Document Title

Summary of the fate and behaviour in the environment for fosetyl

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

2016-07-19

Author(s)

[redacted]

Bayer CropScience

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Version history

Date (yyyy-mm-dd)	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2015-10-05	Original Document MCA – Section 7 of Supplementary Dossier	M-534116-02-1
2016-07-19	Dossier update according to "Request for additional information on the supplementary dossier submitted by Bayer CropScience for the approval renewal of the active substance Fosetyl (2015-5865)" by RMS France on 2016-04-04 and its follow up on 2016-06-02: - BCS responses to RMS requests have been added throughout Section 7. - Summaries (including detailed result tables) of the studies used for the first approval of fosetyl and presented in the DAR and addenda to the DAR which are still relevant for the List of Endpoints have been added throughout Section 7.	M-534116-03-1

[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"

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CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

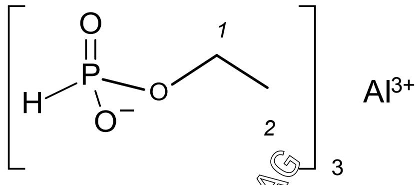
Fosetyl was included in Annex I to Directive 91/414/EEC in 2006 (Directive 2006/64/CE of 18 July 2006, Entry into Force on 1 May 2007). This Supplementary Dossier contains only data which were not submitted at the time of the Annex I inclusion of fosetyl under Directive 91/414/EEC and which were therefore not evaluated during the first EU review. All data which were already submitted by Bayer CropScience (BCS) for the Annex I inclusion under Directive 91/414/EEC are contained in the DAR, its Addenda and are included in the Baseline Dossier provided by BCS. These data are only mentioned in the Supplementary Dossier for the sake of completeness and only general information (e.g. author, reference etc.) is available for these data. In order to facilitate discrimination between new data and data submitted during the Annex I inclusion process under Directive 91/414/EEC, the old data are written in grey typeface. For all new studies, detailed summaries are provided within this Supplementary Dossier. However, for a better understanding of the fate and behaviour in the environment of fosetyl, short summaries including the results of all studies are given at the beginning of the relevant sections. Additional information requested by the RMS France on 2016-04-04 and its follow up on 2016-06-02 during the evaluation of the Supplementary Dossier is highlighted in yellow.

Fosetyl is the ISO common name for ethyl hydrogen phosphonate (IUPAC). Due to the fact that the aluminium salt, a variant of fosetyl, is used in the formulated product, it should be noted that the data in this section belong to the variant fosetyl-aluminium (fosetyl-Al), unless otherwise specified.

In original reports study authors may have used different names or codes for metabolites of fosetyl-Al. In this summary, a single name or a single code is used for each metabolite. A full list containing structural formula, various names, short forms, codes and occurrences of metabolites is provided as Document N3.

As some pragmatic approach "phosphonic acid" formed as a major metabolite is reported in this Supplementary Dossier as the free acid for the sake of clarity and unequivocal handling. After application, aluminium tris-O-ethyl phosphonate (i.e. fosetyl-Al) dissociates into the O-ethyl phosphonate and aluminium ions. Any phosphonate formed from O-ethyl phosphonate in the following would never be present in the form of the free acid (i.e. phosphonic acid) under the conditions of the environment (pH 4 to 9). This conclusion is supported by the molecular structure and by the dissociation constant observed (dissociation constant for the first step of deprotonation: pKa = 2.0). Consequently, phosphonates in their fully protonated form are strong acids that spontaneously form salts in contact with soil or natural water with any suitable counter ion present (i.e. sodium, potassium, magnesium, calcium). With the ability to readily form salts in the environment phosphonates are, in terms of their acidic or alkaline character, similar to the salts of phosphoric acid (i.e. phosphates) in their environmental behaviour.

The studies investigating the environmental fate of fosetyl-aluminium were performed with the following positions of ^{14}C- and ^{32}P-radiolabel:



Label 1: [1-^{14}C]fosetyl-aluminium
Label 2: [2-^{14}C]fosetyl-aluminium
Label 3: [^{32}P]fosetyl-aluminium[1]

In addition and for the metabolite phosphonic acid, some tests were performed with ^{33}P-radiolabelled[1] test item.

CA 7.1 Fate and behaviour in soil

CA 7.1.1 Route of degradation in soil

CA 7.1.1.1 Aerobic degradation

Report:	KCA 7.1.1.1/01 [redacted]; [redacted]; [redacted]; 1978; M-163672-01-1
Title:	Aluminium ethylphosphite - Degradation in the soil
Report No.:	R002963
Document No.:	M-163672-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/02 [redacted]; [redacted]; 1982; M-159391-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil metabolism study
Report No.:	R000825
Document No.:	M-159391-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

[1] It should be noted that the two isotopes of phosphorus, i.e. ^{32}P and ^{33}P, do have a half-life of 14.3 and 25.3 days, respectively. This limits the use for long-term tests, in particular when being compared to tests with ^{14}C-radiolabelled compounds. Test durations at or beyond the half-life of the corresponding phosphorus isotope need to consider the decline from short half-life thus contributing to a higher complexity in interpretation of test results.

Report:	KCA 7.1.1.1/03 [redacted] K; [redacted]; 1999; M-184329-01-1
Title:	The rate of degradation of (14C)-fosetyl-Al in three soils under aerobic conditions at 20 degree Celsius
Report No.:	R011664
Document No.:	M-184329-01-1
Guideline(s):	EU (=EEC): 95/36/EC, (1995); SETAC: (1995); Equivalent to US EPA OPPTS Guideline No. 835.4100
Guideline deviation(s):	none
GLP/GEP:	**yes**

Information on route of degradation in soil for metabolite phosphonic acid/phosphonate

Report:	KCA 7.1.1.1/04 [redacted]; [redacted]; 1953; M-234773-01-1
Title:	Transition of phosphite to phosphate in soils
Report No.:	C034353
Document No.:	M-234773-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/05 [redacted]; 1960; M-234777-01-1
Title:	Microbial oxidation and utilization of orthophosphite during growth
Report No.:	C034355
Document No.:	M-234777-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/06 [redacted]; [redacted]; 1966; M-234784-01-1
Title:	Bacterial oxidation of orthophosphite
Report No.:	C034359
Document No.:	M-234784-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/07 [redacted]; [redacted]; [redacted]; 2001; M-234787-01-1
Title:	Phosphite (phosphorous acid): Its relevance in the environment and agriculture and influence on plant phosphate starvation response
Report No.:	C034360
Document No.:	M-234787-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/08 [redacted]; [redacted]; [redacted]; [redacted]; [redacted]; 2003; M-233852-01-1
Title:	The degradation of phosphorous acid, the main metabolite of fosetyl-Al in soil (Environmental position paper)
Report No.:	C033860
Document No.:	M-233852-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/09 [redacted],; [redacted]; 1957; M-234780-01-1
Title:	Fractionation of soil phosphorus
Report No.:	C034357
Document No.:	M-234780-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.1/10 [redacted]W; 2005; M-248853-01-1
Title:	Assessment of aluminium deposited to soil due to agricultural usage of fosetyl-al Code: AE F053616
Report No.:	C047183
Document No.:	M-248853-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

The route of degradation in aerobic soil of fosetyl-aluminium (fosetyl-Al) had been investigated under laboratory conditions in a total of three studies in:

- three soils (20 and 12 °C, moisture at 70% of water retention capacity for one soil, 50% of water retention capacity for two soils) after application of 1-^{14}C- and ^{32}P-labeled fosetyl-Al (KCA 7.1.1.1/01);
- four soils (20 °C, moisture at 75% of water capacity at 0.33 bar) after application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.1.1/02). In addition and for comparison, investigations were performed with 1-^{14}C-labeled ethanol separately dosed to two soils and incubated under the same conditions as for the active substance;
- three soils under standard conditions (20 °C, moisture at 40% of the maximum water holding capacity (MWHC) after application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.1.1/03).

The data requirement was addressed under Point 7.1.1.1.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

It should be noted that fosetyl-Al has a very simple structure to consist of portions to generate potentially organic ('ethanol') and inorganic (aluminium ions, phosphorus) portions of residues in the environment. This nature to form small, short-lived species (apart from phosphonic acid) is the cause of analytical challenges to detect the active substance as well as for any components formed at trace level. Moreover, a new study according to OECD 307 would not be designed and conducted significantly different from studies available. New data would thus not contribute to a better understanding on route and rate of degradation of fosetyl-Al in soil.
The test designs of studies KCA 7.1.1.1/01 to KCA 7.1.1.1/03 reflect typical designs as for current OECD 307 testing. The studies included analysis of separate soil samples at the various timepoints after application of ^{14}C-labelled active substance. Material balances were established and the distribution of degradation products at the various time points was reported.
In summary it is concluded that the studies are still valid with no major deviation from designs according to OECD 307.

The evaluation revealed that the degradation of fosetyl-Al in aerobic soil proceeded rapidly *via* biologically induced split of the molecule into 'non-organic' parts, i.e. 'phosphonates' (phosphonic acid, see also explanations in the following) and into ethanol being the predecessor of other transient, carbon-containing transformation products. The degradation in aerobic soil was accompanied by formation of non-extractable residues (NER) and significant mineralisation to ^{14}C-carbon dioxide.

Ethanol and 'phosphonate' (phosphonic acid, see below) occurred as major metabolites (>10% AR) in tests on route of degradation in aerobic soil. The transient character of ethanol and its degradation products is clearly indicated by its occurrence and decline within one day of incubation. Besides the active substance, phosphonate in the defined form as the free phosphonic acid had been defined as the residue in soil, groundwater and surface water for consideration in environmental risk assessments for Annex I inclusion.

It should be noted that 'phosphonates' are dealt with as phosphonic acid in this dossier as some pragmatic approach for the sake of clarity and unequivocal naming.
After application, aluminium tris-O-ethyl phosphonate (i.e. fosetyl-Al) dissociates into the O-ethyl phosphonate anions and aluminium kations. Any phosphonate formed in the following from O-ethyl phosphonate would thus never be present as the free acid (i.e. phosphonic acid) under the pH conditions of the environment (pH 4 to 9).

This conclusion is supported by the molecular structure and by the dissociation constant observed[2]. Consequently phosphonates in their fully protonated form are strong acids that spontaneously form salts in contact with soil or natural water with any suitable ubiquitous counter ion present (i.e. sodium, potassium, magnesium, calcium).
For actual environmental risk assessments within the approval renewal of fosetyl, ethanol was not considered due to its transient character in aerobic soil degradation tests. This conclusion is supported by the nature of ethanol to be readily biodegradable. In addition, formation and respiration in natural biological systems like yeasts is well known.
The metabolic pathway resulting from degradation tests in aerobic soil under conditions of the laboratory is summarized in Figure 7.1.1.1-1.

Ethanol is a natural product to predominantly result from fermentation processes. These can also occur for some time in the environment, for example, during the decay of fruits. Following its simple structure to contain two carbon atoms, hydrogen and oxygen only, the compound qualifies for exclusion from risk assessment at the first step when considering the criteria laid down in Guidance Document SANCO/221/2000 rev.10, dated 25 February 2003, to exclude metabolites within the relevance assessment for groundwater.
The data available on route and rate of degradation of ethanol in soil and water from tests with the active substance and from separately applied ethanol support a type of weight of evidence approach that ethanol is readily degraded. Based again on a seasonal application rate of 3 x 3.6 kg a.s./ha = 10.8 kg a.s./ha (please refer to Document D1 of the representative formulation Fosetyl-Al WG 80), this would be formally a maximum relase of 4.2 kg ethanol distributed in 750 000 kg soil (area of 1 ha, 5 cm depth, soil density of 1.5 kg/L) to result in a maximum concentration of about 5.6 mg/kg soil. Considering the high dilution in combination with ready biodegradability, negligible effects can be estimated from ethanol residues in the environment following use of fosetyl-Al in the field.

Within the process of Annex I inclusion of fosetyl under Directive 91/414/EEC, aspects of the fate and potential of aluminium originating from use of fosetyl-Al were also considered, i.e. the potential to set effects in the environment. The request had been addressed in a document included as KCA 7.1.1.1/10.

[2] Dissociation constant of phosphonic acid for the first step of deprotonation: pKa = 2.00; for second step: pKa = 6.59. At environmentally relevant values of pH phosphonates will be thus present in their ionized form as $H_2PO_3^-$ or HPO_3^{2-} ions.

Following use of fosetyl-Al the inorganic portion of residues may be formally described as 'Al^{3+} ions'. For the sake of scientific precision in description it should be considered that Al^{3+} ions definitively do not exist in a free form in the environment. Aluminium (Al) has a very high affinity to oxygen resulting in very tight binding of the two elements. This binding is pre-determined in the molecular structure of fosetyl. In a first approach, Al residues species can be more typically characterised as 'AlO^{+}' upon their release. 'AlO^{+}'-type residues of Al undergo mineralisation by binding to counter-ions found ubiquitously in the mineral fraction of the environment such as Na^{+}, K^{+}, Mg^{2+}, Ca^{2+} as cations, but also to undergo binding to oxgen-containing anions like carbonates ('CO_3^{2-}'), phosphates ('PO_4^{3-}') and silicates ('SiO_4^{2-}'). As a result water-soluble, dissolved residues are fixed to form 'kaolin-type' and other minerals contributing as Al-containing fraction as a predominant portion to the 'earth crust'. The earth crust contains about 8% Al thus being the third most abundant element besides oxgen (about 60%) and silicon (28%). Water-soluble residues of Al are thus found to a negligible extent in the environment. With Al being not defined as a component of concern there was no requirement to set limits or define as a target in the Drinking Water Directive.

The facts should be considered when evaluating the significance of Al residues in the environment released from fosetyl-Al use:

The total mineral portion of an area of 1 hectare in size and of 5 cm depth weighs about 1 250 000 kg (1250 tons). Assuming an abundance of 8% Al thereof this includes 100 000 kg (100 tons) of 'Al'. A maximum annual residue 0.86 kg 'Al^{3+}' results from use of fosetyl-Al when sprayed at the maximum seasonal application rate of 3 x 3.6 kg a.s./ha (= 10.8 kg a.s./ha in total, please refer to Document D1 of the representative formulation Fosetyl-Al WG 80). The annual release reflects about 0.0008% of the total actual Al-content in soil. The contribution to the existing portion of Al in soil is thus minimal.

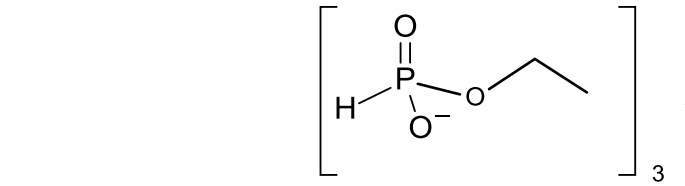
In summary, aluminium and ethanol residues undergo mineralisation either to contribute to the mineral portion of soil and to carbon dioxide via microbial oxidation processes.

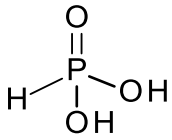
The basic information on transformation of phosphonate (former term: phosphite) into phosphate was demonstrated on the basis of publications (KCA 7.1.1.1/04 to KCA 7.1.1.1/07). The common element of the publications was that the oxidation of phosphonate to phosphate is a biologically induced process by soil microbes. In addition, a method for the extraction and thus characterization of inorganic phosphates occurring in soil was published and submitted as supplementary data in KCA 7.1.1.1/09. A number of aspects dealing with the use of phosphonates in agriculture including the use as fertilizer and the potential influence on plant physiology were reviewed in KCA 7.1.1.1/09. Finally, the various key facts to describe the route and rate of degradation of phosphonates in the soil and aquatic environment were summarized in KCA 7.1.1.1/08.

Phosphate is a mineral being a natural component in the earth crust including soil. A potential release of phosphate in soil and water are strongly dependent on availability to biology/organisms. Phosphonates and their oxidation product phosphate are essential nutrients taken up by plants thus lowering the risk for accumulation in soil. In addition, availability to plants, but also potential for transport in the environment is strongly dependent on the actual form of the phosphate salt in soil. This effect is well known to be a problem in the effectiveness as nutrient for fertilizers. In particular, binding to earth-alkali metals like magnesium and calcium can be very strong to result as a process of ageing in non-solubility in water and non-availability to plants, but also lowering the risk for any transport in the soil and water environment.

Phosphate is an essential nutrient for all living organisms including animals, plants and microbia. For example, for vines in the EU typical annual amounts of phosphate fertilizers applied range from 22 to 110 kg P_2O_5/ha. A maximum of 10.8 kg (3 x 3.6 kg) fosetyl-Al/ha applied (please refer to Document D1 of the representative formulation Fosetyl-Al WG 80) thus may form 8.64 kg phosphate/ha in theory. In case of use in crops with low phosphate application rates, the amount of phosphonates applied should therefore be considered in the total annual phosphate balance.

Figure 7.1.1.1- 1: Existing route of degradation of fosetyl-Al in aerobic soil





Phosphonic acid

Ethanol

Non-extractable Residues

+

Carbon dioxide

Study summaries on rate of aerobic degradation in soil taken from the DAR

In addition and at the special request of the RMS France, summaries of existing studies on aerobic degradation in soil already evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC were taken from the Draft Assessment Report of the RMS France (February 2005) and its Final Addendum (September 2005). Summaries of those studies are provided, from which data were used for the new kinetic evaluations and the actual risk assessment. These study summaries are written in grey typeface in the following to distinguish from new studies.

Report:	KCA 7.1.1.1/01 [redacted]; [redacted]; [redacted]; 1978; M-163672-01-1
Title:	Aluminium ethylphosphite - Degradation in the soil.
Report No.:	R002963
Document No.:	M-163672-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Comment RMS: Study carried out before GLP. No guideline followed. This study can be used for evaluation.

- **Methods**

Aluminium 1-^{14}C-ethylphosphonate (no impurity observed on TLC plates) or Aluminium ^{32}P-ethylphosphonate (a few impurities observed on TLC plates) were applied at 500 mg/kg (about 10 times the normal rate) to 50 g samples of 3 soils (Table 8.1.1.1-1). Incubation was at 12 or 20 °C and at 50% MWHC. Soils were extracted with distilled water. Radioactivity in extracts was measured by LSC (^{14}C) or Cerenkof effect (^{32}P). Extracts were concentrated and analysed by TLC. CO_2 was trapped in methanol-phenethylamine (was checked by barium hydroxide). Unextracted radioactivity (^{14}C) was determined by combustion and was not characterized.

Table 8.1.1.1-1: Soil characteristics

	Versailles soil	**German soil 2.2**	**German soil 2.3**
Clay (< 2 µm) %	20.5	6.6	9.2
Silt (2-20 µm) %	21.1	10.0	12.4
Sand (20-200 µm) %	55.2	28.4	37.6
Sand (> 200 µm) %	2.7	55.0	40.5
Organic matter (OC) %	1.94 (1.13)	4.71 (2.74)	1.72 (1.0)
pH	6.4	6.9	6.1
CEC	10.0	13.2	5.0

Table 8.1.1.1-2: Degradation of ^{14}C-fosetyl-Al in 3 soils at 20 °C (mean of 2 replicates, % AR)

Soil	DAT	CO_2 [a]	Extractable [a]	Non-extractable	Recovery
Versailles	1	18.9 (5.0)	49.8 (84.5)	26.6	95.3
	2	55.2 (16.2)	5.1 (50.8)	38.6	98.9
	4	67.3 (58.7)	2.3 (5.2)	37.6	107.2
	8	67.5 (67.8)	-	29.7	97.2
	16	70.0 (69.3)	-	26.7	96.7
	32	74.7 (74.5)	-	23.9	98.6
German 2.2	1	38.6 (5.3)	21.7 (64.9)	39.7	100.0
	2	58.6 (17.4)	10.4 (41.9)	41.3	110.3
	4	70.7 (59.4)	10.8 (5.9)	36.9	118.4
	8	70.1 (60.9)	8.2	27.1	105.4
	16	70.2 (65.3)	1.6	21.7	93.5
	32	77.8 (68.9)	-	20.4	98.2
German 2.3	1	13.5 (5.9)	53.0	14.1	80.6
	2	58.9 (16.6)	2.9	22.7	84.5
	4	73.0 (57.8)	-	33.5	106.5
	8	76.9 (65.5)	-	27.4	104.3
	16	77.6 (71.1)	-	21.0	98.6
	32	83.0 (75.6)	-	21.8	104.2

[a] values into brackets are from studies at 12° C

- **Results**

For ^{14}C-labelled fosetyl, recoveries were acceptable with a few exceptions (Tables 8.1.1.1-2). For all soils, rapid and significant mineralization of the ethyl group was observed at both temperature (> 50% in 2 or 4 days and > 70% in 4 to 16 d or 16 to 32 d at 20 or 12 °C, respectively). No degradation product was detected in soil extracts at 12 °C (contained the highest amounts of RA). At 20 °C, bound residue peaked at 33 to 41% after 2 to 4 d and was 20.4 to 23.4% after 32 d. For ^{32}P-labelled fosetyl, no figure was presented but no volatile was said to be recovered and phosphonic acid was identified in the 32DAT soil extract from the German soil 2.2 at 12 °C. Assuming no degradation product in soil extracts, DT50 for fosetyl is estimated to be < 1 d at 20 °C and < 2 d at 12 °C.

Report: KCA 7.1.1.1/02 [redacted], [redacted], 1982, M-159391-01-1
Title: Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil metabolism study
Report No.: R001825
Document No.: M-159391-01-1
Guideline(s): none
Guideline deviation(s): not applicable
GLP/GEP: **no**

Comment RMS: Study carried out before GLP. No guideline was followed. This study can be used for evaluation but it should be noticed that very small soil samples were used.

- **Methods**

Aluminium tris-O-[^{14}C-ethyl]phosphonate (purity 97.7%) or 1-^{14}C-ethanol (purity 99%) were applied at 100 or 39 mg/kg, respectively, to 2.5 g samples of sandy loam and clay loam soils (Table 8.1.1.1-3). Incubation was at 20 °C and at 75% of soil moisture at 33 kPa for 15 hours. Volatiles were trapped in NaOH and analysed by LSC and HPLC before and after adding barium hydroxide. Soils were extracted with 0.1N sulfuric acid, 0.1N ammonium hydroxide, methanol and ethyl acetate, and extracts were analysed by LSC and HPLC. Soil residue was quantified by combustion and fractionated into humic substances. For fosetyl, degradation was also studied in 2 additional soils (loamy sand and silt loam, see Table 8.1.1.1-3) for 3 hours and in the 4 sterile soils for 1 day. Influence of soil moisture (25 to 75% of moisture at 33 kPa) and of concentration (20 to 500 mg/kg) was studied using the sandy

loam soil. Influence of repeated applications was also investigated (unlabelled fosetyl was applied 4 times, every 2 d, before adding labelled compound at 100 mg/kg).

Table 8.1.1.1-3: Soils characteristics

	Sandy loam I	Loamy sand I	Silt loam I	Clay loam I
Sand (> 50 µm) %	62.3	81.2	15.2	34.0
Silt (2-50 µm) %	20.2	13.8	55.3	27.6
Clay (< 2 µm) %	13.6	3.1	23.0	37.5
Organic matter (OC) %	3.6 (2.09)	1.3 (0.76)	2.3 (1.34)	2.6 (1.51)
pH	5.3	6.6	6.6	7.6
CEC meq/100 g	13	5	14	21
Moisture 33 kPa %	24	16	26	26
Bulk density	1.4	1.6	1.3	1.25

❑ **Results**

For the main studies with fosetyl (sandy loam and clay loam soils), recoveries were acceptable (Tables 8.1.1.1-4 and -5). Mineralization of the ethyl group was 9.4 to 19.6% after 15 to 16 h and significant amounts of ethanol were detected in traps (up to 36.6% after 15 h). Ethanol losses could be due to the small size of soil samples. Extractable RA was mainly recovered in the acidic extracts, mainly as fosetyl and ethanol (max. 78% after 1.5 h). It was < 8.3% in NH_4OH extracts and neither fosetyl nor ethanol were detected by HPLC. Fosetyl was rapidly degraded (< 4% remaining after 7 h). Unextractable RA was 37 to 47% after 15 to 16 h and it was shown to be associated with the fulvic acid fraction (sandy loam) or the fulvic and humin fractions (clay loam). Neither fosetyl nor ethanol were detected in the fulvic fraction by HPLC. The behaviour of ^{14}C-ethanol was very similar to that of aluminium 1-^{14}C-ethylphosphonate. For fosetyl, a similar pattern of degradation was observed in the additional soils (loamy sand and silt loam). No degradation was observed in the 4 sterile soils (data not shown). Soil moisture had no effect on the rate of degradation of fosetyl but the volatile fraction (probably ethanol) was more important at low soil moisture (Table 8.1.1.1-6). Concentration and previous treatments had no effect on fosetyl degradation in soil (Tables 8.1.1.1-7 and -8).

Table 8.1.1.1-4: Degradation of ^{14}C-fosetyl-Al and ^{14}C-ethanol in sandy loam soil at 20 °C (% AR)

	Fosetyl						Ethanol					
	0	0.75 h	1.5 h	3 h	7 h	15 h	0 h	0.75 h	1.5 h	3 h	7 h	15 h
Total volatile	-	2.8	7.7	30.1	42.8	46.0	-	11.0	19.3	32.3	51.4	54.4
ethanol	-	2.4	6.7	27.9	36.5	36.6	-	10.0	17.5	29.4	44.6	46.7
CO_2	-	0.42	1.0	2.2	6.3	9.4	-	1.0	1.8	2.9	6.8	7.7
Total extract	99.5	91.8	81.0	51.8	15.3	12.6	99.1	80.3	69.9	48.6	10.5	10.6
H_2SO_4 extr.	97.5	89.9	78.3	48.0	5.8	2.0	98.7	79.6	67.3	44.6	2.1	1.4
fosetyl	97	17	0.2	-	-	-	-	-	-	-	-	-
ethanol	-	73	78	48	5	-	99.5	81	67	44	-	-
NH_4OH extr.	2.0	1.6	2.1	2.0	8.0	8.3	0.4	1.1	2.1	3.0	6.3	7.3
Unextract.	0.1	3.7	7.8	14.8	38.4	37.0	0.1	3.5	9.8	16.1	32.5	33.6
Recovery	99.6	98.3	96.5	96.6	96.5	95.6	99.2	95.3	98.9	97.0	94.3	98.6

Table 8.1.1.1-5: Degradation of [14]C-fosetyl-Al and [14]C-ethanol in clay loam soil at 20 °C (% AR)

	Fosetyl					**Ethanol**				
	0	1 h	3 h	7 h	16 h	0 h	1 h	3 h	7 h	16 h
Total volatile	-	2.5	16.1	35.4	37.2	-	17.5	36.3	52.2	54.3
ethanol	-	1.8	12.9	23.3	17.6	-	16.2	32.8	41.7	40.2
CO_2	-	0.7	3.2	12.1	19.6	-	1.3	3.5	10.5	14.1
Total extract	96.5	91.7	67.2	20.1	10.9	95.8	73.4	42.2	9.4	7.8
H_2SO_4 extr.	94.8	89.8	63.8	12.6	3.4	95.3	71.8	38.7	2.9	1.8
fosetyl	95	64	21	4	-	-	-	-	-	-
ethanol	-	27	43	6	-	96	72	38	-	-
NH_4OH extr.	1.5	1.6	2.2	4.1	3.9	0.4	1.0	1.9	3.4	2.9
Unextract.	0.1	3.5	14.7	40.0	47.0	0.2	5.2	17.7	34.4	35.3
Recovery	96.6	97.7	98.0	95.5	95.1	96.0	96.0	96.2	96.0	97.4

Table 8.1.1.1-6: Effect of soil moisture on fosetyl degradation in sandy loam soil at 20 °C (% of applied)

Soil moisture	**25% FC**					**50% FC**					**75% FC**				
HAT	0	0.5	1 h	2.5	6.5	0	0.5	1 h	2.5	6.5	0	0.5	1 h	2.5	6.5
Volatile	-	5.5	18.1	52.4	76.1	-	4.7	11.8	25.9	59.1	-	1.8	5.8	19.6	49.4
Acidic extr.	93.4	86.1	72.9	37.9	8.6	88.2	86.8	75.3	54.3	6.0	93.3	88.6	83.2	63.7	7.7
fosetyl	93	43	23	2	-	88	37	20	1	-	93	49	27	1	-
ethanol	-	43	50	36	-	-	49	55	50	-	-	39	56	63	-
Bound	2.3	2.2	2.4	4.7	10.4	2.1	2.8	4.1	10.8	26.2	2.4	2.9	3.9	11.2	34.6
Recovery	95.7	93.8	93.4	95.0	95.1	90.3	94.3	91.2	91.0	91.3	95.7	93.3	92.9	94.5	91.7

Table 8.1.1.1-7: Effect of concentration on fosetyl degradation in sandy loam soil at 20 °C (% of applied)

Dose	**20 mg/kg**				**100 mg/kg**				**500 mg/kg**			
HAT	0	0.5	1	3	0	0.5	1	3	0	0.5	1	3
Volatile	-	6.1	12.4	31.0	-	4.9	10.4	35.6	-	4.5	9.3	38.7
CO_2	-	1.1	2.0	7.2	-	0.8	0.8	3.0	-	0.4	0.3	1.6
ethanol	-	5.0	10.5	23.8	-	4.1	9.6	32.7	-	4.1	8.9	37.1
Acidic extr.	95.3	83.4	66.8	12.4	94.6	90.5	79.9	44.4	99.0	91.3	82.7	47.5
fosetyl	95	6.5	-	-	84	11	3	-	93	15	5	-
ethanol	-	77	66	[illegible]	10	79	77	44	6	76	78	47
Bound	2.1	10.8	22.0	63.3	2.5	4.2	6.7	19.6	1.9	2.4	2.7	5.0
Recovery	97.4	100	101	107	97.1	99.5	97.0	99.6	101	98.2	94.7	91.2

Table 8.1.1.1-8: Effect of previous treatments on fosetyl degradation in sandy loam at 20 °C (% of applied)

HAT	**0.5 h**		**1 h**		**2.5 h**	**6.5 h**
Number of appl.	1	5	1	5	5	5
Volatile	2.9	3.2	8.1	8.6	19.3	47.3
Acidic extract	88.8	90.4	81.5	78.8	53.8	4.5
fosetyl	40	50	18.5	29	4	-
ethanol	49	40	63	50	50	-
Bound	5.2	5.2	7.4	8.9	21.4	39.2
Recovery	96.9	98.8	97.0	96.3	94.5	91.0

Request from the RMS:
In the study by [redacted] and [redacted] (1982), the amount of the unknown metabolite detected at retention time 0.65 (RRT 0.65) increases until the end of the study. Moreover, it is detected twice at 5% of the applied radioactivity.
A statement justifying that no risk assessment was performed for these compounds should be provided.

Response from BCS:
The unknown RRT 0.65 was observed at 5% in sandy loam soil only and each following application of fosetyl or ethanol, thus suggesting its origin from ethanol. Formation in clay loam soil was sporadic (samples after 7 hours only), again following application of fosetyl and ethanol. Owing to the very short sampling intervals, interim steps in degradation of ethanol in aerobic soil could thus be observed such as the well-known oxidation to the corresponding aldehyde and carboxylic acid, again being very short-lived.
As supported by the existing evaluation in the DAR (see Section B.8, page 401), this indicates that the compounds showed strongly transient character when considering a maximum incubation of 16 hours in the test. As indicated earlier, ethanol is readily degraded in soil at concentrations occurring from use of fosetyl-Al in the field.

Report:	KCA 7.1.1.1/03 [redacted]X; [redacted]; 1999; M-184329-01-1
Title:	The rate of degradation of (14C)-fosetyl-Al in three soils under aerobic conditions at 20 degree Celsius
Report No.:	R011664
Document No.:	M-184329-01-1
Guideline(s):	EU (=EEC): 95/36/EC (1995); SETAC (1995); Equivalent to US EPA OPPTS Guideline No. 835.4100
Guideline deviation(s):	none
GLP/GEP:	yes

Comment RMS: GLP, SETAC guideline. Acceptable.

❑ **Methods**

Pure aluminium 1-^{14}C-ethylphosphonate was applied at 10 mg/kg to 50 g samples of clay loam, sand, or sandy loam soils (Table 8.1.1.1-9). Incubation was at 20 °C and at 40% of MWHC for 120 d. Soils were extracted twice with 0.1 M formic acid. Extracts were analysed by LSC and HPLC. Volatiles from all samples were trapped but not quantified. Bound residue was not determined.

Table 8.1.1.1-9: Soil characteristics

	Clay loam (S261)	Sand (S262)	Sandy loam (S263)
Sand (> 63 µm) %	34.3	86.8	65.4
Silt (2-63 µm) %	35.0	7.0	22.5
Clay %	30.7	6.2	12.1
OC (%)	2.5	1.6	1.8
pH water / $CaCl_2$	6.9 / 6.7	5.4 / 4.6	6.6 / 5.4
CEC meq/100 g	20.6	9.3	18.1
WHC pF0 / pF 2.5 (%)	61.6 / 31.8	55.8 / 19.4	49.6 / 18.6
Biomass start / end (mg C/100 g)	53.4 / 63.8	22.1 / 20.4	17.1 / 22.5

- **Results**

Because volatiles and unextractable RA were not measured, no mass balance could be established. Because i) RA was fully recovered on day 0 and ii) amounts of extractable RA, fosetyl and ethanol were in accordance with data from the previous studies, results can be used for determination of degradation rate of fosetyl and they provide further information on degradation products (tables 8.1.1.1-10 and 11). In addition to ethanol, up to five unknowns were detected in soil extracts of which U1 and U2 were major and could reach 17.2 and 12.8%, respectively, after < 1 h. Because all unknowns were transient and were only detected for the first day, they are deemed to be not relevant and no further information is required. DT50 and DT90 for fosetyl were calculated using different models and results are shown in Table 8.1.1.1-12.

Table 8.1.1.1-10: Degradation of ^{14}C-fosetyl-Al in clay loam soil at 20 °C (mean of 2 replicates, % AR)

Duration	Extractable	Fosetyl	Ethanol	U1	U2	U3	U4	U5
0 h	99.2	29.0	59.4	-	7.1	-	-	-
0.25 h	87.4	15.0	60.3	4.5	7.6	-	-	-
0.5 h	78.3	10.0	55.3	3.5	7.3	-	-	-
1 h	69.7	6.3	51.3	2.5	5.1	4.4	-	-
2 h	37.1	2.0	24.1	2.4	3.0	-	1.6	4.2
4 h	17.8	0.7	9.7	1.3	1.1	4.3	2.1	-
8 h	13.9	-	-	-	-	-	-	-
24 h	10.2	-	-	-	-	-	-	-
7 d	7.5	-	-	-	-	-	-	-
120 d	4.2	-	-	-	-	-	-	-

Table 8.1.1.1-11: Degradation of ^{14}C-fosetyl-Al in 2 soils at 20 °C (mean of 2 replicates, % AR)

Duration	sand soil				sandy loam soil				
	Extractable	Fosetyl	Ethanol	U2	Extractable	Fosetyl	Ethanol	U1	U2
0 h	99.1	36.3	59.3	8.6	100.8	39.7	51.4	9.7	-
0.25 h	96.7	9.2	75.8	11	97.6	15.4	65.0	17.2	-
0.5 h	94.8	3.2	70.1	11.6	92.8	7.0	69.8	16.1	-
1 h	92.0	10.6	68.0	12.8	83.1	-	69.1	14.6	-
2 h	84.7	5.1	67.7	11.5	68.9	-	53.6	15.3	-
4 h	68.8	-	62.4	6.4	31.3	-	21.9	3.3	6.1
8 h	50.2	-	-	-	12.4	-	-	-	-
24 h	30.0	-	-	-	6.8	-	-	-	-
7 d	2.7	-	-	-	4.9	-	-	-	-
120 d	1.5	-	-	-	2.4	-	-	-	-

Table 8.1.1.1-12: Rate of degradation of fosetyl-Al in 3 soils at 20 °C

Soil type	Linear 1st order		KIM model		Timme-Frehse	
	DT50	DT90	DT50	DT90	DT50	DT90
Clay loam	37 min	122 min	17 min	104 min	29 min	96 min
Sand	60 min	200 min	5 min	369 min	21 min	69 min
Sandy loam	12 min	40 min	11 min	37 min	1 min	13 min

Request from the RMS:
In the study by [redacted] and [redacted] (1999), unknown metabolite U2 is a major metabolite in two soils (max. 17.2% of applied radioactivity) and the amount of unknown metabolite U5 increases until the end of the study in two soils (max. 7.1% of applied radioactivity).
A statement justifying that no risk assessment was performed for these compounds should be provided.

Response from BCS:
Unknown U2 was observed at 17.2% in maximum in soil sandy loam after 0.25 hours of incubation showing a decline to 3% after 4 hours. It was observed at 7.6% in soil clay loam to decline to 1.1% after 4 hours. Finally, it was observed at 12.8% in the sandy soil after 1 hour to decline to 6.3% after 4 hours.
The data illustrate that U2 is a very short-lived and thus transient metabolite.
Unknown U5 was observed at 7.1% in soil clay loam after 4 hours and at 6.1% in soil sandy loam again after 4 hours of incubation.
Considering the fact that always several metabolites were observed, an increase of a 'long-lived' single component would be indicated in the course of the study. However, total extractable radioactivity including U2 decreased to 5 to 7.5% in the two soils within 7 days of incubation to decline to 2 to 4% at study end. Conclusively, there was no trend for an increase of an individual component in the course of the study again underlining the very transient character.
The existing evaluation in the DAR (see Section B.8, pages 394 and 401) supports the view that components observed in short-term aerobic soil degradation tests do have a strongly transient character.

[redacted] A.M. (1999). Appendix 7 (Determination of phosphorous acid in soil extracts) of the previous report 17302 (R010664). RPA study 12546. GLP, no guideline followed. Acceptable.

- **Methods**

Acidic extracts were concentrated by freeze drying, residues were dissolved in tartaric acid solution and derivatization was carried out by the use of diazomethane. Methylated phosphonic acid was analysed by GC. Soils were further extracted with ammonium buffer and extracts were analysed as above.

- **Results**

Methylated phosphonic acid was not detected in acidic extracts but substantial amounts were detected in ammonium buffer extracts especially from the clay loam soil and the sandy loam soil (chromatograms not shown, recovery not specify). Thus phosphonic acid was not quantified but it was shown to be a degradation product of fosetyl.

<u>Overall conclusion on studies on route and rate of aerobic degradation of fosetyl-Al in soil</u>

Two out of three studies (KCA 7.1.1.1/01 and KCA 7.1.1.1/02) in total were performed prior to the introduction of GLP for environmental fate data with no citation of a guideline followed. Study KCA 7.1.1.1/03 followed GLP and, formally SETAC guidelines prior to the availability of OECD 307.
Beyond formalistic aspects the laboratory data available are able to reflect adequately the behavior of fosetyl-aluminium (fosetyl-Al) in soil.
For example, study KCA 7.1.1.1/01 was performed by an institution near to the French ministry of agriculture. With full material balances available, the design of the study was able to demonstrate the basic processes contributing to the understanding of the route of degradation in soil. The study has some deficits in analysis since soil extracts were not fully analysed and thus no full pattern of active substance including metabolites was established. This was the major reason to exclude the study from the set used for calculation of degradation rates in soil later (see Section CA 7.1.2).
Results of study KCA 7.1.1.1/02 are well in line with the earlier study KCA 7.1.1.1/01. Again, despite the study was designed prior to the availability of guidelines (which were at least drafted upon conduct of the study and published by the US in 1982) its design and conduct are still able to fully support the understanding of the route of degradation of fosetyl-Al in soil. In this context, it should be noted that results are consistent in demonstrating that fosetyl-Al degradation is a very rapid process which is very consistent with its simple structure. Although criticized by the RMS the design to take small soil samples for investigation was appropriate when considering that the work-up and extraction of a soil sample till analysis is a time-consuming process. Small samples in this context simply eased the handling to result in fast possible work-up – essential and supportive to have consistent results for an active substance degrading within hours when being in contact with soil.
Study KCA 7.1.1.1/03 did not include the determination of volatile and non-extractable radioactivity thus no full material balance was formally established. Again, considering the outcome of the study in context of the two additional studies, the results are fully consistent. Since the active substance fosetyl-Al is not volatile, the results are still adequate to determine degradation rates in aerobic soil.
The overall conclusion is therefore that new information would not contribute to a better understanding of the processes of degradation of fosetyl-Al in aerobic soil. In view of deviations to actual guidelines the data can be understood as a worst case estimate since incubation, for example, under conditions supporting microbial activity in soil is very likely to result in even faster rates of degradation.

Study summaries of existing studies and publications on route of aerobic degradation in soil:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.1.1/01 [redacted]; [redacted]; [redacted]; 1978; M-163672-01-1
Title:	Aluminium ethylphosphite - Degradation in the soil
Report No.:	R002963
Document No.:	M-163672-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The biotransformation of [^{14}C]-fosetyl-Al was investigated under aerobic conditions of the laboratory in three soils, i.e. French soil Versailles and the German soils 2.2 and 2.3, following incubation in the dark at 20 °C and soil moisture of 70% (soil Versailles) or 50% moisture of the maximum water retention capacity (German soils 2.2 and 2.3) for 32 days in maximum. A nominal test concentration of 500 mg active substance/kg soil was applied based on a single maximum rate of 80 kg a.s./ha in the field. The test concentration thus represented a 10fold concentration when compared to the field application rate.

Incubation was also performed at 12 °C for another series of soil samples under the same conditions of moisture and test concentration for 64 days. In addition, the degradation behaviour of [^{32}P]-fosetyl-Al was studied following application to samples of the same soils.

Material balances at 20 °C ranged from 95.2 to 107.2% AR for soil Versailles, 93.5 to 109.9% AR for German soil 2.2 and 93.0 to 106.4% AR for German soil 2.3. Exceptions were for German soil 2.2 by day 4 (117.8% AR) and by days one and two for German soil 2.3 (80.6 and 84.5% AR, respectively).

Material balances at 12 °C ranged from 95.2 to 107.2% AR for soil Versailles, 93.5 to 109.9% AR for German soil 2.2 and 93.0 to 106.4% AR for German soil 2.3. Exceptions were for German soil 2.2 by day 4 (117.8% AR) and by days one and two for German soil 2.3 (80.6 and 84.5% AR, respectively).

No full material balances were determined for samples incubated at 12 °C or for samples incubated with [^{32}P]-fosetyl-Al.

Following incubation at 20 °C the total extractable radioactivity decreased from 48.1% AR (soil Versailles), 11.3% AR (German soil 2.2) and 53.0% AR (German soil 2.3) by day one to 1.3% AR by day 4, 0.5% AR by day 16 and 2.9% AR by day 2, respectively.

Following incubation at 12 °C the total extractable radioactivity decreased from 82.9% AR (soil Versailles), 64.9% AR (German soil 2.2) and 75.1% AR (German soil 2.3) by day one to 0.5% AR by day 32, 0.4% AR by day 32 and 0.7% AR by day 16, respectively.

No quantifation of test item and degradation products was reported for soil extracts.

For samples incubated at 20 C, degradation of [^{14}C]-fosetyl-Al was found to proceed predominantly *via* rapid formation of carbon dioxide starting at the first sampling interval (day one) to reach maxima of 74.7% AR (soil Versailles), 77.8% AR (German soil 2.2) and 82.6% AR at the end of the study (day 32).

For samples incubated at 12 C, maxima of carbon dioxide formation were 74.8% AR (soil Versailles), 71.8% AR (German soil 2.2) and 83.5% AR (German soil 2.3) after 64 days of incubation (study end). For samples incubated at 20 °C non-extractable residues (NER) decreased from 28.4% AR by day one to 23.9% AR by day 32 (soil Versailles) and from 50.2% AR by day one to 20.4% AR by day 32 (German soil 2.2). Values of NER increased for German soil 2.3 from 14.1% AR by day one to 20.8% AR by day 32.

With no quantitation of test item and degradation products reported no degradation rates were estimated for fosetyl-Al in soil in this study.

The study is regarded as valid information to support the understanding of the principles of route of degradation of fosteyl-Al in soil.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[^{14}C]-fosetyl-Al
Specific Activity: not reported
Radiochemical Purity: not reported

[^{32}P]-fosetyl-Al
Specific Activity: not reported
Radiochemical Purity: not reported

Specific activity and radiochemical purity were not reported. However, the identity of test item was clearly indicated described by structure including the position of radiolabel.

2. Test Soils

The study was performed using the three test soils as characterized in Table 7.1.1.1- 1.

Table 7.1.1.1- 1: Physico-chemical properties of test soils

Parameter	Soil		
Soil Designation	Versailles	2.2	2.3
Geographic Location			
City	Versailles	Speyer	Speyer
Country	France	Germany	Germany
Particle size			
Sand [> 200 µm] (%)	2.7	55.0	40.8
Fine Sand[20 – 200 µm] (%)	55.2	28.4	37.6
Silt[2 – 20 µm] (%)	21.1	10.0	12.4
Clay[< 2 µm] (%)	20.5	6.6	9.2
pH	6.4	6.9	6.1
Organic Matter (%)	1.94	4.71	1.72
Organic carbon (%) *	1.13	4.17	1.00
Cation Exchange Capacity (meq/100 g)	10.0	13.2	5.0
Water Holding Capacity	not reported	not reported	not reported

* Calculated by dividing organic matter content by 1.72

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in flow through systems consisting of glass flasks each containing 50 g soil and attached to a trap for volatile radioactivity (mixture of methanol and phenethylamine, 2:1, v/v), i.e. ^{14}C-carbon dioxide. Soil moisture was maintained during incubation by passing humidified air through the samples.

The tests were performed at a concentration of approx. 500 mg/kg dry weight of soil. The test concentration was based on a field rate of 8 g/m² (80 kg a.s./ha), thus being equivalent to a 10-fold concentration in comparison to the field situation. [1-ethyl-^{14}C]- or [^{32}P]-fosetyl-Al was applied as aqueous solution (1 mL) drop wise onto the soil surface of the soil samples. Soil samples had been adjusted to 70% of the water retention capacity (soil Versailles) or 50% of the water retention capacity for German soils 2.2 and 2.3 one week prior to application. The samples were incubated at 20 ± 2 °C under aerobic conditions in the dark for 32 days in maximum. Incubation was 64 days in maximum for samples incubated at 12 ± 1 °C.

2. Sampling

For samples incubated with [^{14}C]-fosetyl-Al, duplicate samples each were removed for analysis after 1, 2, 4, 8, 16 and 32 days of incubation (12 and 20 °C). For tests at 12 °C, additional duplicates per soil were removed after 64 days of incubation.

Sampling intervals for soils incubated with [^{32}P]-fosetyl-Al were not reported.

3. Analytical Procedures

Soil samples were extracted up to three times successively with distilled water at ambient temperature. Radioactivity in extracts was determined by liquid scintillation counting (LSC). Radioactivity present as ^{32}P in extracts was measured and confirmed by applying the Cherenkov effect.

Soil extracts were concentrated and analysed by TLC/radio-detection. No quantitation of test item and degradation products in soil extracts was reported. The identity of test item and degradation products (i.e. phosphonic acid) was confirmed by TLC co-chromatography with reference items.

Volatile radioactivity in traps (methanol/phenethylamine mixture) was determined by LSC. The identity of ^{14}C-carbon dioxide formed and trapped as volatile radioactivity was confirmed by co-precipitation with aqueous barium chloride solution (barite water).

Following homogenisation, non-extractable residues (NER) in extracted soils was determined by combustion/LSC. Selected samples were subject to an additional harsh extraction step using aqueous hydrochloric acid. NER were not quantified for samples incubated at 12 °C. No full material balance was therefore established for these samples. The same applied for extractable and non-extractable radioactivity in samples treated with [^{32}P]-fosetyl-Al.

Degradation kinetics of fosetyl-Al or its degradation products were not evaluated owing to the fact that distribution of extractable radioactivity into the test item and degradation products was not reported.

II. RESULTS AND DISCUSSION

The established full material balances for the three test soils incubated at 20 °C following application of [^{14}C]-fosetyl-Al were summarized in Table 7.1.1.1- 2 to Table 7.1.1.1- 4. The corresponding data available for samples incubated at 12 °C were summarized in Table 7.1.1.1- 5 to Table 7.1.1.1- 7.

A. DATA

Table 7.1.1.1- 2: Degradation of [^{14}C]-fosetyl-Al at 20 °C in French soil Versailles under aerobic conditions

Component		Replicate No.	1	2	4	8	16	32
Ambient extract	1st	Mean	41.9	3.0	1.3	-	-	-
		SD	2.5	0.4	0.4	-	-	-
	2nd	Mean	6.2	1.1	-	-	-	-
		SD	0.3	0.1	-	-	-	-
Total in ambient extracts			48.1	4.1	1.3	-	-	-
Harsh extracts (aqueous hydrochloric acid)	1st	Mean	1.3	1.1	1.0	-	-	-
		SD	0.1	0.1	0.0	-	-	-
	2nd	Mean	0.5	-	-	-	-	-
		SD	0.0	-	-	-	-	-
Total in harsh extracts			1.8	1.1	1.0	-	-	
NER from combustion		Mean	26.6	38.6	37.6	29.7	26.7	23.9
		SD	1.7	1.1	4.4	0.5	0.3	0.7
Total NER			28.4	39.7	38.6	29.7	26.7	23.9
Volatiles (^{14}C-Carbon dioxide)		Mean	18.9	55.2	67.3	67.5	70.0	74.7
		SD	0.5	1.4	1.0	3.0	0.0	0.2
Total radioactivity		Mean	95.2	98.9	107.2	97.1	96.7	98.6
		SD	0.4	2.1	3.0	3.4	0.3	0.5

* All values expressed as percentage of total applied radiolabel
NER = non-extractable residues, SD = standard deviation
Total NER = sum of harsh extracts and radioactivity determined after combustion

Table 7.1.1.1- 3: Degradation of [^{14}C]-fosetyl-Al at 20 °C in German soil 2.2 under aerobic conditions

Component		Replicate No.	1	2	4	8	16	32
Ambient extract		Mean	11.3	2.5	1.6	-	0.5	-
		SD	0.7	0.3	0.1	-	0.1	-
Harsh extracts (aqueous hydrochloric acid)	1st	Mean	6.1	4.2	4.5	4.3	1.6	-
		SD	0.0	0.0	0.1	0.1	0.5	-
	2nd	Mean	4.4	3.4	4.7	3.9	-	-
		SD	0.0	0.2	0.2	0.1	-	-
Total in harsh extracts			10.5	7.6	9.2	8.2	1.6	-
NER from combustion		Mean	39.7	41.3	36.9	27.1	21.7 [1]	20.4
		SD	0.6	1.1	0.3	0.3	-	2.8
Total NER			50.2	48.9	46.1	35.3	23.3	20.4
Volatiles (^{14}C-Carbon dioxide)		Mean	38.6	58.6	70.7	70.1	70.5	77.8
		SD	0.1	1.2	0.3	2.8	0.3	2.9
Total radioactivity		Mean	100.0	109.9	117.8	105.3	93.5 [1]	98.2
		SD	1.1	2.4	0.8	2.5	-	0.1

[1] single replicate
* All values expressed as percentage of total applied radiolabel
NER = non-extractable residues, SD = standard deviation
Total NER = sum of harsh extracts and radioactivity determined after combustion

Table 7.1.1.1- 4: Degradation of [^{14}C]-fosetyl-Al at 20 °C in German soil 2.3 under aerobic conditions

Component		Replicate No.	Incubation time (days)					
			1	2	4	8	16	32
Ambient extract	1st	Mean	43.9	2.9	-	-	-	-
		SD	8.3	0.3	-	-	-	-
	2nd	Mean	9.1	-	-	-	-	-
		SD	0.6	-	-	-	-	-
Total in ambient extracts			53.0	2.9	-	-	-	-
NER		Mean	14.1	22.7	33.5	27.4	21.0	20.8
		SD	0.3	0.2	0.8	0.5	0.5	0.0
Volatiles (^{14}C-Carbon dioxide)		Mean	13.5	58.9	73.0	76.9	77.6	82.6
		SD	0.2	1.2	0.0	0.9	0.6	0.8
Total radioactivity		Mean	80.6	84.5	106.4	104.2	98.6	93.0
		SD	9.4	1.7	0.9	0.3	1.1	1.2

* All values expressed as percentage of total applied radiolabel
NER = non-extractable residues, SD = standard deviation

Table 7.1.1.1- 5: Degradation of [^{14}C]-fosetyl-Al at 12 °C in French soil Versailles under aerobic conditions

Component		Replicate No.	Incubation time (days)						
			1	2	4	8	16	32	64
Ambient extracts	1st	Mean	69.4	50.8	5.2	-	1.1	0.5	-
		SD	1.8	1.4	0.4	-	0.1	0.2	-
	2nd	Mean	12.2	-	-	-	-	-	-
		SD	0.2	-	-	-	-	-	-
	3rd	Mean	1.3	-	-	-	-	-	-
		SD	0	-	-	-	-	-	-
Total in ambient extracts			82.9	50.8	5.2	-	1.1	0.5	-
NER		Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Volatiles (^{14}C-Carbon dioxide)		Mean	5.0 [1]	16.2	58.7	67.8	69.3	74.5 [1]	74.8
		SD		0.05	0.5	0.5	0.2		0.4
Total radioactivity		Mean	89.5 [1]	67.0	63.9	67.8	70.4	75.1 [1]	74.8
		SD		1.4	0.1	0.5	0.1		0.4

[1] single replicate
* All values expressed as percentage of total applied radiolabel
NER = non-extractable residues, SD = standard deviation, n.d. = not determined

Table 7.1.1.1- 6: Degradation of [^{14}C]-fosetyl-Al at 12 °C in German soil 2.2 under aerobic conditions

Component		Replicate No.	Incubation time (days)						
			1	2	4	8	16	32	64
Ambient extracts	1st	Mean	47.8	36.9	5.2	1.1	0.6	0.4	-
		SD	3.2	0.6	0.0	0.1	0.1	0.0	-
	2nd	Mean	17.1	5.0	0.7	-	-	-	-
		SD	1.4	0.7	0.1	-	-	-	-
Total in ambient extracts			64.9	41.9	5.9	1.1	0.6	0.4	-
NER		Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Volatiles (^{14}C-Carbon dioxide)		Mean	5.3	17.4	59.4	60.9	65.3	68.9 [1]	71.8
		SD	0.2	0.3	0.3	0.6	0.8		1.5
Total radioactivity		Mean	70.2	59.2	65.3	62.0	65.8	69.3 [1]	71.8
		SD	2.0	0.1	0.4	0.6	0.9		1.5

[1] single replicate
* All values expressed as percentage of total applied radiolabel
NER = non-extractable residues, SD = standard deviation, n.d. = not determined

Table 7.1.1.1- 7: Degradation of [^{14}C]-fosetyl-Al at 12 °C in German soil 2.3 under aerobic conditions

Component		Replicate No.	Incubation time (days)						
			1	2	4	8	16	32	64
Ambient extracts	1st	Mean	63.7	58.2	7.5	1.4	0.7	-	-
		SD	0.9	5.1	0.2	0.1	0	-	-
	2nd	Mean	10.5	6.3	-	-	-	-	-
		SD	0.5	1.2	-	-	-	-	-
	3rd	Mean	0.9	-	-	-	-	-	-
		SD	0	-	-	-	-	-	-
Total in ambient extracts			75.1	64.5	7.5	1.4	0.7	-	-
NER		Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Volatiles (^{14}C-Carbon dioxide)		Mean	5.9	16.6	57.8	65.5	71.1	75.0	83.5
		SD	0.3	0.2	1.2	0.4	0.5	1.3	1.4
Total radioactivity		Mean	81	81	65.3	66.9	71.8	75.0	83.5
		SD	1.1	6.4	1.4	0.5	0.5	1.3	1.4

[1] single replicate
* All values expressed as percentage of total applied radiolabel
NER = non-extractable residues, SD = standard deviation, n.d. = not determined

B. MATERIAL BALANCE

For samples incubated with [^{14}C]-fosetyl-Al at 20 °C, material balances ranged from 95.2 to 107.2% AR (soil Versailles), from 93.5 to 109.9% AR (German soil 2.2) and from 93.6 to 106.4% AR (German soil 2.3). An exception occurred for both replicates of German soil 2.2 after 4 days of incubation to result in a mean material balance of 117.8% AR. No explanation was given for the values being out of range for acceptance. Another exception was observed for German soil 2.3 to result in 80.6 and 84.5% AR mean total recoveries for samples incubated for one day and two days, respectively. Again, no explanation was given in the study report.
No full material balances were reported and thus established for samples incubated at 12 °C since no NER was determined.
No material balances were reported for samples following incubation with [^{32}P]-fosetyl-Al.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

For samples incubated with [^{14}C]-fosetyl-Al at 20 °C, total extractable radioactivity decreased from 48.1% AR by day one to 1.3% AR after 4 days of incubation (soil Versailles), from 11.3% AR by day one to 0.5% AR after 16 days (German soil 2.2) and from 53.0% AR by day one to 2.9% AR after 2 days in German soil 2.3.
The total of non-extractable residues (NER) resulting from combustion and harsh extractions (hydrochloric acid) was 28.4% AR by day one, to peak by day two (39.7% AR) and to decrease to 23.9% AR after 32 days of incubation (soil Versailles). For German soil 2.2, total NER were 50.2% AR by day one to decrease to 20.4% AR by day 32. For German soil 2.3, total NER were 14.1% AR by day one to peak by day 4 (33.5% AR) and to decrease to 20.8% AR at the end of the study (day 32).

For samples incubated with [^{14}C]-fosetyl-Al at 12 °C, total extractable radioactivity decreased from 82.9% AR by day one to 0.5% AR by day 32 (soil Versailles), from 64.9% AR by day one to 0.4% AR after 32 days (German soil 2.2) and from 75.1% AR by day one to 0.7% AR after 16 days in German soil 2.3.
No values for extractability of residues at the various time points were reported for samples following application of [^{32}P]-fosetyl-Al.
No values for NER at the various time points were reported for samples following application of [^{32}P]-fosetyl-Al at 20 °C and for samples incubated with [^{14}C]-fosetyl-Al at 12 °C.

D. VOLATILE RADIOACTIVITY

For samples incubated with [^{14}C]-fosetyl-Al at 20 °C, values of ^{14}C-carbon dioxide formed were 18.9% AR by day one to reach a maximum of 74.7% AR at the end of the study (day 32, soil Versailles). For German soil 2.2, values were 38.6% AR by day one to increase to 77.8% AR by day 32. Finally, ^{14}C-carbon dioxide was 13.5% AR by day one and the maximum of 82.6% AR by day 32 for German soil 2.3.

For soil samples incubated with [^{14}C]-fosetyl-Al at 12 °C, maximum values of ^{14}C-carbon dioxide formed were 5.0% AR by day one to reach a maximum of 74.8% AR at the end of the study (day 64, soil Versailles). For German soil 2.2, values were 5.3% AR by day one to increase to 71.8% AR by day 64. Finally, ^{14}C-carbon dioxide was 5.9% AR by day one and the maximum of 83.5% AR by day 32 for German soil 2.3.

For [^{32}P]-fosetyl-Al no volatile radioactivity was observed in traps thus serving as an indication that no volatile phosphorus-originating components had been formed during incubation.

E. DEGRADATION OF PARENT COMPOUND

As demonstrated by TLC/^{14}C-radio-detection, [^{14}C]-fosetyl-Al was the only ^{14}C-containing compound detected in soil extracts of samples incubated up to four days after application.

As a result of processing, a volatile component was observed that occurred in traps of the rotary evaporator after concentration of soil extracts. There was the hypothesis that the volatile component observed was ^{14}C-ethanol. However, no identification of the component was reported.
Following observations made for soil extracts of day one, about 50% of the radioactivity was lost by processing. Although not further quantified, this underlined qualitatively the fast formation of ethanol from the active substance [^{14}C]-fosetyl-Al and the rapid conversion of ^{14}C-residues in soil to ^{14}C-carbon dioxide.

Following application of [^{32}P]-fosetyl-Al, analysis of concentrated soil extracts was performed by thin-layer chromatography (TLC) starting by day two. Besides the presence of [^{32}P]-fosetyl-Al, analysis revealed the formation of one ^{32}P-containing degradation product, i.e. phosphonate, formed from biotically induced hydrolysis of [^{32}P]-fosetyl-Al.

III. CONCLUSIONS

Following application of [^{32}P]- or [^{14}C]-labelled fosetyl-Al to soil, residues were readily degraded to form [^{32}P]-phosphonate, ^{14}C-carbon dioxide and, concluded from its behaviour, ethanol as degradation products of fosetyl-Al in aerobic soil.

Conclusively, the degradation of fosetyl-Al in aerobic soil was driven by hydrolysis into the carbon chain containing part, i.e. ethanol and the phosphonate moiety, i.e. phosphonic acid[3].
For the carbon containing part the biotic transformation resulted in rapid mineralisation to form ^{14}C-carbon dioxide as the predominant product. This finding is consistent with the very simple structure and in line with microbiological and biochemical pathways for short-chained aliphatic carbon compounds.

[3] As some pragmatic approach 'phosphonic acid' formed as a major metabolite was handled as the free acid in this dossier for the sake of clarity and unequivocal handling. Starting with application ethyl-phosphonate-aluminium (i.e. fosetyl-Al) is dissociated in the spray mixture into the ethyl-phosphonate and aluminium ions. The phosphonates formed from ethyl-phosphonate in the following are never present in the form of the free acidic (i.e. phosphonic acid) under the conditions of the environment. This conclusion is supported by the molecular structure and by the dissociation constant observed (see below). Consequently phosphonates in their fully protonated form are strong acids that spontaneously form salts in contact with soil or natural water with any suitable counter ion present (i.e. sodium, potassium, magnesium, calcium).
Dissociation constant of phosphonic acid for first step of deprotonation: pKa = 2.00.

The microbiologically induced hydrolysis of the phosphonic acid ester compound fosetyl-Al to phosphonate was additionally confirmed by investigations with [^{32}P]-labelled fosetyl-Al.

The study did not allow for the calculation of rates of degradation in aerobic soil, however, it is able to strongly support the understanding of the principles of route of degradation of fosetyl-Al in soil.

Study evaluation:
The study was performed prior to availability of official EU, national and US guidelines for testing. However, its design and conduct included important key elements that can be found in actual designs of soil degradation testing.

The first major reason to exclude the study from kinetic evaluation was the fact that the design of the study did not include the generation of day zero samples. The lack of day zero samples did not allow for the formal confirmation that extraction efficiency was given and, as an early control, for the correct amount of radioactivity applied to samples. Day zero samples are important to serve as the starting point for kinetic evaluation.
Furthermore, at least some analysis of soil extracts was performed, but not reported. Apart from ^{14}C-carbon dioxide, there was no quantification of the distribution of radioactivity in soil extracts into the various components formed for each sampling interval. The latter is the ultimate prerequisite to reliably include any soil degradation data into a kinetic evaluation of the experiment.

Considering the structure of the test item and the behaviour of residues described in the study, the results fully and consistently confirm the understanding of the behaviour of fosetyl-Al in soil - as can be expected already from theory.
Overall the study design was able to characterise the key principles in the degradation behaviour of fosetyl-Al residues in soil.

Although analysis and analytical methods have made progress, it should be noted that some principles observed in this study still apply thus making soil tests with fosetyl-Al a very challenging task. These challenges include, but are not limited to the fact of very fast formation of at least two volatile degradation products (ethanol and carbon dioxide) within hours after application, combined with analytical limitations when soil extract analysis has to be performed very rapidly after extraction of soil. The ionic character of the active substance and phosphonates serve as additional issues for the trace analysis in environmental matrices like soil.

Conclusively, the study is regarded as valid to support the understanding of the route of degradation of fosetyl-Al in soil.

Report:	KCA 7.1.1.1/02 [redacted]; [redacted]; 1982; M-159391-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil metabolism study
Report No.:	R000825
Document No.:	M-159391-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	no

Executive Summary
The biotransformation of [^{14}C]-fosetyl-Al was investigated under aerobic conditions of the laboratory in four soils Sandy loam, Clay loam, Loamy sand and Silt loam following incubation in the dark at 20 °C and soil moisture of 75% of water holding capacity at 0.33 bar for 16 hours in maximum. A nominal test concentration of 100 mg active substance/kg soil was applied based on a single maximum rate of 80 kg a.s./ha in the field.

In addition, the biotransformation of [^{14}C]-ethanol was investigated under aerobic conditions of the laboratory in the two soils Sandy loam and Clay loam following incubation in the dark at 20 °C and soil moisture of 75% of water holding capacity at 0.33 bar for 16 hours in maximum. A nominal test concentration of 39 mg ethanol/kg soil was applied based on a single maximum rate of 80 kg a.s./ha in the field and assuming quantitative conversion to ethanol.

Total recovery of applied radioactivity (AR) ranged from 95.6 to 99.6% AR (Sandy loam), 95.1 to 98.0% AR (Clay loam), 96.7 to 99.5% AR (Loamy sand) and from 95.8 to 100% AR (Silt loam).

For the active substance fosetyl-Al, total extractable radioactivity decreased from 99.5% AR (Sandy loam), 96.5% AR (Clay loam), 98.8% AR (Loamy sand) and 98.5% AR (Silt loam) by zero hours to 12.6% AR after 15 hours, 10.9% AR after 16 hours, 64.8% AR after 3 hours and 52.3% AR after 3 hours, respectively.
The decrease of extractable radioactivity was paralleled by formation of non-extractable residues (NER) to account for 37.0% AR after 15 hours (Sandy loam), 47.0% AR after 16 hours (Clay loam), 5.2% AR after 3 hours (Loamy sand) and 21.4% AR after 3 hours (Silt loam).
Microbiological degradation resulted in spontaneous ^{14}C-carbon dioxide formation at 9.4% AR after 15 hours (Sandy loam) and 19.6% AR after 16 hours (Clay loam) in maximum. Ethanol was formed and detected as other organic volatile radioactivity. Ethanol amounted to 36.6% AR after 15 hours (Sandy loam) and 17.6% AR after 16 hours (Clay loam) in maximum. Volatile radioactivity was not separately investigated for the two soils Loamy sand and Silt loam.

For ethanol, total extractable radioactivity decreased from 99.5% AR (Sandy loam) and 96.5% AR (Clay loam) by zero hours to 10.6% AR after 15 hours and 7.8% AR after 16 hours, respectively.
The decrease of extractable radioactivity was paralleled by formation of non-extractable residues (NER) to account for 33.6% AR after 15 hours (Sandy loam) and 35.3% AR after 16 hours (Clay loam.
Microbiological degradation resulted in spontaneous ^{14}C-carbon dioxide formation at 7.7% AR after 15 hours (Sandy loam) and 14.1% AR after 16 hours (Clay loam) in maximum. Ethanol was detected as other organic volatile radioactivity to account for 46.7% AR after 15 hours (Sandy loam) and 40.2% AR after 16 hours (Clay loam) in maximum.

Values of fosetyl-Al decreased from 97.0% AR (Sandy loam), 95% AR (Clay loam), 97% AR (Loamy sand) and 98% AR (Silt loam) by zero hours to 1.2% AR after 1.5 hours, 4% AR after 7 hours, 17% AR after 3 hours and 5% AR after 3 hours, respectively.
Degradation of ^{14}C-fosetyl-Al proceeded very rapidly via biologically induced phosphonate ester hydrolysis to ethanol observed at maximum values of 84.7% AR after 1.5 hours (Sandy loam) and 55.9% AR after 3 hours (Clay loam). Values of ethanol extractable from soil decreased to 5% AR (Sandy loam) and 6% AR (Clay loam) each after 7 hours of incubation.

Following separate application of ^{14}C-ethanol values of ethanol decreased from 99.1% AR (Sandy loam) and 96% AR (Clay loam) by zero hours to 48.1% AR after 15 hours and 42% AR after 16 hours, respectively.
Degradation again proceeded very rapidly *via* microbial induced processes to result in values of ethanol extractable from soil to decrease to 1.4% AR (Sandy loam) and 1.8% AR (Clay loam) after 15 hours and 16 hours of incubation, respectively.

For fosetyl-Al the kinetic evaluation of degradation data was performed graphically to result in half-lives estimated to 0.33 hours (Sandy loam) and 1.5 hours (Clay loam).
For ethanol the corresponding half-lives were 2.5 hours for each of the two soils Sandy loam and Clay loam.

Fosetyl-Al and its readily and rapidly formed metabolite ethanol were spontaneously degraded in contact with soil to form non-extractable residues and carbon dioxide as the result of biological processes.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

[ethyl-1-^{14}C]-fosetyl-Al
Batch ID: KWC-1110
Specific Activity: 1.3 MBq/mg (35.2 µCi/mg)
Radiochemical Purity: 97.7%

Fosetyl-Al
Batch ID: EA-1167.1
Chemical Purity: > 99%

[1-^{14}C]-ethanol
Batch ID: 120
Specific Activity: 44.4 MBq/mg (1200 µCi/mg)
Radiochemical Purity: 99%

If necessary, the radio-labelled test substance was diluted with unlabelled fosetyl-Al.

2. Soil

The soils had been sieved to 2 mm. The physico-chemical characteristics were summarized in Table 7.1.1.1- 8.

Table 7.1.1.1- 8: Physico-chemical properties of test soils

Parameter	Soil			
Soil ID	Sandy loam	Clay loam	Loamy sand	Silt loam
Textural Classification	sandy loam	clay loam	loamy sand	silt loam
Sand[50 -2000 µm] (%)	62.3	34.0	81.2	15.2
Silt [2 µm – 50 µm] (%)	20.2	27.6	13.8	55.3
Clay [< 2 µm] (%)	13.6	37.5	3.1	23.0
pH [a)]	5.3	7.6	6.6	6.6
Organic Matter (%)	3.6	2.6	1.3	2.3
Organic Carbon (%) [b)]	2.1	1.5	0.8	1.3
Cation Exchange Capacity (meq/100 g)	13	21	5	14
Water Capacity @ 0.33 bar (%)	24	26	16	26

[a)] Method not reported
[b)] Calculated from organic matter content by dividing by a factor of 1.72

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in flow-through systems consisting of glass flasks each containing 2.5 g of soil and attached to two successive traps for volatile radioactivity (0.1 N aqueous sodium hydroxide solution). For the two soils Sandy loam and Clay loam and late sampling intervals of seven hours and 15 hours, the traps were amended by another trap containing concentrated sulfuric acid. Soil moisture during incubation was maintained by passing humidified air through the test samples.

For fosetyl-Al, the tests were performed at a test concentration of 100 mg a.s./kg dry weight of soil, based on a field rate of 8 g/m² (80 kg a.s./ha) and assuming homogenous distribution in the top 6 cm of soil.
Soils Sandy loam and Clay loam were incubated separately with [^{14}C]-ethanol at a test concentration of 39 mg/kg dry weight of soil since results of preliminary studies suggested ethanol to be a major metabolite of fosetyl-Al. Separate application to soil also allowed for a comparison of degradation patterns. The test concentration was derived from assuming complete hydrolysis of fosetyl-Al at 100 mg/kg to ethanol.

The test substances [ethyl-1-^{14}C]-fosetyl-Al or [1-^{14}C]-ethanol were applied as aqueous solution drop wise onto the soil surface of the soil samples. Soil samples were adjusted to 75% of the soil water capacity at 0.33 bar. The samples were incubated at 20 ± 2 °C under aerobic conditions in the dark for 16 hours (0.67 days) in maximum.
For soils Sandy loam and Clay loam investigations included the incubation of sterilised soils to demonstrate the biotic, microbial nature of degradation in soil. Being not regarded as key, results were not summarized in this summary in view of the significant portion of carbon dioxide formed within the very short incubation times. The biotic nature of degradation was thus clearly demonstrated by the key results.
Finally, additional potential parameters of influence were investigated for soil Sandy loam by variation of soil test moisture, variation of test concentration and the influence of repeated applications. Being beyond the standards in actual test designs in soil degradation and by not contributing to an overall better understanding of the behaviour of fosetyl-Al in soil, the results were not subject of this summary.
Non-extractable residues (NER) were characterized by organic matter fractionation into humins, humic and fulvic acids. Owing to the very short incubation times the results did not contribute to a significantly better understanding of the behaviour of fosetyl-Al in soil. The corresponding details were therefore not subject of this summary.

2. Sampling
Samples treated with active substance ^{14}C-fosetyl-Al:
For the two soils Sandy loam and Clay loam, single replicates were removed for analysis following 0, 0.75, 1.5, 3, 7 and 15 hours of incubation (Sandy loam) or 0, 1, 3, 7 and 16 hours (Clay loam). Samples of soils Loamy sand and Silt loam were removed for analysis after 0, 0.75, 1.5 and 3 hours of incubation.

Samples treated with ^{14}C-ethanol:
For soils Sandy loam and Clay loam, single replicates were removed for analysis following 0, 0.75, 1.5, 3, 7 and 15 hours of incubation (Sandy loam) or 0, 1, 3, 7 and 16 hours (Clay loam).

3. Analytical Procedures
Following incubation, total volatile radioactivity collected in traps was determined by liquid scintillation counting (LSC).
Following precipitation as barium carbonate, ^{14}C-carbon dioxide was quantified by determination of the difference between total radioactivity and the radioactivity that remained in solution. The radioactivity remaining in solution after precipitation was ethanol. This was confirmed by reversed phase HPLC analysis combined with ^{14}C-radio-detection and comparison with authentic ^{14}C-reference standard.
The soil was extracted successively twice with 25 mL 0.1 N aqueous sulfuric acid, each followed by a rinsing step with 25 mL water. Another extraction step was performed with 25 mL 0.1 N aqueous ammonium hydroxide solution, again followed by rinsing with 25 mL water. Finally, methanol and ethyl acetate were formally included in soil extraction as organic solvents. As expected, radioactivity in organic solvent extracts ranged from below 1 to 3% AR in maximum. Recoveries from extraction with organic solvents were therefore not considered in the reporting of material balances.

Total radioactivity in soil extracts was determined by LSC. Dependent on total radioactivity, extracts were analysed by HPLC combined with ^{14}C-radio-detection.
Non-extractable residues (NER) were quantitated by combustion followed by LSC.

4. Determination of degradation kinetics:
The kinetic evaluation of degradation data was performed graphically.

II. RESULTS AND DISCUSSION

A. DATA

The results of aerobic biotransformation of [1-^{14}C]fosetyl-Al after incubation in soils Sandy loam, Clay loam, Loamy sand and Silt loam were summarised in Table 7.1.1.1- 9 to Table 7.1.1.1- 12.
The results on aerobic transformation of [1-^{14}C]ethanol in soils Sandy loam and Clay loam were presented in Table 7.1.1.1- 13 and Table 7.1.1.1- 14.

Table 7.1.1.1- 9: Degradation of [^{14}C]-fosetyl-Al at 20 °C in soil Sandy loam under aerobic conditions

	Incubation Time (hours)					
Component	**0**	**0.75**	**1.5**	**3**	**7**	**15**
Fosetyl-Al	97.0	100	1.2	n.d.	n.d.	-
Ethanol (extractable)	<1	73.0	78.0	48.0	5	-
Ethanol (volatile)	-	2.4	6.7	27.9	36.5	36.6
Total ethanol **	<1	75.4	84.7	75.9	41.5	36.6
Unknown RRT 0.65 (alkaline extract)	2.2*	1.8*	2.5*	3.4*	5	5
Others (alkaline extract)	n.d.	n.d.	n.d.	n.d.	3.9	4.5
^{14}C-Carbon dioxide	-	0.4	1.0	2.2	6.3	9.4
Total extractable radioactivity	99.5	91.8	81.0	51.8	15.3	12.6
Non-extractable residues	0.1	3.7	7.8	14.8	38.4	37.0
Total volatile radioactivity***	-	2.8	7.7	30.1	42.8	46.0
Total radioactivity	99.6	98.3	96.5	96.6	96.5	95.6

All values expressed as percentage of total applied radioactivity
n.d.: not detected
* Includes other compounds in alkaline extract (ammonium hydroxide extract)
** Separates into extractable and volatile portion
*** Separates into carbon dioxide and volatile portion of ethanol

Table 7.1.1.1- 10: Degradation of [^{14}C]-fosetyl-Al at 20 °C in soil Clay loam under aerobic conditions

Component	Incubation Time (hours)				
	0	**1**	**3**	**7**	**16**
Fosetyl-Al	95	64	21	4	-
Ethanol (extractable)	1	27	43	6	-
Ethanol (volatile)	-	1.8	12.9	23.3	17.6
Total ethanol*	1	28.8	55.9	29.3	17.6
Unknown RRT 0.65 (alkaline extract)	-	-	-	-***	-
Others (alkaline extract)	1.7	1.8	2.6	6.3	5.0
^{14}C-Carbon dioxide	-	0.7	3.2	12.1	19.6
Total extractable radioactivity	96.5	91.7	67.2	20.1	10.9
Non-extractable residues	0.1	3.5	17.4	40.0	47.0
Total volatile radioactivity**	-	2.5	16.1	35.4	37.2
Total radioactivity	96.6	97.7	98.0	95.5	95.1

All values expressed as percentage of total applied radioactivity
n.d.: not detected
* Separates into extractable and volatile portion
** Separates into carbon dioxide and volatile portion of ethanol
*** Presence of Unknown RRT reported in extract, but not quantified

Table 7.1.1.1- 11: Degradation of [^{14}C]-fosetyl-Al at 20 °C in soil Loamy sand under aerobic conditions

Component	Incubation Time (hours)			
	0	**0.75**	**1.5**	**3**
Fosetyl-Al	97	63	41	17
Ethanol (extractable)	n.d.	30	39	44
Ethanol (volatile)	-	-***	-***	-***
Total ethanol*	-	-	-	-
Unknown RRT 0.65 (alkaline extract)	-	-	-	-
Others (alkaline extract)	-	-	-	-
^{14}C-Carbon dioxide	-	-	-	-
Total extractable radioactivity	98.8	92.9	81.7	64.8
Non-extractable residues	0.7	1.8	3.1	5.2
Total volatile radioactivity**	-	4.0	12.0	26.7
Total radioactivity	99.5	98.7	96.8	96.7

All values expressed as percentage of total applied radioactivity
n.d.: not detected
* Separates into extractable and volatile portion
** Separates into carbon dioxide and volatile portion of ethanol
*** not determined

Table 7.1.1.1- 12: Degradation of [^{14}C]-fosetyl-Al at 20 °C in soil Silt loam under aerobic conditions

Component	Incubation Time (hours)			
	0	0.75	1.5	3
Fosetyl-Al	98	60	36	5
Ethanol (extractable)	n.d.	25	44	46
Ethanol (volatile)	-	-***	-***	-***
Total ethanol*	-	-	-	-
Unknown RRT 0.65 (alkaline extract)	-	-	-	-
Others (alkaline extract)	-	-	-	-
^{14}C-Carbon dioxide	-	-	-	-
Total extractable radioactivity	98.5	89.7	81.3	52.3
Non-extractable residues	1.5	5.1	6.5	21.4
Total volatile radioactivity**	-	2.9	8.0	23.1
Total radioactivity	100	97.7	95.8	96.8

All values expressed as percentage of total applied radioactivity
n.d.: not detected
* Separates into extractable and volatile portion
** Separates into carbon dioxide and volatile portion of ethanol
*** not determined

Table 7.1.1.1- 13: Degradation of [^{14}C]-ethanol at 20 °C in soil Sandy loam under aerobic conditions

Component	Incubation Time (hours)					
	0	0.75	1.5	3	7	15
Ethanol (extractable)	99.1	81	67	44	2	1.4
Ethanol (volatile)	-	10.0	17.5	29.4	44.6	46.7
Total ethanol**	99.1	91.0	84.5	73.4	46.6	48.1
Unknown RRT 0.65 (alkaline extract)	0.4*	1.2*	2.4*	3.5*	5	5
Others (alkaline extract)	-	-	-	-	2.4	3.3
^{14}C-Carbon dioxide	-	1.0	1.8	2.9	6.8	7.7
Total extractable radioactivity	99.5	80.9	69.9	48.6	10.5	10.6
Non-extractable residues	0.1	3.5	9.8	16.1	32.5	33.6
Total volatile radioactivity***	-	11.0	19.2	32.3	51.4	54.4
Total radioactivity	99.6	96.4	100.7	99.9	101.2	106.3

All values expressed as percentage of total applied radioactivity
n.d.: not detected
* Includes other compounds in alkaline extract (ammonium hydroxide extract)
** Separates into extractable and volatile portion
*** Separates into carbon dioxide and volatile portion of ethanol

Table 7.1.1.1- 14: Degradation of [^{14}C]-ethanol at 20 °C in soil Clay loam under aerobic conditions

Component	Incubation Time (hours) 0	1	3	7	16
Ethanol (extractable)	96	72	38	2.9	1.8
Ethanol (volatile)	-	16.2	32.8	41.7	40.2
Total ethanol*	96	88.2	70.8	44.6	42.0
Unknown RRT 0.65 (alkaline extract)	-	-	-	-***	-
Others (extractable)	0.5	1.2	2.4	4.4	3.8
^{14}C-Carbon dioxide	-	1.3	3.5	10.5	14.1
Total extractable radioactivity	96.5	73.4	42.2	9.4	7.8
Non-extractable residues	0.2	5.2	17.7	34.4	35.3
Total volatile radioactivity**	-	17.5	36.3	52.2	54.3
Total radioactivity	96.7	97.4	99.7	106.5	111.5

All values expressed as percentage of total applied radioactivity
n.d.: not detected
* Separates into extractable and volatile portion
** Separates into carbon dioxide and volatile portion of ethanol
*** Presence of Unknown RRT reported in extract, but not quantified

B. MATERIAL BALANCE

Following application of ^{14}C-fosetyl-Al, total material balances of radioactivity ranged from 95.6 to 99.6% AR for soil Sandy loam, from 95.1 to 98.0% AR for soil Clay loam, from 96.7 to 99.5% AR for soil Loamy sand and from 96.7 to 99.5% AR for soil Silt loam. The results were more detailed in Table 7.1.1.1- 15. Conclusively, material balances were in the acceptable range.

Following application of ^{14}C-ethanol, the values for total material balances of radioactivity ranged from 96.4 to 106.3% AR for soil sandy loam and from 96.7 to 111.5% AR for soil clay loam. The results are more detailed in Table 7.1.1.1- 16. In conclusion, there were no signs for losses of radioactivity during work-up and processing.

Table 7.1.1.1- 15: Total material balances of radioactivity of ^{14}C-fosetyl in four soils

Soil	Sandy loam	Clay loam	Loamy sand	Silt loam
Total Recovery (% AR)	95.6 – 99.6	95.1 – 98.0	96.7 – 99.5	95.8 – 100
Mean (% AR)	97.2	96.6	97.9	97.6
Rel. standard deviation	1.3	1.2	1.2	1.6

Values given as percentages of initially applied radioactivity
n.a. = not applicable since single replicates were analysed

Table 7.1.1.1- 16: Total material balances of radioactivity of ^{14}C-ethanol in two soils

Soil	Sandy loam	Clay loam
Total Recovery (% AR)	96.4 – 106.3	96.7 – 111.5
Mean (% AR)	100.7	102.4
Rel. standard deviation	2.9	5.7

Values given as percentages of initially applied radioactivity
n.a. = not applicable since single replicates were analysed

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Values of extractable radioactivity decreased rapidly with time accompanied by formation of NER as summarised in Table 7.1.1.1- 17 for fosetyl-Al and in Table 7.1.1.1- 18 for ethanol.

Following application of fosetyl-Al, quantitative extractability (98.5 to 99.5% AR) was given by zero hours indicating extraction efficiency, to decrease to 10.9 to 12.6% AR within less than one day, i.e. after 15 to 16 hours of incubation.
In turn, formation of NER was fast starting from 0.1 to 1.5% AR by zero hours to 37.0 to 47.0% AR after 15 to 16 hours of incubation.

Following application of ethanol, complete extractability (96.5 to 99.5% AR) was given by zero hours, to decrease again to 7.8 to 10.6% AR within less than one day, i.e. after 15 to 16 hours of incubation. Formation of NER was fast starting from 0.1 to 1.2% AR by zero hours to 33.6 to 35.3% AR after 15 to 16 hours of incubation.

Table 7.1.1.1- 17: Extractable and non-extractable residues of 14C-fosetyl-Al in four soils

Soil	Extractable residues (%)		Non-extractable residues (%)	
	(0 hours)	(15/16 hours)	(0 hours)	(15/16 hours)
Sandy loam	99.5	12.6	0.1	37.0
Clay loam	96.5	10.9	0.1	47.0
Soil	**Extractable residues (%)**		**Non-extractable residues (%)**	
	(0 hours)	(3 hours)	(0 hours)	(3 hours)
Loamy sand	98.8	64.8	0.7	5.2
Silt loam	98.5	52.3	1.5	21.4

Values given as percentages of initially applied radioactivity

Table 7.1.1.1- 18: Extractable and non-extractable residues of ^{14}C-ethanol in two soils

Soil	Extractable residues (%)		Non-extractable residues (%)	
	(0 hours)	(15/16 hours)	(0 hours)	(15/16 hours)
Sandy loam	99.5	10.6	0.1	33.6
Clay loam	96.5	7.8	0.2	35.3

Values given as percentages of initially applied radioactivity

D. VOLATILE RADIOACTIVITY

Formation of volatiles was significant for all soils and test items.
Following application of ^{14}C-fosetyl-Al, the total portion of volatiles recovered in traps was 46.0% AR for soil Sandy loam and 37.2% AR for soil Clay loam after 15 and 16 hours of incubation, respectively. Volatile radioactivity was separated into ethanol and carbon dioxide. Ethanol accounted for 36.6% AR (Sandy loam) and 17.6% AR (Clay loam) after 15 to 16 hours of incubation while carbon dioxide was formed in parallel to 9.4% AR (Sandy loam) and 19.6% AR (Clay loam) at the same time.
Detection of volatile radioactivity was also significant for soils Loamy sand and Silt loam (i.e. 44 and 46% AR after 3 hours). However, no separation of volatiles was reported for the two soils.

Following application of ^{14}C-ethanol, the total portion of volatiles recovered in traps was 54.4% AR for soil Sandy loam and 54.3% AR for soil Clay loam after 15 and 16 hours of incubation, respectively. Volatile radioactivity was separated into ethanol and carbon dioxide. Ethanol accounted for 46.7% AR (Sandy loam) and 40.2% AR (Clay loam) after 15 to 16 hours of incubation while carbon dioxide was formed in parallel to 7.7% AR (Sandy loam) and 14.1% AR (Clay loam) at the same time.

E. TRANSFORMATION OF TEST SUBSTANCE

Following application of ^{14}C-fosetyl-Al, the active substance was extensively transformed to result in ethanol, NER and mineralisation to carbon dioxide as predominant transformation products (see Table 7.1.1.1- 9 to Table 7.1.1.1- 12).
The transformation of the active substance was very fast to decrease from 97.0% AR after zero hours to 1.2% AR after 1.5 hours (Sandy loam), from 95% AR after zero hours to 4% AR after 7 hours (Clay loam), from 97% AR after zero hours to 17% AR after 3 hours (Loamy Sand) and from 98% AR after zero hours to 5% AR after 3 hours (Silt loam).
Ethanol was observed at peak levels of 84.7% AR after 1.5 hours (Sandy loam) and 55.9% AR after 3 hours (Clay loam).

Following application of ^{14}C-ethanol, the test substance was extensively transformed to result in NER and mineralisation to carbon dioxide as predominant transformation products (see Table 7.1.1.1- 13 and Table 7.1.1.1- 14).
The transformation of the test substance ethanol was very fast to decrease from 99.1% AR after zero hours to 48.1% AR after 15 hours (Sandy loam) and from 96% after zero hours to 42% AR after 16 hours (Clay loam).

Following application of ^{14}C-fosetyl-Al or ^{14}C-ethanol, an unknown component (RRT 0.65)[4] was observed at 5% AR in soil Sandy loam after 7 or 15 hours of incubation. The component was thus observed following analysis of alkaline (i.e. aqueous ammonium hydroxide) soil extracts at the last sampling intervals of the study. From the same metabolic pattern resulting from following application of the active substance or its metabolite ethanol, it is concluded that Unknown RRT 0.65 was not formed from the active substance, but is the result of microbial degradation of ethanol in aerobic soil. Owing to the fact that the study had very short overall incubation times the metabolite is regarded as transient component in metabolism of ethanol in aerobic soil. Moreover, Unknown RRT 0.65 was not observed in study KCA 7.1.1.1/01 thus with no indication for an accumulation of this residues in soil samples with prolonged incubation times.
In addition, the extraction behaviour of this compound should be considered: Unknown RRT 0.65 was found in alkaline ammonium hydroxide extracts only. Efficiency of extraction was shown to reach a plateau for acidic extraction after 15 minutes, while 2 hours were found necessary for the alkaline extraction. While the extraction solvent was the same (i.e. water), conditions of hydrolysis changed from acidic to alkaline. By prolongation of the extraction time and in combination pH changed enabling hydrolysis this suggests that Unknown RRT 0.65 was an artificial component resulting from the hydrolysis of radioactivity bound complex to the matrix/soil organic matter.

The biotic character of degradation of fosetyl-Al residues in soil was underlined by the formation carbon dioxide including non-extractable (bound) residues that could not be converted further during the runtime of the study. The very fast transformation in aerobic soil till mineralisation serves as a strong indication that formation of NER as intermediates are caused by soil biological activity.

F. DEGRADATION KINETICS

No formal kinetic evaluation was performed. Values of the DT_{50} in soil Sandy loam were estimated graphically to 0.33 hours for fosetyl-Al and to 2.5 hours for ethanol.
For soil Clay loam values of the DT_{50} were estimated to 1.5 hours for fosetyl-Al and to 2.5 hours for ethanol.

[4] RRT = relative retention time derived from HPLC analysis

III. CONCLUSIONS

In contact with aerobic soil, fosetyl-Al was very rapidly degraded under the conditions of the laboratory to form ethanol (maximum: 84.7% AR after 1.5 hours, soil Sandy loam), non-extractable residues (maximum: 47.0% AR after 16 hours, soil Clay loam) and ^{14}C-carbon dioxide (maximum: 19.6% AR after 16 hours, soil Clay loam) as predominant transformation products of microbial induced degradation.

Half-lives for the degradation were estimated to 0.33 hours (soil Sandy loam) and 1.5 hours (soil Clay loam) for fosetyl-Al and to 2.5 hours for ethanol in each of the two soils.

Degradation in aerobic soil therefore contributes significantly to the overall elimination of residues of fosetyl-Al and its rapidly, but transient metabolite ethanol from the environment.

Study evaluation:
The study was performed prior to availability of official EU guidelines. However, first official US national guidelines for testing became available at about the time of study conduct. The design and conduct of the study included all the essential elements necessary and that can be found in actual designs of soil degradation testing.

With the key elements in design and conduct given along with consistency of results there is no reason to exclude the study from kinetic evaluation and thus from use in environmental risk assessment.

The results are well in line with other data available on route of degradation (see study KCA 7.1.1.1/01) and confirm the understanding of the behaviour of fosetyl-Al residues in soil.
The study design was thus able to demonstrate qualitatively and quantitatively the key principles in degradation of fosetyl-Al residues in soil.
The study confirmed ethanol to be the volatile, transient product of degradation besides carbon dioxide as terminal mineralisation product within very short time, i.e. hours after application.

Despite progress made in analysis and analytical methods, the results of the study clearly indicate also the challenges (i.e. material balances, distribution of radioactivity in soil extracts and volatiles and their kinetic evaluation) in the investigation of extremely rapidly degradable active substances forming volatile, fast degrading components in the following.
Any repetition would therefore not result in a different understanding of transformation processes, transformation products formed and thus the behaviour of fosetyl-Al residues in aerobic soil.

Conclusively, the study is regarded as valid for use in environmental risk assessment to provide information about the route and rate of degradation of fosetyl-Al and ethanol in soil.

Report:	KCA 7.1.1.1/03 [redacted] ダ; [redacted]; 1999; M-184329-01-1
Title:	The rate of degradation of (14C)-fosetyl-Al in three soils under aerobic conditions at 20 degree Celsius
Report No.:	R011664
Document No.:	M-184329-01-1
Guideline(s):	EU (=EEC): 95/36/EC, (1995); SETAC: (1995); Equivalent to US EPA OPPTS Guideline No. 835.4100
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The biotransformation of [^{14}C]-fosetyl-Al was investigated under aerobic conditions of the laboratory in three UK soils Clay loam S261, Sand/Sandy loam S262 and Sandy loam S263 following incubation in the dark at 20 °C and soil moisture of 40% of the maximum water holding capacity (MWHC) for 120 days in maximum. A nominal test concentration of 19 mg active substance/kg soil was applied based on a single maximum rate of 20 kg a.s./ha in the field.

The study was originally designed and conducted to establish a full material balance. The study focused later on the extractable portion of radioactivity thus, in character, serving as a rate study in aerobic soil. No full material balances were thus determined.

The total extractable radioactivity decreased from 99.2% AR (Clay loam S261), 99.1% AR (Sand/Sandy loam S262) and 100.8% AR (Sandy loam S263) by day zero to 4.2, 1.5 and 2.4% AR each after 120 days of incubation, respectively.
Owing to the change in focus of the study the extent of formation of non-extractable residues (NER), other volatile radioactivity and ^{14}C-carbon dioxide was not determined.

Values of fosetyl-Al decreased from 28.9% AR (Clay loam S261), 36.2% AR (Sand/Sandy loam S262) and 39.7% AR (Sandy loam S263) by zero hours to 0.5% AR after 4 hours, 11.0% AR after 2 hours and 7.0% AR after 0.5 hours, respectively.
In contact with soil, degradation of ^{14}C-fosetyl-Al thus proceeded spontaneously *via* biologically induced phosphonate ester hydrolysis to ethanol extractable from soil observed at maximum values of 57.5% AR after 0.5 hours (Clay loam S261), 75.8% AR after 0.25 hours (Sand/Sandy loam S262) and 69.8% AR after 0.5 hours (Sandy loam S263).
Values for ethanol extractable from soil decreased to 1.7% AR (Clay loam S261), 62.4% AR (Sand/Sandy loam S262) and 21.9% AR (Sandy loam S263) each after 4 hours of incubation.

The kinetic evaluation of degradation data was performed by three approaches (i.e. Timme-Frehse, software KIM and linear regression analysis) to result in half-lives to range from 17 to 37 minutes (Clay loam S261), five to 60 minutes (Sand/Sandy loam S262) and one to 12 minutes (Sandy loam S263).

The results confirmed the findings of earlier studies that fosetyl-Al and its readily and rapidly formed metabolite ethanol were spontaneously degraded in soil.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

[ethyl-1-^{14}C]-fosetyl-Al

Sample ID:	LBE0088
Specific Activity:	2.2 MBq/mg
Radiochemical Purity:	> 99%
Chemical Purity:	not reported

2. Soil

Prior to start of the test the soils had been sieved to 2 mm. The physico-chemical characteristics were summarized in Table 7.1.1.1- 19.

Table 7.1.1.1- 19: Physico-chemical properties of test soils

Parameter	Soil		
Soil	Clay loam	Sand	Sandy loam
Code	S261	S262	S263
Geographic Location			
OS Grid Ref	NS 378225	NS 295167	NS 379234
Country	United Kingdom	United Kingdom	United Kingdom
Textural Classification (USDA)	Clay loam	Sand/Loamy Sand	Sandy loam
Sand [63µm – 2 mm] (%)	34.3	86.8	65.4
Silt [2 µm - 63µm] (%)	35.0	7.0	22.5
Clay [< 2µm] (%)	30.7	6.2	12.1
pH (water)	6.9	5.4	6.6
pH (1 M KCl)	6.7	4.6	5.4
Organic carbon (%)	2.5	1.6	1.8
Organic matter (%)*	4.3	2.8	3.1
Cation Exchange Capacity [meq/100 g]	20.6	9.3	18.1
Water Holding Capacity @ pF 0 (%)	61.6	-**	49.6
Water Holding Capacity @ pF 2.5 (%)	31.8	-**	18.6

* Calculated from organic carbon content by use of a factor of 1.72
** Not reported

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in flow-through systems consisting of glass flasks each containing 50 g of soil and attached to two successive traps for volatile radioactivity (ethanediol to collect non-specific volatiles formed and ethanolamine for carbon dioxide). Soil moisture during incubation was maintained by passing humidified, carbon dioxide-free air through the test systems.

The tests were performed at a test concentration of 19 mg a.s./kg dry weight of soil, based on a field rate of 2 g/m² (20 kg a.s./ha) and assuming homogenous distribution in the top 6 cm of soil.

The test substance [ethyl-1-^{14}C]-fosetyl-Al was applied as aqueous solution drop wise onto the soil surface of the soil samples. Soil samples were adjusted to 40% of the water holding capacity at zero bar (MWHC). The samples were incubated at 20 ± 2 °C under aerobic conditions in the dark for 120 days in maximum.

2. Sampling

Duplicate samples were removed for analysis following 0, 0.25, 0.5, 1, 2, 4 and 8 hours and 1, 2, 7, 14, 30, 60 and 120 days of incubation. Microbial biomass of soil was determined prior to application and at end of the study.

3. Analytical Procedures

Soil samples were extracted twice with 150 mL 0.1 M aqueous formic acid at ambient temperature for 1 hour. Radioactivity in soil extracts was determined by liquid scintillation counting (LSC). Soil extracts were analysed by HPLC combined with ^{14}C-radio-detection. Components were identified by comparison with authentic reference material.
For determination of phosphonic acid/phosphonates formed from application of fosetyl-Al, extracted soil samples were further extracted twice with ammonia buffer. Following a derivatisation step (diazomethane) analysis was performed by gas chromatography (GC).

Non-extractable radioactivity was not determined.
Volatile radioactivity was collected during the incubation phase, but traps were not processed following removal of soil samples for analysis.

4. Determination of degradation kinetics

The kinetic evaluation of data was performed via various approaches including the approach by Timme and Frehse (non-specified software as tool), the software KIM and linear regression assuming first order kinetics to obtain fits to measured data.

II. RESULTS AND DISCUSSION

A. DATA

The results of aerobic biotransformation of [ethyl-1-^{14}C]fosetyl-Al after incubation in soils Clay loam S261, Sand/Sandy loam S262 and Sandy loam S263 were summarised in Table 7.1.1.1- 20 to Table 7.1.1.1- 22.

Table 7.1.1.1- 20: Degradation of [^{14}C]-fosetyl-Al in Clay loam soil S261 under aerobic conditions

Component		Incubation time													
		(hours)							(days)						
	Replicate	0	0.25	0.5	1	2	4	8	1	2	7	14	30	60	120
Fosetyl-Al	mean	28.9	15.0	10.0	6.3	2.0	0.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	0.6	0.9	0.2	1.1	0.1	0.0	-	-	-	-	-	-	-	-
Ethanol	mean	59.4	60.3	57.5	51.3	20.1	1.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	1.6	1.4	1.0	0.6	6.2	0.0	-	-	-	-	-	-	-	-
Unknown 2	mean	7.1	7.6	7.3	5.1	2.9	1.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	2.2	0.8	0.1	0.0	0.9	0.1	-	-	-	-	-	-	-	-
Unknown 5	mean	n.d.	n.d.	n.d.	n.d.	4.2	7.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	-	-	-	-	0.9	0.0	-	-	-	-	-	-	-	-
Total of other Unknowns*	mean	3.8	4.5	3.5	6.9	7.8	7.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total extractable radioactivity	mean	99.2	87.4	78.3	69.7	37.1	17.8	13.9	10.2	10.4	7.5	6.8	5.5	6.1	4.2
	SD	1.3	1.9	1.6	0.9	5.7	0.0	2.8	1.4	0.4	0.1	0.4	0.2	1.8	0.3
Non-extractable radioactivity	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
^{14}C-carbon dioxide	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total radioactivity	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-

All values expressed as percentage of total applied radioactivity
n.d.: not detected; n.a.: not analysed
* Includes total of Unknowns reported as Unknown 1, Unknown 3 and Unknown 4. Maximum occurrence for each of the individual components was below 5% AR at any sampling interval.

Table 7.1.1.1- 21: Degradation of [^{14}C]-fosetyl-Al in Sand/sandy loam soil S262 under aerobic conditions

Component		Incubation time													
		(hours)							(days)						
	Replicate	0	0.25	0.5	1	2	4	8	1	2	7	14	30	60	120
Fosetyl-Al	mean	36.2	9.2	13.2	10.6	11.0	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	5.3	5.0	3.3	2.1	0.0	-	-	-	-	-	-	-	-	-
Ethanol	mean	54.3	75.8	70.1	68.6	67.7	62.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	2.5	4.7	3.4	0.6	4.4	4.5	-	-	-	-	-	-	-	-
Unknown 2	mean	8.6	11.7	11.6	12.8	11.5	6.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	1.6	0.5	0.2	2.0	2.1	1.0	-	-	-	-	-	-	-	-
Total of other Unknowns*	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total extractable radioactivity	mean	99.1	96.7	94.8	92.0	84.7	68.8	50.2	10.0	11.6	2.7	4.0	2.9	1.8	1.5
	SD	1.1	0.2	0.1	0.4	1.0	5.5	0.5	0.3	2.9	0.3	0.8	0.4	0.4	0.4
Non-extractable radioactivity	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
^{14}C-carbon dioxide	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total radioactivity	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-

All values expressed as percentage of total applied radioactivity
n.d.: not detected; n.a.: not analysed
* Includes total of Unknowns reported as Unknown 1, Unknown 3, Unknown 4 and Unknown 5.

Table 7.1.1.1- 22: Degradation of [^{14}C]-fosetyl-Al in Sandy loam soil S263 under aerobic conditions

Component	Replicate	Incubation time													
		(hours)							(days)						
		0	0.25	0.5	1	2	4	8	1	2	7	14	30	60	120
Fosetyl-Al	mean	39.7	15.4	7.0	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	1.2	1.4	0.2	-	-	-	-	-	-	-	-	-	-	-
Ethanol	mean	51.4	65.0	69.8	69.1	53.6	21.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	1.7	1.1	1.0	0.3	2.9	1.7	-	-	-	-	-	-	-	-
Unknown 2	mean	9.7	17.2	16.1	14.6	15.3	3.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	0.7	0.3	0.3	1.6	5.5	0.2	-	-	-	-	-	-	-	-
Unknown 5	mean	n.d.	n.d.	n.d.	n.d.	n.d.	6.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	-	-	-	-	-	0.7	-	-	-	-	-	-	-	-
Total of other Unknowns*	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total extractable radioactivity	mean	100.8	97.6	92.9	83.6	68.9	31.3	12.4	6.8	7.5	4.9	4.6	5.4	2.6	2.4
	SD	0.2	0.1	1.5	1.3	2.6	2.3	2.7	0.2	0.1	1.0	0.6	1.8	0.0	0.6
Non-extractable radioactivity	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
^{14}C-carbon dioxide	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total radioactivity	mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-

All values expressed as percentage of total applied radioactivity
n.d.: not detected; n.a.: not analysed
* Includes total of Unknowns reported as Unknown 1, Unknown 3 and Unknown 4.

B. MATERIAL BALANCE

No full material balance was established for this study. The study was originally designed and conducted during the incubation phase to establish a full material balance of radioactivity. The study focused later on the extractable portion radioactive residues in soil. The results therefore represent values for the degradation of the active substance and for the dissipation of the portion of ethanol formed not being subject to volatilisation under the conditions of the test.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Values of extractable radioactive residues decreased very rapidly with time as summarized in Table 7.1.1.1-23.

Quantitative extractability (98.5 to 99.5% AR) was given by zero hours for all soils indicating extraction efficiency to decrease to 1.5 to 4.2% AR after 120 days of incubation. The decline in extractability was most pronounced within the first day after application, to result in values of total extractable radioactivity to range from 6.8 to 10.2% AR by day 1 after application.

Independent of a full material balance given this allowed for the conclusion that the DT_{90} expressed on the basis of extractable radioactivity was reached by day 1.

Owing to a change in conduct in comparison to test design NER were not determined and thus not quantified.

Table 7.1.1.1- 23: Extractable and non-extractable residues of ^{14}C-fosetyl-Al in three soils

Soil	Extractable residues (%)		Non-extractable residues (%)	
	(0 days)	(120 days)	(0 days)	(120 days)
Clay loam S261	99.2	4.2	n.d.	n.d.
Sand/Sandy loam S262	99.1	1.5	n.d.	n.d.
Sandy loam S263	100.8	2.4	n.d.	n.d.

Values given as percentages of initially applied radioactivity
n.d. = not determined

D. VOLATILE RADIOACTIVITY

Owing to a change in conduct in comparison to its design, volatile radioactivity was collected, however, not investigated following removal of samples for analysis.

E. TRANSFORMATION OF TEST SUBSTANCE

The active substance ^{14}C-fosetyl-Al was extensively transformed to result in ethanol detected as the predominant transformation product (see Table 7.1.1.1- 20 to Table 7.1.1.1- 22).
Since the portion of NER and carbon dioxide or other volatiles formed was not determined, no results were available to formally confirm that degradation was driven by microbial processes.
It should be noted that the results were very well in line and fully consistent with the behaviour observed in other tests performed with the active substance and its metabolite ethanol in aerobic soil (see KCA 7.1.1.1/01 and KCA 7.1.1.1/02).
The transformation of the active substance was very fast to decrease from 28.9% AR after zero hours to 0.5% AR after 4 hours (Clay loam S261), from 36.2% AR after zero hours to 11.0% AR after 2 hours (Sand/Sandy loam S262) and from 39.7% AR after zero hours to 7.0% AR after 0.5 hours (Sandy loam S263).
The portion of ethanol extracted from soil was observed at peak levels of 57.5% AR after 0.5 hours (Clay loam S261), 75.8% AR after 0.25 hours (Sand/Sandy loam S262) and 69.8% AR after 0.5 hours (Sandy loam S263).

A total of five unknown components were observed in soil extracts in the course of incubation. Three components (reported as Unknowns 1, 3 and 4) showed a maximum occurrence below 5% AR for all soils at any sampling interval in the course of the tests.

Unknown 5 was detected in soil Clay loam S261 and Sandy loam S263 at maximum values of 7.1 and 6.1% AR at the last sampling interval analysed (i.e. after 4 hours of incubation), respectively. These values should be put into the context of significant decline of extractability and thus maximum of potential occurrence of Unknown 5 in the course of the test: Total extractability declined from 17.8% AR after 4 hours to 10.4% AR after 1 day for soil Clay loam S261 and from 31.3% AR after 4 hours to 6.8% AR after 1 day for soil Sandy loam S263.
When considering that the origin of radioactive residues is known from the degradation pathway, i.e. ethanol, this additionally lowers any risk to originate from carbon-containing residues in soil following use of fosetyl-Al.

Unknown 2 was detected at maximum levels to occur rather early in the course of incubation, i.e. 7.6% AR after 0.25 hours (Clay loam S261), 12.8% AR after one hour (Sand/Sandy loam S262) and 17.2% AR after 0.25 hours (Sandy loam S263). Values of Unknown 2 showed a decline to 1.1% AR after 4 hours (Clay loam S261), 6.3% AR after 4 hours (Sand/Sandy loam S262) and 3.3% AR after 4 hours (Sandy loam S263) of incubation. Unknown 2 thus showed very transient behaviour to result in half-lives significantly below one day.
Considering again that radioactive residues originate from ethanol, this additionally lowers any risk to originate from carbon-containing residues in soil following use of fosetyl-Al.

Keeping in mind that total extractable radioactivity always consisted of more than a single compound at all sampling intervals, there was no situation given for a single compound to 'accumulate' in the total course of the experiment.

Analysis of extracted soils for phosphonic acid/phosphonates by GC did not result in a clear trend for values determined with time. On the other hand results clearly demonstrated that the degradation of fosetyl-Al had resulted in the presence of substantial amounts of phosphonic acid/phosphonates.

Overall, the results of the study were very well in line and thus fully consistent with the behaviour observed in other tests performed with the active substance and its metabolite ethanol in aerobic soil (see KCA 7.1.1.1/01 and KCA 7.1.1.1/02).

F. DEGRADATION KINETICS

Degradation rates of fosetyl-Al in aerobic soil were calculated using the Timme-Frehse approach, the software KIM and linear regression analysis. The results were summarized in Table 7.1.1.1- 24.

Dependent on method of calculation values of the DT_{50} ranged from 17 to 37 minutes in soil Clay loam S261, 5 to 60 minutes in soil Sand/Sandy loam S262 and 1 to 12 minutes in soil Sandy loam S263.

Table 7.1.1.1- 24: Rate of degradation of fosetyl-Al in three soils under aerobic conditions

Soil	Method	DT_{50} (minutes)	DT_{90} (minutes)	Kinetic model
Clay loam S261	TF	29	96	SFO
	KIM	17	104	SFO
	Linear	37	122	SFO
Sand/Sandy loam S262	TF	21	69	SFO
	KIM	5	369	SFO
	Linear	60	200	SFO
Sandy loam S263	TF	1	13	SFO
	KIM	11	37	SFO
	Linear	12	40	SFO

TFM: Timme-Frehse approach
KIM: software Kinetic Modelling (Thomae)
Linear: Linear regression analysis

III. CONCLUSIONS

Fosetyl-Al and its readily and rapidly formed metabolite ethanol were spontaneously degraded in contact with soil under the aerobic conditions of the test as the result of biological processes.

Half-lives for the degradation of fosetyl-Al were estimated to 17 to 29 minutes (soil Clay loam S261), five to 60 minutes (soil Sand/Sandy loam S262) and one to 12 minutes (soil Sandy loam S263).

The results of the study confirmed earlier information that degradation in aerobic soil contributes significantly to the overall elimination of residues of fosetyl-Al including its rapidly, but transient metabolite ethanol from the environment.

Study evaluation:

The study was performed according to SETAC (1995) guidelines for testing. Therefore, its design and conduct included the essential elements necessary and that can be found in actual designs in testing, in particular for determination of the rate of degradation in soil.

With the key elements in design and conduct given along with consistency of results there is no reason to exclude the study from kinetic evaluation and thus from use in environmental risk assessment.

The results are well in line with other data available on route of degradation (see study KCA 7.1.1.1/01) and confirm the understanding of the behaviour of fosetyl-Al residues in soil.
The study design was thus able to demonstrate qualitatively and quantitatively the key principles in degradation of fosetyl-Al residues in soil.
The study confirmed ethanol to be the volatile, transient product of degradation besides carbon dioxide as terminal mineralisation product within very short time, i.e. hours after application.

Despite progress made in analysis and analytical methods, the results of the study clearly indicate also the challenges (i.e. material balances, distribution of radioactivity in soil extracts and volatiles and their kinetic evaluation) in the investigation of extremely rapidly degradable active substances forming volatile, fast degrading components in the following.
Any repetition would therefore not result in a different understanding of transformation processes, transformation products formed and thus the behaviour of fosetyl-Al residues in aerobic soil.

Conclusively, the study is regarded as valid for use as information the route and rate of degradation of fosetyl-Al and ethanol in soil.

Report:	KCA 7.1.1.1/04 [redacted]; [redacted]; 1953; M-234773-01-1
Title:	Transition of phosphite to phosphate in soils
Report No.:	C034352
Document No.:	M-234773-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	no

Executive Summary

The objective of the publication was to determine the mechanism of oxidation involved in the transformation of phosphonates to phosphate in aerobic soil.
The biotransformation of phosphonate, applied in the form of the disodium penta hydrate, Na_2HPO_3 x 5 H_2O, was investigated under aerobic conditions of the laboratory in US soil San Joaquin clay loam. Soils samples were incubated in the dark at 28 °C and soil moisture at field capacity for 16 weeks (approx. 112 days) in maximum. The nominal test concentration was 80 mg 'phosphorus trioxide' (P_2O_3) equivalents/kg soil.

Chemical analysis for phosphonate (phosphite) was performed indirectly by determination of the amount of phosphate in soil extracts prior to and the total phosphate after oxidation of phosphonates by iodine for the same soil sample.
Following application of phosphonate, values of phosphonate residues decreased from 1.95 mg[5] by week four to 0.97 mg by week 16.
At the same time, values of phosphate residues increased from 9.5 mg by week four to 10.4 mg by week 16.

[5] Residues of phosphonates in soil were expressed by the term phosphorus trioxide (P_2O_3) equivalents recovered/25 g subsample of soil in order to make the various portions of phosphorus involved comparable.

The influence of chemicals like toluene impacting as fumigating-type agents on microbial activity in soil was investigated in parallel.
Following application of phosphonate and incubation under the influence of toluene, values of phosphonate residues were 1.95 mg by week four to remain constant at 1.95 mg by week 16.
At the same time, values of phosphate residues remained also nearly constant, i.e. 9.3 mg by week four and 9.4 mg by week 16.

The fact that the phosphonate concentration declined in soil combined with an increase of the total phosphate concentration during the same time served as the indication that phosphonate had been transformed in soil to phosphate.
The results from samples incubated under the influence of toluene indicated that the transformation of phosphonate in soil was hindered by fumigating, soil sterilizing agents thus reducing soil microbial activity and its ability for transformation of phosphonate to phosphate in soil.

It was therefore concluded that the transformation process of phosphonate to phosphate in soil was related to microbial processes.
There were also indications that the process of microbial oxidation of phosphonates was not a sole surface phenomenon, but phosphonates to be absorbed or assimilated as a nutrient by actively growing microorganisms before being oxidized.

No kinetic evaluation of the data for a rate of degradation in soil was performed.

In view of major deviations from actual standards in testing of route and rate of degradation in soil and the low number of sampling intervals the results of the study was excluded from use in environmental risk assessment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Disodium phosphonate penta hydrate (Na_2HPO_3 x 5 H_2O)

Sample ID:	not reported
Specific Activity:	not reported
Radiochemical Purity:	not reported
Chemical Purity:	not reported

2. Test Soils

The soil reported as San Joaquin clay loam had been sieved to≤ 0.8 mm in comparison to the standard of 2 mm. No physico-chemical characteristics were reported.

B. STUDY DESIGN

1. Experimental Conditions

Particular incubation conditions such as the use of flow-through or static conditions were not reported. The test substance was applied to 400 g soil samples of which a 25 g subsample was removed for analysis after incubation.
The incubation was performed under aerobic conditions in the laboratory in the dark at 28 °C for 16 weeks (approx. 112 days) in maximum. Soil moisture was adjusted to field capacity with distilled water.

The tests were performed at a test concentration of 100 mg disodium phosphonate/kg dry weight of soil, applied in the form of its penta hydrate ($Na_2HPO_3 + 5\ H_2O$) and equivalent to 80 mg 'phosphorus trioxide' (P_2O_3) equivalents/kg soil. No reference was made to a field rate.
The investigations included the incubation of soil treated with toluene as sterilizing/fumigating agent to demonstrate the influence of biotic, microbial nature of conversion of phosphonate to phosphate in soil.

Additional potential parameters of influence on microbial activity in soil samples were investigated by variation and maintenance of sterile conditions of soil (for example, toluene *versus* autoclavation and autoclavation plus toluene during incubation) or, the amendment starch to samples to support microbial activity in soil. Being beyond the standards in actual test designs in soil degradation and by not contributing to an overall better understanding of the behaviour of phosphonate in soil, the results were not summarized in detail.

2. Sampling

Single subsamples (i.e. 25 out of 400 g) were removed for chemical analysis 4, 8, 12 and 16 weeks after treatment.

3. Analytical Procedures

The soil subsamples of 25 g were extracted by boiling the mixture gently with 250 mL 2 N aqueous hydrochloric acid for 15 minutes. Aliquots of soil extract were passed through an ion exchange column filled with the sodium-saturated resin Amberlite IR.

Chemical analysis for phosphonate (phosphite) was performed indirectly by determination of the amount of phosphate in soil extracts prior to and the total phosphate after oxidation of phosphonates by iodine.
For determination of phosphate a modification of the method of Deniges (i.e. colorimetric method) was used. Reference to the method was given, however, no details were reported nor modifications made to the original method described.
Oxidation of phosphonates was performed by slightly alkalisation of the acidic soil extract (10 mL aliquot) with saturated aqueous sodium hydrogen carbonate ($NaHCO_3$) solution followed by addition of 5 mL aqueous 0.01 N iodine solution. The mixture was allowed to stand at room temperature for 15 minutes. Following acidification (2 mL aqueous 2 N sulphuric acid, H_2SO_4) the excess of iodine was back-titrated with 0.01 N aqueous sodium thiosulfate ($Na_2S_2O_3$) solution (disappearance of brown iodine colour).
Again, the determination of phosphate after oxidation of phosphonates followed the modified method of Deniges.

4. Determination of degradation kinetics

No kinetic evaluation of degradation data for a rate of degradation in soil was performed.

II. RESULTS AND DISCUSSION

A. DATA

The results of aerobic biotransformation of disodium phosphonate after incubation in San Joaquin clay loam soil were summarised in Table 7.1.1.1- 25 to Table 7.1.1.1- 26.

Table 7.1.1.1- 25: Dissipation of disodium phosphonate and determination of phosphate in San Joaquin clay loam soil incubated at 28 °C under aerobic conditions

Component	Sample	Sampling interval (weeks)				
		0	4	8	12	16
Phosphonate	Mean *	n.d.	1.95	1.51	1.15	0.97
	SD	n.d.	n.d.	n.d.	n.d.	n.d.
Phosphate	Mean *	n.d.	9.5	9.8	10.2	10.4
	SD	n.d.	n.d.	n.d.	n.d.	n.d.

Values given as mg 'phosphorus trioxide' (P_2O_3) equivalents/25 g subsample of soil recovered

* Averages of four 25 g subsamples of one soil sample each extracted with 2 N aqueous hydrochloric acid. The nominal amount applied to 25 g subsample of soil was 2.04 mg.

SD = standard deviation, n.d. = not determined/not reported

Table 7.1.1.1- 26: Dissipation of disodium phosphonate and determination of phosphate in San Joaquin clay loam soil under aerobic conditions at 28 °C - influence of toluene as fumigant

Component	Sample	Sampling interval (weeks)				
		0	4	8	12	16
Phosphonate	Mean *	n.d.	1.95	2.04	1.95	1.95
	SD	n.d.	n.d.	n.d.	n.d.	n.d.
Phosphate	Mean *	n.d.	9.3	9.2	9.4	9.4
	SD	n.d.	n.d.	n.d.	n.d.	n.d.

Values given as mg 'phosphorus trioxide' (P_2O_3) equivalents/25 g subsample of soil recovered

* Averages of four 25 g subsamples of one soil sample each extracted with 2 N aqueous hydrochloric acid. The nominal amount applied to a 25 g subsample of soil was 2.04 mg.

SD = standard deviation

B. Verification of extraction procedures

Recoveries of phosphonate applied to soil samples at day zero were not reported.

C. Decline of residues of phosphonate in soil

Residual concentrations of phosphonate in soil in terms of the amount of phosphonate recovered in a 25 g subsample showed a decline from 1.95 phosphorus trioxide (P_2O_3) equivalents/kg soil after four weeks to 0.97 phosphorus trioxide (P_2O_3) equivalents/kg soil after 16 weeks (approx.112 days) of incubation.

In turn, values of phosphate determined in the same samples showed an increase with time, *i.e.* from 9.5 phosphorus trioxide (P_2O_3) equivalents/kg soil after four weeks to 10.4 phosphorus trioxide (P_2O_3) equivalents/kg soil after 16 weeks (approx.112 days) of incubation.

For samples incubated under the influence of toluene as soil fumigant, no decline of the concentration of phosphonate was observed, i.e. values were 1.95 phosphorus trioxide (P_2O_3) equivalents/kg soil after four weeks and 1.95 phosphorus trioxide (P_2O_3) equivalents/kg soil after 16 weeks (approx.112 days) of incubation.

Values of phosphate determined in the same samples were nearly constant, i.e. 9.3 phosphorus trioxide (P_2O_3) equivalents/kg soil after four weeks and 9.4 phosphorus trioxide (P_2O_3) equivalents/kg soil after 16 weeks (approx.112 days) of incubation.

The fact that the phosphonate concentration declined in soil combined with an increase of the total phosphate concentration during the same time served as the indication that phosphonate had been transformed in soil to phosphate.

The results from samples incubated under the influence of toluene indicated that the transformation of phosphonate in soil was hindered by such fumigating, soil sterilizing agents thus influencing soil microbial activity and its ability for transformation of chemicals in soil.
The influence of toluene was documented by no decline of phosphonate concentration in soil and the concentration of phosphate measured being nearly constant throughout incubation.

The mechanisms of oxidation processes in soils were discussed to consist of at least three general categories: (a) chemical or catalytic, (b) enzymatic, and (c) biological. Explaining the transformation in soil by category a) would result in phosphonate oxidation to proceed at about equal rates for all treatments. The involvement of category b) would result in the oxidation to proceed equally for all samples, but not for sterilised (autoclaved) soils. Obviously, the findings could not be explained by the first two categories.

The oxidation of phosphonates was observed for soil samples when microbial activity was not inhibited. In turn, little or no oxidation of phosphonates occurred microbial activity was hindered by toluene. It was therefore concluded that the transformation process in soil was related to microbial processes.

There were also indications that the process of microbial oxidation of phosphonates was not a sole surface phenomenon, but phosphonates to be absorbed or assimilated as a nutrient by actively growing microorganisms before it was oxidized.

III. CONCLUSIONS

The study results showed that the transformation of phosphonates to phosphate in soil was driven by microbial processes.
The objective of the study thus focused on principles of phosphonate biotransformation in soil.

Owing to the focus of the study it was not a major objective in design to follow accurately the decline of phosphonate concentration in soil with time in the sense of actual designs of studies on route and rate of degradation.
No efforts were thus undertaken to confirm essential details like the concentration of test item applied by day zero and, in parallel, the extraction efficiency. The latter is standard in actual designs of tests on route and rate of degradation in soil.
Moreover, four subsamples of 25 g were taken from a sample containing 400 g in total. Actual standards in tests on route and rate of degradation in soil require the processing of the whole soil sample at date of analysis. Such processing allows for clear material balances thus avoiding potential inconsistencies of results from sample inhomogeneity.
With no analysis performed for samples of day zero the total number of sampling intervals available for kinetic analysis was reduced to just four.
In view of major deviations from actual standards in soil degradation testing in the laboratory, the study was not regarded as valid to derive a reliable degradation rate for phosphonates in aerobic soil.

The study thus served as supplemental information on the route of degradation of phosphonates in aerobic soil.

Report:	KCA 7.1.1.1/05 [redacted] L; 1960; M-234777-01-1
Title:	Microbial oxidation and utilization of orthophosphite during growth
Report No.:	C034355
Document No.:	M-234777-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary
The objective of the publication was to find microorganisms able to take up phosphorus originating from phosphonate and to accumulate the oxidation product, phosphate in the growing medium. This would have given an insight into the mechanism phosphonates to become available for microbial growth.
Experiments were performed on culture media for microbes only and thus in the absence of soil or soil extracts.

Out of 23 microbial cell cultures investigated, a number of 14 utilised phosphonate for growth, however, only the bacterial strain *Pseudomonas fluorescens* 195 'accumulated' phosphate in the medium following the objectives of the study.
Further investigations with *Pseudomonas fluorescens* 195 resulted in reduced phosphate release to the medium.

The information therefore does not contribute directly to the understanding of the route of degradation in soil. The publication thus served as supplemental information about the potential mechanisms of uptake and use of phosphonate by microbes.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item
Unlabelled Na_2HPO_3 was used as phosphonate source for the microorganisms tested.

2. Test Microorganisms
In total 23 microbial cultures representing different genera (e.g. *Pseudomonas*, *Rhizobium*, *Agrobacterium*, *Azotobacter*) and species (*P. fluorescens*, *P. denitrificans*, *A. radiobacter*, *A. tumefaciens*) were used in the experiments.

3. Test Medium
For the inoculum a liquid phosphonate medium (pH 7) was used consisting of glucose (0.5 g/L), yeast extract (Difco, 0.1 g/L); $(NH_4)_2SO_4$ (2 g/L), KCl (0.1 g/L); $FeSO_4 \times 7H_2O$ (0.01 g/L), $MnSO_4 \times H_2O$ (0.01 g/L), $MgSO_4 \times 7H_2O$ (0.03 g/L), $CaCl_2$ (trace), $Na_2HPO_3 \times 5H_2O$ (2 g/L). The latter compound, as a 10% solution, was adjusted to pH 7 with HCl and sterilized separately by passage through a glass filter or by autoclaving 10 min at 121 °C (15 lb pressure). The medium used for growth and phosphonate oxidation studies differed from the above only in that the glucose concentration was at 2.5 g/L.

B. STUDY DESIGN

1. Experimental Conditions
For growth and phosphonate oxidation studies the growth medium was dispensed at 50 or 75 ml in a 250 mL Erlenmeyer flask and was inoculated with 3 drops of a respective culture which had been shaken 48 h at 25 °C. These flasks then were shaken on a Brunswick rotary shaker at 25 °C for up to four days. For experiments conducted at 37 °C a reciprocating shaker was used.

2. Sampling
Samples were taken on a daily basis.

3. Analytical Procedures
Samples were centrifuged to remove the cells and orthophosphate phosphorous in the supernatant was determined by the method of Dickman and Bray[6]. Orthophosphonate phosphorous was determined by the modified procedure of [redacted] and [redacted][7] using enough sulphuric acid to adjust pH to < 6. Residual carbohydrate in culture broth was determined by the anthrone method[8]. The number of viable microorganisms in culture broths was determined by the plate count technique.

For fermentation analysis for growth of strain 195 daily samples taken during 4 days of shaking at 25 °C were centrifuged and the supernatant solutions were analysed for orthophosphate phosphorus, total of orthophosphonate plus orthophosphate phosphorus, pH, viable cells and residual carbohydrate as glucose.

The effect of the source of carbon for growth was studied by replacing the glucose of the medium with other carbon sources at the same concentration and with DL-alanine.

II. RESULT AND DISCUSSION

A. SURVEY OF MICROORGANISMS
Nineteen cultures, including bacteria, yeasts, actinomycetes and fungi were initially tested. Ten of these cultures grew during shaking for 3 days at 25 °C. It has been shown that certain microorganisms can utilize orthophosphonate phosphorus as a source of phosphorus for growth. Nine out of the 10 were gram-negative bacteria. Analyses for orthophosphate in 0.5 mL samples of these cultures revealed that only *Pseudomonas fluorescens* strain 195 had accumulated free orthophosphate in the medium.

Other members of the genus *Pseudomonas* were tested to see whether orthophosphate accumulation during growth on orthophosphonate might be a general characteristic of this genus. The plate count determinations revealed that all of the *Pseudomonas* strains grew well with phosphonate phosphorus at 25 and 37 °C (except for one strain). Except for strain 195, no orthophosphate phosphorus was detected in the supernatants of the other cultures regardless of whether grown at 25 or 37 °C.

B. FERMENTATION ANALYSIS FOR GROWTH OF STRAIN 195 ON PHOSPHONATE MEDIUM'
Fermentation analysis for growth of strain 195 showed that although the most rapid rate of growth occurred within the first 24 hours, phosphate phosphorus did not begin to appear in the medium until the second day, from which time the concentration increased in a linear fashion through the third or fourth day. Cessation of the linear appearance of phosphate phosphorus coincided approximately with the initiation of a maximal stationary phase of growth and with the disappearance of carbohydrate from the medium. Thus the accumulation of orthophosphate occurs during rapid cell multiplication and carbohydrate utilization and is not necessarily a result of death and autolysis of old cells.

[6] Dickman, S. R. and Bray, R. H. 1940 Colorimetric determination of phosphate. Ind. Eng. Chem. Anal. Ed., 12, 665-66S.
[7] [redacted], F. and [redacted], J. P. 1953 Transition of phosphite to phosphate in soils. Soil Sci., 76, 361-371.
[8] Morris, D.L. 1948 Quantitative determination of carbohydrates with Dreywood's anthrone reagent. Science, 107, 254-255.

C. EFFECT OF MEDIUM CONSTITUENT VARIATION ON PHOSPHONATE OXIDATION

If phosphonate oxidation is a function of cell growth and metabolism then variations in the medium constituents should have a marked effect on the rate of orthophosphate accumulation in culture broths. Investigations on the effect of the source of carbon for growth revealed that orthophosphate accumulation occurred only with glucose and alanine. When the salt solution, which consisted of trace amounts of iron, manganese, magnesium and calcium, was not present phosphate accumulation did not occur and the amount of growth was negligible. The absence of yeast extract in the medium also had a marked effect on orthophosphate accumulation. Where no yeast extract was added to the medium, growth was retarded by one day and orthophosphate did not accumulate until the third day, at which tune a relatively large accumulation occurred. Initial addition of trace amounts of orthophosphate to these flasks did not have any appreciable effect. Also, in media containing yeast extract the effect of orthophosphate was negligible. All variations tried in the growth medium resulted in reduced accumulation of orthophosphate phosphorous.

III. CONCLUSIONS

It was shown that soil microorganisms utilized orthophosphate for growth under aerobic conditions and that one strain of *Pseudomonas fluorescens* (strain 195) was able to also accumulate the oxidation product, orthophosphate, in the growth medium. This accumulation occurred after most of the initial phosphorus demands for growth was met and continued in a linear fashion as long as carbohydrate was present. Cessation of the linear appearance of orthophosphate in the medium coincided with the onset of a maximum stationary phase of growth. Thus the accumulation of orthophosphate occurred during rapid cell multiplication and carbohydrate utilization and was not necessarily a result of death and autolysis of old cells.

Conclusively, the information therefore does not contribute directly to the understanding of the route of degradation in soil. The publication thus served as supplemental information about the potential mechanisms of uptake and use of phosphonate by microbes.

Report:	KCA 7.1.1.1/06 [redacted], [redacted]; 1966; M-234784-01-1
Title:	Bacterial oxidation of orthophosphite
Report No.:	C034350
Document No.:	M-234784-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	no

Executive Summary

Relying on the earlier publications referring to bacterial oxidation, the objective of the publication was to provide information on the processes involved to oxidise phosphonate to phosphate by microorganisms.

The investigations were performed against the background as to whether the change of the oxidation state of phosphorus from +3 (phosphonate) to +5 (phosphate) might play a role in biological phosphorus cycles.

Experiments were performed on culture media for microbes only and thus in the absence of soil or soil extracts.

The ability to utilize phosphonate as a sole source of phosphorus for growing in cell media was shown for a number of bacteria. The two bacteria *Pseudomonas fluorescent 195* and *Serratia marcescens 24* were investigated in more detail. From growth rates and total cell yields of the bacteria it was concluded that the bacteria could use phosphonate as efficient as phosphate.

The information therefore does not contribute directly to the understanding of the route of degradation in soil. The publication thus served as supplemental information about the potential mechanisms of uptake and oxidation of phosphonate by microbes.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Unlabelled sodium orthophosphonate (Na_2HPO_3) was used as phosphorus source for the microorganisms tested. It was shown that the sodium phosphonate reagent used did not contain significant amounts of phosphate.

2. Test Microorganisms

In total eight microbial cultures representing different genera and species were used in the experiments: *Aerobacter aerogenes* 68, *Bacillus megaterium* WS, *B. subtilis* 19, *Escherichia coli* H, *Pseudomonas aeruginosa* Lilly, *P fluorescens* 195, *Serratia marcescens* 24, *S. marcescens* 235.

3. Test Medium

Cultures were grown under shaking in sterilized basal medium (glucose, NH_4Cl, Na_2SO_4, $MgCl_2$ x $6H_2O$, tris(hydroxymethyl)aminomethane (Tris)), adjusted to pH 7.0 with HCl. Liquid media contained a single filter-sterilized phosphorus source added to the basal medium at a final concentration of 10 µg of phosphorus per mL. Solid media were prepared by the addition of Ionagar and a phosphorus source (phosphate or phosphonate) to the basal medium to final concentrations of 0.85% and 20 µg/mL, respectively. It was shown that the basal medium did not contain a significant amount of phosphorus contamination.

B. STUDY DESIGN

1. Experimental Conditions

All cultures were grown at 30 °C, with the exception of *Bacillus subtilis*, *B. megaterium*, and *Escherichia coli* which were grown at 37 °C, and *Pseudomonas fluorescens* 195 which was grown at 25 °C.

2. Sampling

Samples were taken at intervals during the incubation period.

3. Analytical Procedures

Phosphate and phosphonate were isolated by anion-exchange chromatography and the phosphorus content of each fraction was determined by a modification of the phosphovanadomolybdate method [9]. The anions were eluted from the column at room temperature by a gradient of KCl (buffered at pH 6.8 with ammonium acetate). The method of Chen, Toribara, and Warner[10] was employed in all other phosphorus assays.

The number of viable microorganisms in culture broths was determined by the plate count technique. Bacteria grown in liquid phosphate medium were plated after appropriate dilution on solid medium containing phosphate, phosphonate or no added source of phosphorus. The plates were incubated at the appropriate temperatures for 3 to 12 days.

[9] Pollard, F. H., D. E. Rogers, M. T. Rothwell, G. Nickless. 1962. Separation of hypophosphite, phosphite, and phosphate by anion exchange chromatography. J. Chromatog. 9:227-230.

[10] Cen, P. S., T. Y. Toribara, H. Warner. 1956. Microdetermirmtion of phosphorus. Anal. Chem. 28:1756-1758.

Assay of phosphonate-oxidizing activity of resting-cell suspensions
Cells were harvested from liquid media containing either phosphate or phosphonate as the sole phosphorus source, washed once with KCl, and re-suspended in Tris-maleic acid buffer (0.1 M, pH 7.0) to a protein concentration of 3.8 mg/mL. To initiate the reaction, sodium phosphonate was added to the cell suspension and, at intervals during shaking at 25 °C, 0.5 mL samples were diluted into KCl and centrifuged. The supernatant liquids were stored at 2 °C until assayed for phosphate.

Assay of phosphonate-oxidizing activity of cell-free extracts
Cells were harvested from either the phosphonate or phosphate medium, washed once with acetate buffer (0.1 M, pH 6.0), re-suspended in buffer, and crushed in a French press. After centrifugation, the extract was diluted in buffer to a protein concentration of 2 mg/mL. An acetate-buffered sodium phosphonate solution (100 mg/mL) was added to the extract to initiate the reaction. For the measurement of the endogenous accumulation of inorganic phosphate, acetate buffer was added to the extract. The reaction mixtures were incubated at 25 °C. At intervals, 0.4 mL samples were withdrawn and added to an equal volume of 10% trichloroacetic acid. After standing for 10 min, distilled water was added, and the suspensions were centrifuged. The supernatant liquids were stored at 2 °C until assayed for phosphate.

II. RESULTS AND DISCUSSION

A. ABILITY OF BACTERIA TO UTILIZE PHOSPHONATE AS SOLE SOURCE OF PHOSPHORUS

Several strains of bacteria were found to be capable of growth in the liquid medium containing phosphonate as a sole source of phosphorus. However, phosphate-grown cells inoculated in phosphonate medium seldom attained an exponential growth rate within 48 hours.

Those bacteria capable of growth on phosphonate acquired the ability to utilize phosphonate by adaptation of the entire population rather than by the growth of small numbers of mutants, since the colony counts on phosphonate solid medium were equal to the colony counts on phosphate medium. No growth of any of bacteria examined was observed on the solid medium lacking an added phosphorus source.

When phosphate-grown *P. fluorescens* 195 and *S. marcescens* 24 were transferred to medium containing a growth-limiting amount of phosphate and excess phosphonate, a typical diauxie effect was observed. The initial long lag which preceded growth in fresh liquid medium was characteristic of *P. fluorescens* 195 and was independent of the age or size of the inoculum, the carbon or phosphorus source and the incubation temperature. After adaptation to growth on phosphonate, the reaction of the bacterium when it was transferred to phosphonate liquid medium was identical to that of phosphate-grown cells when they were transferred to phosphate liquid medium. The growth rates were identical in both phosphonate and phosphate liquid media.

Since only those varieties of bacteria which were able to grow on the synthetic medium were tested, the possibility exists that several other types of bacteria not examined possess the ability to utilize phosphonate. The period of adaptation observed prior to growth on phosphonate and the absence of phosphonate-oxidizing activity of extracts obtained from cells grown in liquid phosphate medium are similar to the characteristics of the well-documented inducible enzyme systems for the utilization of carbon sources and suggest that the induction period is required for the synthesis of an enzyme responsible for the oxidation of phosphonate.

It was reported in previous studies that phosphate is reduced by microorganisms under anaerobic conditions to phosphonate and hypophosphonate and that detectable amounts of these compounds appeared in the culture medium. Since most phosphorus assays involve the oxidation of all phosphorus materials to inorganic orthophosphate, small amounts of phosphonate in nature may have escaped detection. Various species of bacteria may, therefore, have retained the ability to oxidize phosphonate as a result of continual exposure to the anion.

B. OXIDATION OF PHOSPHONATE BY RESTING CELLS

Resting cell suspensions prepared from *P. fluorescens* 195 grown in phosphonate medium were capable of oxidizing phosphonate to phosphate, although the activity was quite low. However, no activity was detected in phosphate-grown cells.

C. OXIDATION OF PHOSPHONATE BY CELL-FREE EXTRACTS

Cell-free extracts of *P. fluorescens* 195 prepared from cells harvested during the exponential phase of growth in phosphonate medium possessed considerable phosphonate-oxidizing activity. No activity was detected in cell-free extracts prepared from phosphate-grown cells. Heating the active preparations at 70 °C for 2 min completely destroyed the activity.

The large difference in activity between intact and cell-free systems is not readily explained. However, it was observed that the presence of an oxidisable carbon source enhanced whole-cell phosphonate-oxidizing activity. This suggests that the uptake of the anion may be coupled to an energy-requiring step. Alternatively, since the assay system employed is dependent upon the oxidation product's being present in the supernatant liquid, the observed low rate of phosphonate oxidation may indicate that the discharge of phosphate from the cells is the rate-limiting step in the process.

III. CONCLUSIONS

The results of the experiments presented have confirmed previous reported results and, in addition, that the ability of certain bacterial populations to utilize phosphonate as a sole source of phosphorus is obtained through induction of the entire population rather than by selection of small numbers of mutant organisms. Since only those varieties of bacteria which were able to grow on the synthetic medium were tested, the possibility exists that several other types of bacteria not examined possess the ability to utilize phosphonate.

The information therefore does not contribute directly to the understanding of the route of degradation in soil. The publication thus served as supplemental information about the potential mechanisms of uptake and oxidation of phosphonate by microbes.

Report:	KCA 7.1.1.1/07 [redacted],; [redacted]; [redacted]; 2001; M-234787-01-1
Title:	Phosphite (phosphorous acid): Its relevance in the environment and agriculture and influence on plant phosphate starvation response
Report No.:	C034360
Document No.:	M-234787-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The publication is a review article dealing with the relevance of phosphonate following its use in agriculture and industry. The review summarizes aspects of potential input of phosphonates into food products and the impact in the environment.

Phosphonic acid [HPO(OH)$_2$] applied in the form of alkali metal salts, i.e. as phosphonates ($H_2PO_3^-$), may act as a fungicide or, as a phosphorus source for plant nutrition.

Evidence that phosphonate can be directly used by plants as a sole source of nutritional phosphorous is lacking. However, transformation of phosphonate to phosphate (HPO_4^{2-}) may take place as the result of microbial oxidation processes.

The information does not contribute directly to a better understanding of the route of degradation in soil. The publication thus served as supplemental information about some principles of occurrence and oxidation of phosphonate in the environment.

I. INTRODUCTION

Phosphorus is one of the major and essential elements required by all living species. Phosphorus does not occur as the free element in nature being very reactive, in particular when combining with oxygen.

When Phosphorus is oxidised to the fullest extent, the product is phosphate (PO_4^{3-}) being present at neutral pH in the form of HPO_4^{2-} or $H_2PO_4^-$ ions. $H_2PO_4^-$ ions are transported into plant cells to serve for cellular bioenergetics, metabolic regulation and as important structural component of macromolecules such as nucleic acids and phospholipids.

Phosphorus in the form of phosphate thus also plays a critical role in metabolic processes in plants, including photosynthesis and respiration. However, phosphate is one of the least available nutrients in many aquatic and terrestrial ecosystems resulting in the need to use phosphate as fertilizer.

In addition, phosphonates ($H_2PO_3^-$) have been applied to improve the yield of many crops. The article tried to provide an objective summary of phosphonate's chemistry and biology.

II. CHEMISTRY OF PHOSPHATE VERSUS PHOSPHONATE

In phosphonate, the formal replacement of an oxygen atom by hydrogen results in the oxidation form +3 in comparison to +5 for phosphate.

The oxidation stage and the molecular structure in comparison to phosphate influence the binding to enzymes and phosphonate cannot enter into the same biochemistry as phosphate.

III. BACTERIAL PHOSPHONATE METABOLISM

In soil, the oxidation of phosphonate to phosphate in soil was found to be largely due to the microbial activity within the soil to be enzymatically oxidized to phosphate before being incorporated into organic forms or plants.

The existence of a chromosomal region dedicated to the microbial metabolism of reduced phosphorous compounds indicates that a redox cycle for phosphorous may be important in the metabolism of phosphonates by microbes.

IV. THE USE OF PHOSPHONATE IN AGRICULTURE

Phosphonate was determined to be a very poor source of phosphorus, owing to the conversion to phosphate necessary first before to become relevant for plant nutrition.

Phosphonate was shown to effectively suppress several fungal plant diseases when being applied in the form of the ethyl ester derivative fosetyl-Al or in the form of the potassium salt. It is assumed that direct deleterious effects of phosphonate on Phytophthora metabolism are important in controlling the diseases which it causes in plants.

V. INFLUENCE OF PHOSPHONATE ON PLANT AND YEAST PHOSPHATE STARVATION RESPONSES

Since phosphonate is phloem mobile and accumulates in sink tissues, plants treated with fosetyl-Al or phosphonate rapidly amass phosphonate within their cells. As plants are unable to metabolize phosphonate, it persists in tissues for extensive periods.

The effect of phosphonate on different plant was investigated in several studies and it was hypothesized that phosphonate exerts its effect on the signalling pathway(s) responsible for the detection of. and response to, internal phosphate levels. Phosphonate treatment negates the acclimation of plants to phosphate deficiency by disrupting the induction of enzymes (e.g., acid phosphatase) and transporters (e.g., high affinity plasma lemma phosphate translocator) characteristic of their phosphate starvation response. Thus, phosphonate intensifies deleterious effects of phosphorus-deficiency by 'tricking' phosphate-deprived plant cells into sensing that they are phosphate-sufficient, when, in fact, their cellular phosphate content is extremely low.

VI. PHOSPHONATE AS PHOSPHORUS FERTILIZER

There is no evidence published in peer-reviewed scientific journals which clearly documents that plants can use phosphonate as a direct source of phosphorus. Phosphonate could, of course, be indirectly providing phosphorous to the plant after its oxidation to phosphate by soil dwelling bacteria. However, relative to phosphate fertilizers, this is not a cost effective or efficient means of meeting the phosphorous requirements of plants. If anything, phosphonate functions as an 'antifertilizer' as it has a profoundly negative influence on plant growth and metabolism when nutritional phosphate levels are not optimal.

VII. PHOSPHONATE IN THE ENVIRONMENT

There may be several concerns regarding the use of phosphonates in agriculture and high-tech industries. Phytophthora species may become resistant and phosphonate treatment of plants may have a side effect on soil microflora.

Besides this, it is important that farmers ensure that crops are in a well fertilized stage with phosphate prior to phosphonate application.

Anyway, phosphonate residues levels in food are well regulated to ensure that chronic consumption of phosphonate treated products do not pose a threat to the consumer.

VIII. CONCLUSIONS

The information does not contribute directly to a better understanding of the route of degradation in soil. The publication thus served as supplemental information about some principles of occurrence and oxidation of phosphonate in the environment.

Report:	KCA 7.1.1.1/09 [redacted],; [redacted]; 1957; M-234780-01-1
Title:	Fractionation of soil phosphorus
Report No.:	C034357
Document No.:	M-234780-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The objective of the publication was to introduce a method for fractionation of soil phosphorus in order to identify the portion available to plants.

The total phosphorus present in soil in the form of inorganic phosphate can be classified into the four main groups calcium phosphate, aluminium phosphate, iron phosphate, and reductant-soluble phosphate being the extractable portion after removal of the first three forms.

The method for fractionation of soil inorganic phosphate was established using synthetic forms of iron phosphate and aluminium phosphate and, of an apatite of known composition for tests with soil samples.

Soil phosphorus availability to plants is suggested to depend on the extensity of the phosphate surface of the various chemical species. Conventional methods for the determination of available phosphorus may extract a portion of all chemical forms. In contrast, the approach presented in the publication allows for the fractionation of inorganic soil phosphorus into the total amount of each discrete chemical form. This would permit the determination of the chemical status of native soil phosphorus and of the fate of applied phosphate fertilizer with or without the effect of cropping.

The information therefore does not contribute directly to the understanding of the route of degradation of fosetyl-Al in soil. The publication thus served as supplemental information about the separation, nature and behaviour of phosphate residues in soil.

I. MATERIALS AND METHODS

A. MATERIALS

For control tests of the new system of soil inorganic phosphate fractional on, synthetic iron phosphate, synthetic aluminium phosphate, and apatite of known composition were employed. The methods were then tested with soil samples.

Table 7.1.1.1- 27: Physico-chemical properties of test soils

Parameter	**Soil**			
Soil Designation	Catalina	Wahiawa clay loam	Miami silt loam	Barnes silt loam
Soil type	Latosol	Latosol (low humic)	Podzol	Chernozem
Geographic Location				
City	Catalina	Wahiawa	Miami	Barnes
Country	Puerto Rico	USA	USA	USA
Texture	not reported	Clay loam	Silt loam	Silt loam
pH	6.2	6.7	4.9	8
Extractable Fe_2O_3 (%)	18.2	10.1	1.7	0.93
Total P (%)	not reported	not reported	0.036	0.02

B. FRACTIONATION PROCEDURE FOR SOIL PHOSPHOROUS

1. Extraction and determination of phosphorus in aluminium phosphate

Soil samples were extracted with 1 N NH_4Cl to remove water soluble and loosely bound phosphorus and the exchangeable calcium. After separation from the supernatant, the soil was further extracted using neutral 0.5 N NH_4F. The soil was separated from solution by centrifugation and decantation. The clear supernatant was used for determination of phosphorus and the extracted soil was used for the extraction of iron phosphate. For determination of aluminium phosphate in the extract subsequently distilled water, 0.8 M boric acid and chloromolybdic acid solution were added to an aliquot of NH_4F-extract and the solution was well mixed after each addition. Then, chlorostannous reductant ~~A~~ (10 g $SnCl_2$ x $2H_2O$ dissolved in 25 HCl conc.) was added to develop the colour. After addition of water, the colour was measured on a photoelectrocolorimeter at 660 nm within 5 to 20 minutes.

2. Extraction and determination of phosphorous in iron phosphate

The soil sample left after the extraction of aluminium phosphate was washed twice with saturated NaCl solution. It was then extracted with 0.1 N NaOH. After centrifugation and decantation of the supernatant, the soil sample was saved for extraction of calcium phosphate. The extract was used to determine the phosphorus. Therefore, an aliquot (usually 2 mL) was supplemented with water. The solution was adjusted to about pH 3 by addition of 2 N NaOH until 2,6 dinitrophenol indicator colour turned to yellow and then was brought back to colourless by addition of 2 N H_2SO_4. Then sulfomolybdic acid solution and water were added. The solution was mixed and three drops of chlorostannous reductant ~~B~~ (25 g $SnCl_2$ x $2H_2O$ dissolved in 100 HCl conc., diluted to 1 L) were added to develop the colour. Water was added to volume and the solution mixed. The colour was measured within 5 to 10 minutes at 660 nm.

For surface soils the decanted extract was usually highly coloured with considerable organic matter, in which case 2 N H_2SO_4 were added, prior to preparation for determination of phosphorus, to the solution and then one or a few drops of concentrated H_2SO_4 until the organic colloids began to flocculate. The suspension was then centrifuged and the clear supernatant collected.

3. Extraction and determination of phosphorus in calcium phosphate

The soil sample left after extraction of iron phosphate was washed twice with saturated NaCl solution and then extracted with 0.5 N H_2SO_4. After centrifugation and decantation an aliquot of the supernatant was mixed with water. The solution was adjusted to about pH 3 by addition of 2 N NaOH until 2,6 dinitrophenol indicator colour turned to yellow and the solution is brought back to colourless by addition of 2 N H_2SO_4. The colour was then developed and measured as for iron phosphate. To test the non-interference of ferric ions, two identical aliquots were taken. To one enough standard phosphorus solution was added to give a final concentration of 0.2 mg/kg of the added phosphorus. Then phosphorus was determined in both aliquots. The complete recovery of the added phosphorus established the non-interference of the ferric ions in the solution. Lower recovery, indicating ferric ion interference, could be diminished by additional chlorostannous acid or by use of [redacted] reductor.

4. Extraction and determination of reductant soluble iron phosphate

The soil sample left after the extraction of calcium phosphate was washed twice saturated NaCl. Afterwards, it was suspended in 0.3 M sodium citrate solution and then solid $Na_2S_2O_4$ was added. The suspension was heated in a water bath and centrifuged. The soil was washed twice with saturated NaCl solution, the washings being combined with the extract. The sample was saved for extraction of occluded aluminium phosphate. The solution in the flask was filled up to volume and aliquots taken for phosphorus (and Fe, if desired) analysis. A suitable aliquot taken for phosphorus determination was mixed and with distilled water and 30% P-free H_2O_2. During heating the mixture, one drop of 0.5 M $FeCl_3$ was added to moderate the oxidation. After completion of oxidation, the solution was boiled for an additional 1 or 2 minutes and then dried on a steam plate. Afterwards, 2 N NaOH was added and the solution was boiled for 1 to 2 minutes and digested on a steam plate for 5 minutes. The suspension was centrifuged to throw down the iron oxide precipitate and the supernatant liquid was decanted. The original flask was washed twice with water and centrifuged together with the extracted soil. The combined supernatant solutions were made to volume and the phosphorus determined by the same method as for iron phosphate.

5. Extraction and determination of phosphorous in aluminium phosphate

For soils high in iron oxide, the residue was extracted with neutral NH_4F to remove occluded aluminium phosphate. Alternatively, the residue was extracted with 0.1 N NaOH to remove occluded aluminium-iron phosphate (barrandite-like). The phosphorus in the solution was determined in the same way as aluminium phosphate or iron phosphate, respectively. In a complete system of fractionation of soil phosphorus, total phosphorus and organic phosphorus were determined on two separate samples.

II. RESULTS AND DISCUSSION

1. Solubility of pure phosphates

The separate extraction methods were systematized in proper sequence in a complete system of fractionation to remove the respective discrete chemical form of inorganic phosphate. The percentage of phosphate dissolved in the fluoride solution increased continuously with the decrease of the solid-solvent ratio. A small percentage of iron phosphate also was dissolved in the NH_4F, and the amount increased with decrease of solid-solvent ratio. For soil containing 50 to 200 mg/kg iron phosphate or 0.05 to 0.2 mg P per gram of soil, not more than 5-10% of iron phosphate would be dissolved during the extraction of aluminium phosphate. To correct for this, a second extraction with NH_4F may be made and the amount of P thus extracted subtracted from the aluminium phosphate obtained in the first extraction and added to the subsequent iron phosphate extracted by NaOH. For convenience, 10% of the iron phosphate as obtained by subsequent NaOH extraction may be subtracted from aluminium phosphate and added to the iron phosphate. Solubility of phosphorus in the form of aluminum phosphate and iron in 0.1 N NaOH was high (4100 and 3400 mg/L), while the solubility of apatite in the same extract was negligible. Therefore, on the sample from which aluminum phosphate was removed, the separation of iron phosphate is complete.

Solubility of apatite is high in 0.5 N H_2SO_4 (3400 mg/L), but a very large quantity of aluminum phosphate and iron phosphate could also be dissolved in it. Thus, it was shown that the NH_4F and NaOH extractions must be carried out in the procedure before the acid extraction.

2. Extraction of Al-, Fe-, and Ca- phosphate from soils

Two soil samples, an iron-rich latosol (Catalina) and a grey-brown podzolic soil (Miami) were used to test the method for fractionation of aluminium, iron, and calcium phosphorus. One gram of each sample, after treatment with NH_4Cl, was extracted successively with neutral 0.5 N NH_4F, 0.1 N NaOH, and 0.5 NH_2SO_4 for one to three times each. The Catalina latosol contains a negligible amount of aluminium phosphate and also a relatively small amount of iron phosphate. The second and third extractions with NH_4F dissolved, therefore, only a negligible amount of phosphate. The Miami silt loam contains relatively large amounts of aluminium and iron phosphates. The phosphate dissolved in the second and third extractions with NH_4F, as shown above, can be attributed to iron phosphate. The next extraction with NaOH, therefore, gave only 94 mg/kg phosphorus in comparison with 128 mg/kg in the second sample given only one extraction of NH_4F. Considerable iron phosphate was dissolved in the second and third extractions with NaOH in both Catalina latosol and Miami silt loam. Phosphorus in synthetic iron phosphate (equivalent to 3400 mg/kg in 1 g soil) can be completely dissolved in one extraction of NaOH, yet successive NaOH extractions of soils which contain much less P continuously dissolve a portion of iron phosphate in the second and third extractions.

The Catalina latosol and the Miami silt loam contain about 320 mg/kg and 150 mg/kg P, respectively, in reductant soluble (occluded) iron phosphate. The portion of iron phosphate dissolved in the second and third extracts must come from the occluded form, through diffusion or from the freshly exposed iron phosphate surface formed by the breaking of particles during the 17 hour shaking. The occluded form is only physically different from that unoccluded so the distinction between them would not be very sharp. The sudden drop from amount of phosphorus dissolved from the first extraction to that of the second extraction fully justifies placing the iron phosphate dissolved in the first extraction in a different category from that of subsequent extractions. One single extraction with NaOH was adopted, therefore, to separate the iron phosphate from occluded phosphorus. The second extraction with H_2SO_4 also dissolved a small amount of phosphorus, attributed also to slow removal of some occluded phosphate.

3. Reductant soluble iron phosphate

The portion of phosphorus not extracted by the NH_4F, NaOH, and H_2SO_4 treatments was almost completely dissolved by a dithionite-citrate reduction-chelation procedure for dissolving free iron oxide coatings. The reduction-chelation treatment was given separately to synthetic iron phosphate and aluminium phosphate. Within the analytical error, 100% of the iron phosphate and a negligible amount of the aluminium phosphate dissolved. The soil phosphorus dissolved by this treatment may properly be termed, therefore, reductant soluble iron phosphate. An iron oxide precipitate apparently was formed on the surface of iron phosphate and on the surface of aluminium-iron phosphate (barrandite-like) in the course of chemical weathering in soils by hydrolysis of iron phosphate and other iron salts. The relative insolubility of iron oxide in the NH_4F, NaOH, or H_2SO_4 extraction must account for the fact that the phosphate thus covered can only be dissolved after the removal of the iron oxide coating. The Wahiawa latosol, the Catalina latosol, and a Miami silt loam after removal of aluminium, iron, and calcium phosphate by successive extraction with NH_4F, NaOH, and H_2SO_4 were treated once with sodium dithionite-citrate and yielded 504, 320, and 150 mg/kg of reductant soluble phosphorus, respectively. Further extraction with either NaOH or NH_4F dissolved appreciable amounts of phosphorus. Since only aluminium phosphate is soluble in either NaOH or neutral NH_4F, most of the residual phosphate must be aluminum phosphate. The somewhat higher amount extracted by NaOH than by NH_4F indicated that there was also some iron phosphate left after the reduction-chelation, most likely in aluminium-iron phosphate (barrandite-like) since any pure iron phosphate would have dissolved in the dithionite-citrate extraction.

4. Fractionation of phosphorous

The phosphorus of soils belonging to the different soil types was fractionated. The results of the replicated samples were in good agreement. Iron phosphate, particularly the reductant soluble form, dominated highly-weathered soils, but these forms were also the most abundant in the Miami silt loam soil. Aluminium phosphate and calcium phosphate occurred in significant amounts in the Miami silt loam soil, while calcium phosphate is dominant in the calcareous subsoil of the Barnes silt loam soil. The ratio of aluminium phosphate to iron phosphate varies from 0.2 in Miami silt loam soil to 2 in the little-weathered Barnes silt loam subsoil. In this connection fractionation of phosphorus in several soil profiles was found to vary even more widely as a function of the degree of chemical weathering. The fusion analysis of the residual samples of both Catalina latosol and Miami silt loam after all extractions yielded 15 and 4 mg/kg of P, respectively. The difference between the added total and determined total amount of P in the soils was within the cumulative experimental error.

III. CONCLUSIONS

A method for fractionation of inorganic soil phosphorus into the total amount of each discrete chemical form was developed. It permits determination of the chemical status of native soil phosphorus and of the fate of applied phosphate fertilizer with or without the effect of cropping.

Overall, the information therefore does not contribute directly to the understanding of the route of degradation of fosetyl-Al in soil. The publication therefore served as supplemental information about the separation, nature and behaviour of phosphate residues in soil.

CA 7.1.1.2 Anaerobic degradation

Report:	KCA 7.1.1.2/01 [redacted],; 1984; M-159549-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Anaerobic aquatic metabolism study.
Report No.:	R000917
Document No.:	M-159549-01-1
Guideline(s):	USEPA (=EPA): D, 162-3
Guideline deviation(s):	none
GLP/GEP:	**no**

The route of degradation in anaerobic soil of fosetyl-aluminium (fosetyl-Al) had been investigated in one study under laboratory conditions in:

- two water-logged soils under standard conditions (20 °C) following application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.1.2/01). In addition, investigations were performed in one soil following the application of 1-^{14}C-labeled ammonium ethylphosphonate or 1-^{14}C-labeled ethanol to one soil.

The data requirement was addressed under Point 7.1.1.1.2.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The evaluation revealed that fosetyl-Al was degraded rapidly under the anaerobic conditions of the test to result in values of the half-life of 1.67 days (40 h, silty clay loam soil) and 0.35 days (14 h, sandy loam), respectively.

Ethanol was observed as the major degradation product and the route of degradation was thus the same as for aerobic degradation in soil. No other metabolites were observed at levels requiring further assessment following actual data requirements according to Commission Regulation (EC) No 283/2013 amending Regulation (EC) No 1107/2009.

The study was considered as indicative during the Annex I inclusion of fosetyl under Directive 91/414/EEC. The reason for assessment of the study as indicative was not clearly given in the existing DAR. Also considering the simple structure of fosetyl-Al the results of the study are very conclusive in comparison to aerobic degradation (see Section CA 7.1.1.1). Nor the active substance, neither its residues formed contain structural elements that are susceptible for a reduction and to form unique transformation products under the anaerobic conditions of the test (example: nitro to amino group). This observation is common for the predominant portion of active substances and documented by meanwhile numerous EFSA Conclusions. As stated in the existing DAR, a new study is not expected to provide more significant information.

Study summaries of existing studies and publications on route of anaerobic degradation in soil:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.1.2/01 [redacted]; 1984; M-159549-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Anaerobic aquatic metabolism study.
Report No.:	R000917
Document No.:	M-159549-01-1
Guideline(s):	USEPA (=EPA): D, 162-3
Guideline deviation(s):	none
GLP/GEP:	**no**

Executive Summary

The biotransformation of [^{14}C]-fosetyl-Al was investigated under anaerobic conditions of the laboratory in the two soils sandy loam and silty clay loam following incubation in the dark at 20 °C for 1.33 days (32 hours, sandy loam) and 10 days (240 hours, silty clay) in maximum. A nominal test concentration of 88 to 100 mg/kg soil was applied based on a single maximum rate of 80 kg a.s./ha in the field.

The biotransformation of [^{14}C]-fosetyl-ammonium was also investigated under the same conditions in soil silty clay loam following incubation for 10 days (240 hours) in maximum.

In addition, the biotransformation of [^{14}C]-ethanol was investigated under the same conditions in soil silty clay loam for 5 days (120 hours) in maximum following application at a test concentration of 44 mg/kg soil.

Following application of ^{14}C-fosetyl-Al material balances ranged from 92.2 to 101.8% AR for silty clay loam soil and 91.9 to 100.0% AR for the sandy loam soil. Following application of ^{14}C-fosetyl-ammonium material balances ranged from 90.6 to 101.9% AR in samples of silty clay loam soil.

Minor losses in the material balance were observed each for two additional sampling intervals per incubation series. With losses being slightly below 90% for most samples this was not regarded to have an impact on the overall outcome of the study.

Following application of ^{14}C-ethanol to silty clay loam soil, material balances were from 90.3 to 100.0% AR, except for the sampling interval 18 hours (89.5% AR).

For the silty clay loam soil values of non-extractable radioactivity from soil were 1.0% AR (fosetyl-Al) and 0.5% AR (fosetyl-ammonium) at time zero to increase to 5.3% AR (fosetyl-Al) and 7.1% AR (fosetyl-ammonium) after 240 hours of incubation. Non-extractable residues from sandy loam soil samples were 0.3% AR at study start (0 hours) and 6.0% AR at study end (32 hours).

Following application of ^{14}C-ethanol non-extractable residues from silty clay loam samples increased from 0.9% AR at study start (0 hours) to 5.6% AR at study end (120 hours).

For the silty clay loam soil the maximum of ^{14}C-carbon dioxide formed was 48.0% AR (fosetyl-Al) and 47.0% AR (fosetyl-ammonium) each after 240 hours of incubation. The maximum of carbon dioxide formed was 16.6% AR for the sandy loam soil after 32 hours of incubation.

Finally, 60.2% AR carbon dioxide were formed in maximum in silty clay loam soil following application of ^{14}C-ethanol after 120 hours of incubation.

Formation of other volatile compounds was insignificant (values of ≤ 0.1% AR) at all sampling intervals).

For the total samples of soil silty clay loam values of the active substances decreased from 89% AR (fosetyl-Al) and 86% AR (fosetyl-ammonium) at study start (0 hours) to 7 and 9% AR at study end (240 hours), respectively. For total samples of soil sandy loam values of fosetyl-Al decreased from 86% AR at study start (0 hours) to 13% AR at study end (32 hours).
For the total samples of soil silty clay loam values of the test substance ^{14}C-ethanol decreased from 83% AR at study start (0 hours) to 5% AR at study end (120 hours).

Conclusively, fosetyl-Al or fosetyl-ammonium was rapidly degraded in anaerobic soil under conditions of the laboratory *via* biotical induced ester hydrolysis to result in formation of ethanol (maximum of 22% AR after 120 hours, soil silty clay loam) and carbon dioxide (maximum 48% AR after 240 hours, soil silty clay loam).
Very rapid degradation was also observed following application of ethanol and separate incubation in samples of silty clay loam soil. The biotransformation of ethanol resulted in formation of carbon dioxide (60.2% AR after 120 hours) as the predominant product of conversion.

Half-lives for fosetyl were 1.67 days (40 hours) in a silty clay loam and 14 hours in a sandy loam soil. The half-life of ethanol in silty clay loam soil was estimated to 0.33 days (8 hours).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

[ethyl-1-^{14}C]-fosetyl-Al	
Sample ID:	GHS 352-I
Specific Activity:	0.9 MBq/mg
Radiochemical Purity:	98%
[ethyl-1-^{14}C]-fosetyl-ammonium	
Sample ID:	MJA-413
Specific Activity:	1.3 MBq/mg
Radiochemical Purity:	100%
Fosetyl-Al	
Batch ID:	EA-1167.1
Specific Activity:	Non-labelled
Radiochemical Purity:	Non-labelled
Chemical Purity:	> 99%

Due to limitations in availability of the test substance fosetyl-Al, the study was conducted in part with the ammonium salt coded MJA-413. Considering that fosetyl salts readily dissociate in aqueous solution to the separate ions, the use of ammonium as counter-ion was regarded to have no impact on the study objective, i.e. to correctly reflect the behaviour of fosetyl under anaerobic conditions.

Samples of soil silty clay loam were incubated with [^{14}C]-ethanol in parallel in order to compare the degradation pattern with [^{14}C]-fosetyl-Al.

2. Test Soils

The tests were performed in two soils each sieved to a particle size ≤ 2 mm as characterised detailed in Table 7.1.1.2- 1.

Table 7.1.1.2- 1: Physico-chemical properties of test soils

Parameter	Soil	
Soil Designation	Sandy loam	Silty clay loam
Particle size		
Sand [50 µm – 2 mm] (%)	62.3	12.7
Silt [2 µm – 50 µm] (%)	20.2	54.7
Clay [< 2 µm] (%)	13.6	32.6
pH	5.3	6.8
Organic Matter (%)	3.6	3.9
Organic carbon (%) *	2.1	2.3
Cation Exchange Capacity (meq/100 g)	13	39
Water Holding Capacity at 0.33 bar (%)	24	26

* Calculated by dividing the organic matter content by 1.72.

B. STUDY DESIGN

1. Experimental Conditions

The half-life of fosetyl-Al in soil under aerobic conditions was known to be very short as compared to the time required for establishing anaerobic conditions in soil samples by flooding. Therefore, the study design formally followed the protocol of anaerobic aquatic metabolism i.e. the application of the test substance when anaerobic conditions had been established.

The alternative design (anaerobic soil metabolism) would have been to apply fosetyl to aerobic soil followed by an ageing period to then establish anaerobic conditions. In view of the very short half-lives of fosetyl in aerobic soil, this design can hardly be followed when considering that the establishment of anaerobic conditions typically requires at least several days.

However, it is concluded that degradation in soil under anaerobic conditions follows the same fundamental pathways as under aerobic conditions with no additional metabolites formed when considering the absence of susceptible functional groups under such reductive conditions in the molecule fosetyl-Al.

The tests were performed in 50 mL glass centrifuge bottles each containing 5.0 g of soil. Following flooding with 20.0 mL of water and amendment of 50 mg alfalfa meal, anaerobic conditions were established by storage of flasks in the dark at 20 ± 2 °C for 29 to 34 days prior to application.

At date of application each sample was treated at a concentration of 88 to 100 mg fosetyl-Al/kg soil, equivalent to 20 to 25 mg fosetyl-Al/L water, based on a maximum single application rate of 80 kg a.s./ha in the field. Samples of silty clay loam soil were treated with ^{14}C-ethanol at a concentration of 44 mg/kg soil, equivalent to 11 mg/L in the water phase.

Following addition of the test substance, flasks were stoppered and samples homogenized for 10 minutes. Stoppers on flasks were replaced by manifold caps to allow flow-through conditions resulting from a stream of nitrogen to pass through each sample during incubation. Volatile radioactivity was collected by passing the nitrogen stream successively through two traps containing 0.1 N aqueous sodium hydroxide solution and one containing concentrated sulphuric acid.

The samples were incubated at 20 ± 2 °C in the dark for 240 hours (10 days) in maximum.

2. Sampling

Duplicates of silty clay loam samples treated with ^{14}C-fosetyl-Al were removed for analysis after 0, 2, 5, 8, 16, 32, 120 and 240 hours of incubation.

Single replicates of silty clay loam samples treated with ^{14}C-fosetyl-ammonium were removed at the same at the same sampling intervals.

Single replicates of sandy loam were removed for analysis after 0, 3 and 17 hours of incubation while duplicates were processed after 8 and 32 hours of incubation.

Following application of ^{14}C-ethanol, silty clay loam samples were processed after 0, 2.5, 5, 18 and 120 hours of incubation.

3. Analytical Procedures

The water was separated from soil by centrifugation. Radioactivity was determined by liquid scintillation counting (LSC) followed by HPLC analysis/^{14}C-radio-detection. For silty clay loam samples treated with ^{14}C-fosetyl-ammonium, analysis was repeated each after removal of ^{14}C-carbonate by precipitation with barium.

Soils were extracted successively with 0.1 N aqueous sulphuric acid, water, 0.1 N ammonium hydroxide, water, and finally methanol. Radioactivity in extracts was determined by LSC. No chromatographic analysis of soil extracts was performed due to low radioactivity in most of the individual extracts.
Radioactivity in extracted and air-dried soils was determined by combustion followed by LSC.

The radioactivity collected in traps was determined by LSC followed by HPLC analysis/^{14}C-radiodetection of first traps. Identity of ^{14}C-carbon dioxide was confirmed by co-precipitation as barium carbonate.

4. Determination of degradation kinetics

The kinetic evaluation of degradation data was performed graphically.

II. RESULTS AND DISCUSSION

A. DATA

The results of biotransformation in anaerobic soil were summarized for [^{14}C]-fosetyl-Al and the two soils silty clay loam and sandy loam in Table 7.1.1.2- 2 and Table 7.1.1.2- 3, for [^{14}C]-fosetyl-ammonium and the silty clay loam in Table 7.1.1.2- 4, and, finally, for [^{14}C]-ethanol and the silty clay loam in Table 7.1.1.2- 5.

Table 7.1.1.2- 2: Degradation of [^{14}C]-fosetyl-Al at 20 °C under anaerobic conditions in soil silty clay loam [% AR]

Compound		Incubation time (hours)							
		0	**2**	**5**	**8**	**16**	**32**	**120**	**240**
Fosetyl-Al	mean SD	89 ±1	87 ±2	77 ±1	80 ±2	73 ±3	50 ±2	25 ±2	7 ±0
^{14}C-Carbon dioxide in traps	mean SD	n.a. -	0.3 ±0.1	0.7 ±0.2	0.9 ±0.1	2.0 ±0.1	5.9 ±0.6	27.1 ±4.2	48.0 ±0.3
Total radioactivity in water	mean SD	88.3 ±0.7	89.7 ±0.6	86.0 ±0.6	84.5 ±2.4	82.1 ±0.5	70.8 ±1.2	51.2 ±2.4	24.7 ±3.3
Total extractable from soil [1]	mean SD	10.3 ±1.3	10.6 ±0.7	9.6 ±0.6	8.0 ±1.2	8.7 ±1.2	8.4 ±0.4	10.2 ±1.0	10.7 ±0.8
Total extractable radioactivity	mean SD	98.1 ±0.1	100.2 ±0.3	95.0 ±0.6	95.0 ±0.5	89.9 ±1.0	79.6 ±1.4	61.0 ±2.8	33.8 ±1.5
Non-extractable radioactivity	mean SD	1.0 ±0.2	1.4 ±0.1	2.0 ±0.5	1.8 ±0.0	1.7 ±0.1	3.1 ±0.1	4.1 ±0.0	5.3 ±0.3
^{14}C-Carbon dioxide including other volatiles	mean SD	n.a. -	0.3 ±0.1	0.7 ±0.2	0.9 ±0.1	2.0 ±0.1	5.9 ±0.6	27.2 ±4.2	48.1 ±0.3
Total radioactivity	mean SD	99.1 ±0.3	101.8 ±0.2	97.6 ±0.9	97.7 ±0.4	93.5 ±1.1	88.6 ±1.8	92.2 ±1.4	87.1 ±0.8

All values expressed as percentages of total applied radioactivity
SD: standard deviation; n.a. = not analysed
Other volatile radioactivity was ≤ 0.1 % AR at any time point
[1] Sum of successive extraction using sulphuric acid, water, ammonium hydroxide, water and methanol.

Table 7.1.1.2- 3: Degradation of [^{14}C]-fosetyl-Al at 20 °C under anaerobic conditions in soil sandy loam [% AR]

Compound		Incubation time (hours) [1] 0	3	8	17	32
Fosetyl-Al	mean	86	70	64	44	13 [4]
	SD	-	-	±4	-	-
^{14}C-Carbon dioxide in traps	mean	n.a.	0.6	2.4	7.7	16.6
	SD	-		±1.1		±2.2
Total radioactivity in water	mean	85.9	78.8	77.4	60.5	43.3
	SD			±0.9	-	±2.7
Total extractable from soil [2]	mean	13.8	11.0	10.7	14.2	14.0
	SD			±0.3	-	±1.6
Total extractable radioactivity	mean	99.7	89.8	88.1	74.7	57.3
	SD			±1.2		±1.1
Non-extractable radioactivity	mean	0.3	1.5	2.8	5.0	6.0
	SD			±0.3	-	±0.3
^{14}C-Carbon dioxide including other volatiles	mean	n.a.	0.6	2.4	7.7	16.6
	SD	-		±1.1	±0.0	±2.2
Total radioactivity	mean	100.0	91.9	93.3	87.4	79.9
	SD			±2.6		±0.9

All values expressed as percentages of total applied radioactivity
n.a.: not analysed, SD: standard deviation
Other volatile radioactivity was ≤ 0.1 % AR at any time point
[1] Duplicates removed for analysis after 8 and 32 hours of incubation
[3] Sum of successive extraction using sulphuric acid, water, ammonium hydroxide, water and methanol.

Table 7.1.1.2- 4: Degradation of [^{14}C]-fosetyl-ammonium at 20 °C under anaerobic conditions in soil silty clay loam [% AR]

Compound	Incubation time (hours) 0	2	5	8	16	32	120	240
Fosetyl-ammonium	86	85	80	77	64	40	27	9
Ethanol in water [1]	n.a.	5.0	5.0	5.0	10 [4]	16.5	22.0	13.5
^{14}C-Carbon dioxide in water [1]	n.a.	2	3	7	11	13	10	6
^{14}C-Carbon Dioxide in traps	n.a.	0.1	0.8	1.0	1.0	7.1	21.0	41.0
Total carbon dioxide	n.a.	2.1	3.8	8.0	12.0	20.1	31.0	47.0
Total radioactivity in water	87.3	88.8	86.3	81.2	82.3	70.6	50.5	29.1
Total extractable from Soil [2]	12.1	11.5	10.4	6.3	10.3	7.8	11.6	9.7
Total extractable radioactivity	99.4	100.3	96.7	87.5	92.6	78.4	62.1	38.8
Non-extractable radioactivity	0.5	0.5	0.9	2.7	1.4	5.1	5.1	7.1
^{14}C-Carbon dioxide including other volatiles	n.a.	2.1	3.8	8.0	12.0	20.1	31.1	47.0
Total radioactivity	101.9	100.9	98.4	91.2	95.0	90.6	88.3	86.9

All values expressed as percentages of total applied radioactivity
Other volatile radioactivity was ≤ 0.1 % AR at any time point
n.a. = not analysed
[1] Difference between ethanol + CO_2 before and after barium precipitation
[2] Sum of successive extractions (sulphuric acid, water, ammonium hydroxide, water and methanol)

Table 7.1.1.2- 5: Degradation of [^{14}C]-ethanol at 20 °C under anaerobic conditions in soil silty clay loam [% AR]

Compound	Incubation time (hours)				
	0	2.5	5	18	120
Ethanol	83	70	59	20	5
^{14}C-Carbon dioxide in water [1]	12	9	16	19	9
^{14}C-Carbon dioxide in traps	n.a.	2.6	3.2	14	51.2
Total ^{14}C-carbon dioxide	12	11.6	19.2	33.0	60.2
Total radioactivity in water	89.0	76.6	77.3	56.5	12.9
Total extractable radioactivity from soil	10.1	13.9	12.4	14.6	15.5
Total extractable radioactivity	99.1	90.5	89.7	71.1	28.4
Non-extractable radioactivity	0.9	1.3	2.6	4.1	5.6
^{14}C-Carbon dioxide including other volatiles	12	11.9	19.2	33.3	65.3
Total radioactivity	100.0	94.7	95.5	89.5	90.3

All values expressed as percentages of total applied radioactivity
n.a.: not analysed
[1] Difference between ethanol + CO_2 before and after barium precipitation

B. MATERIAL BALANCE

Following application of ^{14}C-fosetyl-Al to silty clay loam soil, material balances ranged from 92.2 to 101.8% AR, except for the two sampling intervals 32 hours (89.2% AR) and 240 hours (87.0% AR).
For the sandy loam soil incubated with fosetyl-Al, material balances were 91.9 to 100.0% AR, except for samples of 17 hours (87.4% AR) and 32 hours (79.9% AR).
For the silty clay loam incubated with ^{14}C-fosetyl-ammonium, material balances ranged from 90.6 to 101.9% AR, except for samples of 120 hours (88.3% AR) and 240 hours (86.9% AR).
Following application of ^{14}C-ethanol to silty clay loam soil, material balances were from 90.3 to 100.0% AR, except for the sampling interval 18 hours (89.5% AR).

Losses of radioactivity to result in total material balances below 90% AR were thus observed for a limited number of samples and minor (i.e. about 1 to 3% AR below 90% AR) for most of these samples. Losses were preferably occurred at later sampling intervals. The significant portion of volatile radioactivity formed starting already at short time intervals during incubation can serve as an indication that losses occurred from leaks in flow through systems and during processing of samples. With losses being slightly below 90% for most samples, this did not affect the overall outcome and integrity of the study.

C. DISSIPATION OF RADIOACTIVITY FROM WATER

Residues in water of silty clay loam samples decreased from 88.3% AR (fosetyl-Al) and 87.3% AR (fosetyl-ammonium) at study start (0 hours) to 24.7 and 29.1% AR at study end (240 hours), respectively.
Residues in water of sandy loam soil samples decreased from 85.9% AR at study start (0 hours) to 43.3% AR at study end (32 hours).

Following application of ^{14}C-ethanol radioactive residues in the water of silty clay loam samples decreased from 89.0% AR at study start (0 hours) to 12.9% AR at study end (120 hours).

D. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Values of extractable radioactivity from soil were 10.3% AR (fosetyl-Al) and 12.1% AR (fosetyl-ammonium) for the silty clay loam soil at time zero to remain nearly constant at 10.7% AR (fosetyl-Al) and 9.7% AR (fosetyl-ammonium) after 240 hours of incubation.
Extractable residues from sandy loam soil samples were 13.8% AR at study start (0 hours) and 14.0% AR at study end (32 hours).
Following application of ^{14}C-ethanol residues extractable from soil of silty clay loam samples increased from 10.1% AR at study start (0 hours) to 15.5% AR at study end (120 hours).

Values of non-extractable radioactivity from soil were 1.0% AR (fosetyl-Al) and 0.5% AR (fosetyl-ammonium) for the silty clay loam soil at time zero to increase to 5.3% AR (fosetyl-Al) and 7.1% AR (fosetyl-ammonium) after 240 hours of incubation.
Non-extractable residues from sandy loam soil samples were 0.3% AR at study start (0 hours) and 6.0% AR at study end (32 hours).
Following application of ^{14}C-ethanol non-extractable residues from silty clay loam samples increased from 0.9% AR at study start (0 hours) to 5.6% AR at study end (120 hours).

E. VOLATILES

The maximum of carbon dioxide formed was 48.0% AR (fosetyl-Al) and 47.0% AR (fosetyl-ammonium) for the silty clay loam soil each after 240 hours of incubation.
The maximum of ^{14}C-carbon dioxide formed was 16.6% AR for the sandy loam soil after 32 hours of incubation.
Finally, 60.2% AR carbon dioxide were formed in maximum in silty clay loam soil following application of ^{14}C-ethanol after 120 hours of incubation.

Formation of other volatile compounds was insignificant (values of ≤ 0.1% AR at all sampling intervals).

F. TRANSFORMATION OF TEST SUBSTANCE

Following application of fosetyl-Al or fosetyl-ammonium, the test substances were extensively transformed by biotical induced ester hydrolysis to result in ethanol, NER and mineralisation to carbon dioxide as predominant transformation products (see Table 7.1.1.2- 2 to Table 7.1.1.2- 5).

The transformation was very fast to decrease from 89% AR (fosetyl-Al) and 86% AR (fosetyl-ammonium) by zero hours to 7 and 9% AR each after 240 hours of incubation in soil silty clay loam.
For soil sandy loam values of fosetyl-Al decreased from 86% AR (zero hours) to 13% AR (32 hours) at the end of the study.
For silty clay loam samples treated with fosetyl-ammonium, ethanol was observed as a major transformation product at peak levels of 22.0% AR after 120 hours of incubation.

Following application of ^{14}C-ethanol to silty clay loam samples, the test substance was extensively transformed to result in ^{14}C-carbon dioxide as the predominant biotransformation product formed at 60.2% AR by the end of the study (120 hours of incubation).
Values of ^{14}C-ethanol applied decreased from 83% AR (zero hours) to 5% AR after 120 hours.

G. DEGRADATION KINETICS

No formal kinetic evaluation was performed. The degradation data was evaluated graphically to result in half-lives of 1.67 days (40 hours) for fosetyl in the silty clay loam and of 14 hours in the sandy loam soil.
The half-life of ethanol in the silty clay loam soil was estimated to 0.33 days (8 hours).

III. CONCLUSIONS

Fosetyl-Al or fosetyl-ammonium was rapidly degraded in anaerobic soil under conditions of the laboratory to result in ethanol (22% AR after 120 hours, soil silty clay loam) and carbon dioxide (48% AR after 240 hours, soil silty clay loam).
The same applied for the degradation of ethanol applied and incubated separately in samples of silty clay loam soil. The biotransformation of ethanol resulted in formation of carbon dioxide (60.0% AR after 120 hours) as the predominant product of conversion.

Half-lives for fosetyl were 1.67 days (40 hours) in a silty clay loam and 14 hours in a sandy loam soil.
The half-life of ethanol in silty clay loam soil was estimated to 0.33 days (8 hours).

Study evaluation:

Considering the simple structure of fosetyl-Al the results of the study were very consistent and well in line with the tests in aerobic soil.

Nor the active substance, neither its residues formed contain structural elements that are susceptible for a reduction and to form unique transformation products under the anaerobic conditions of the test (example: nitro to amino group). This observation is common for the predominant portion of active substances and documented by meanwhile numerous EFSA Conclusions.

Also in line with this observation the conduct of a new study is not expected to provide new substantial information about the behaviour of fosetyl-Al in anaerobic soil.

CA 7.1.1.3 Soil photolysis

Report:	KCA 7.1.1.3/01 [redacted], [redacted]; 2000; M-179065-01-1
Title:	Phosphorous acid: Soil photolysis.
Report No.:	R009319
Document No.:	M-179065-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.3/02 [redacted]; [redacted]; 2001; M-201629-01-1
Title:	Photodegradation of phosphorous acid in soil Code: AE 0540099
Report No.:	C011841
Document No.:	M-201629-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**yes**

Report:	KCA 7.1.1.3/03 [redacted]; [redacted]; [redacted]; [redacted]; [redacted]; 2003; M-233852-01-1
Title:	The degradation of phosphorous acid, the main metabolite of fosetyl-Al in soil (Environmental position paper)
Report No.:	C033806
Document No.:	M-233852-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.3/04 [redacted]; 1999; M-234789-01-1
Title:	Predicting photoreaction rates in surface waters
Report No.:	C034561
Document No.:	M-234789-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.1.3/05 [redacted]; [redacted]; 1990; M-234783-01-1
Title:	Depth dependence of direct and indirect photolysis on soil surfaces
Report No.:	C034558
Document No.:	M-234783-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

In view of the spontaneous degradation in aerobic soil, no photolysis study on soil surfaces was performed with the active substance fosetyl-aluminium.

Instead, the potential for <u>degradation of phosphonic acid on soil surfaces</u> following irradiation had been investigated under laboratory conditions in:

- one soil at 30 °C following application of non-labeled phosphonic acid (KCA 7.1.1.3/01);
- one soil at 22 °C following application of non-labeled phosphonic acid (KCA 7.1.1.3/02).

The data requirement was addressed under Point 7.1.1.1.2.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

Study KCA 7.1.1.3/01 was submitted as preliminary data to finally serve as supplemental information. Study KCA 7.1.1.3/02 was a follow up of the first study conducted at a lower incubation temperature (i.e. 22 versus 30 °C) and prolonged irradiation time (45 versus 21 days).

The evaluation revealed that the decrease of phosphonic acid was faster under irradiated conditions in comparison to dark controls. It was concluded that photolytical transformation had some effect on the degradation of phosphonic acid on soil surfaces to result in about the half of the half-life as observed for degradation in dark controls. The DT_{50} of phosphonic acid in dark controls was estimated to range between 50 and 60 days.

Due to the nature of the test compound and the analysis, no pattern of metabolites could be described for extracts from irradiated samples or from dark controls.

Since the potential for direct absorption of light by phosphonic acid is very limited (i.e. no significant absorption at wavelengths of more than 290 nm), the actual degradation observed is explained by indirect photolytic effects, i.e. the reaction of singlet oxygen, hydroxyl radicals and peroxy radicals as oxidative species formed in the top 2 mm of soil from irradiation as indicated by publications submitted (KCA 7.1.1.3/04 and KCA 7.1.1.3/05).

No other metabolites were observed at levels requiring further assessment following actual data requirements according to Commission Regulation (EC) No 283/2013 amending Regulation (EC) No 1107/2009.

Studies KCA 7.1.1.3/01 and KCA 7.1.1.3/02 were considered as indicative during the Annex I inclusion of fosetyl under Directive 91/414/EEC. Due to negligible light absorption above 290 nm, only indirect photolysis of fosetyl-Al could occur. Therefore, no new information will be obtained performing a direct photolysis study with fosetyl-Al. Photolysis is more likely based on the reaction with photo-generated transient oxidants like singlet oxygen, hydroxyl radicals and peroxy radicals. All of these photooxidants cause an oxidation reaction which is expected to result in case of phosphonates in phosphate. A new study is not expected to provide more significant information.

Study summaries of existing studies and publications on soil photolysis:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.1.3/01 [redacted];[redacted]; 2000; M-179065-01-1
Title:	Phosphorous acid: Soil photolysis.
Report No.:	R009319
Document No.:	M-179065-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The photolytic transformation of phosphonate was investigated by application of phosphonic acid at a nominal test concentration of 4 mg a.s./kg soil onto the surface of samples of soil [redacted] followed by irradiation at 30 C under simulated sunlight for 21 days in maximum. Investigations were performed against dark controls.

For irradiated samples, extractability of residues identified as phosphonate decreased from 4.6 mg/kg soil by day zero to 2.2 mg/kg by day 21.
Extractability of residues identified as phosphonate decreased from 4.6 mg/kg soil by day zero to 3.3 mg/kg after 21 days for dark controls.

It was concluded that phosphonate was not subject to ready photo-transformation on soil surfaces.

This study provided preliminary data thus being regarded as supplemental information. The study was replaced by study KCA 7.1.1.3/02 conducted at a lower test temperature (22 °C) and prolonged time of irradiation (45 days).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Analytical grade phosphonic acid was used, batch EA5152SD2.

2. Soil

The test soil originated from [redacted], France. The soil was air-dried and sieved to a particle size ≤ 2 mm. No further details of soil characteristics were reported.

B. STUDY DESIGN

1. Experimental Conditions

The test was performed in 'static' systems consisting of stainless steel dishes each covered to a depth of approximately 1 cm with moistened soil to result in 50 g soil per sample.
The test was performed at a concentration of 4 mg/kg via drop wise application of the aqueous solution of the test material to the soil surface.
Samples were irradiated with a xenon burner (Hanau Suntest) simulating natural sunlight at an intensity of 602 W/m^2. Soil samples were cooled during irradiation to maintain a temperature of 30 ± 1 °C at the soil surface. Additional samples were incubated in the dark in parallel.
Loss of soil moisture was compensated for by daily weighing and appropriate addition of deionised

water.

2. Sampling

Duplicates of irradiated samples and dark controls were removed for analysis by day zero and after 1, 3, 7, 15 and 21 days of incubation.

3. Analytical Procedures

Soil samples were extracted with aqueous ammonia buffer solution at ambient temperature for one hour followed by rinsing of extracted soil twice with isopropanol. Combined extract and rinses were filled up to the mark with isopropanol followed by de-cationisation of an aliquot by use of a cation exchange resin. Following addition of trimethylsilyl diazomethane as derivatizing reagent the aliquot was concentrated to a final volume of approx. 2 mL and filled up to the mark with isopropanol.

The purified, derivatised and concentrated aliquots were analysed for the phosphonic acid dimethyl ester derivative by gas chromatography (GC) and the use of a photometric flame detector. Phosphonic acid was quantified by use of external standards.

II. RESULTS AND DISCUSSION

A. DATA

The results of photo-transformation tests of phosphonic acid onto the surface of [redacted] soil were summarized along with dark controls in Table 7.1.1.3- 1.

Table 7.1.1.3- 1: Photo-transformation of phosphonic acid on [redacted] soil

Component	Irradiated / Dark control	mean SD	Incubation time					
			0	1	3	7	15	21
Phosphonic acid	irradiated	mean	4.6	3.9	3.6	3.5[1]	2.6	2.2
		SD	0.2	0.1	0.1		0.2	0.0
	dark	mean	4.6	[2]	3.7	3.6	3.1	3.3
		SD	0.2		0.0	0.3	0.1	0.0

All values expressed as residues recovered in terms of mg/kg soil
DAT: days after treatment
[1] Single value due to problems during extraction for one replicate
[2] No value due to problems during extraction

B. MATERIAL BALANCE

Following use of non-labelled test material no material balance including the determination of non-extractable residues could be established.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

For irradiated samples, extractability of residues decreased from 4.6 mg/kg soil by day zero to 2.2 mg/kg by day 21.

Extractability of residues in dark controls decreased from 4.6 mg/kg soil by day zero to 3.3 mg/kg after 21 days.

D. VOLATILES

Owing to the nature of the test material the formation of volatile components was not expected and thus not determined.

E. TRANSFORMATION OF TEST SUBSTANCE

For irradiated samples, extractability of residues identified as phosphonic acid decreased from 4.6 mg/kg soil by day zero to 2.2 mg/kg by day 21.

Extractability of residues identified as phosphonic acid decreased from 4.6 mg/kg soil by day zero to 3.3 mg/kg after 21 days for dark controls.

III. CONCLUSIONS

Following irradiation at soil surfaces residues of phosphonate extractable from soil were found to decrease slowly with time.
The dissipation of the test substance could be affected by at least three factors, i.e. a decrease of extractability from soil in general, due to the influence of irradiation and, to some extent, due to microbial transformation as indicated by the dark controls investigated.

In total, it was concluded that phosphonate was subject to slow photo-degradation at soil surfaces.
This study was submitted as preliminary data to finally serve as supplemental information while study KCA 7.1.1.3/02 was submitted as a follow up, conducted at a lower test temperature (i.e. 22 °C) and for prolonged period of time (i.e. 45 days).

Report:	KCA 7.1.1.3/02 [redacted] B[redacted]; 2001; M-201629-01-1
Title:	Photodegradation of phosphorous acid in soil Code: AE 0540099
Report No.:	C011841
Document No.:	M-201629-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**yes**

Executive Summary
The photolytic transformation was investigated by application of phosphonic acid at a nominal test concentration of 4 mg a.s./kg soil onto the surface of samples of soil [redacted] followed by irradiation at 22 C under simulated sunlight for 45 days in maximum. Investigations were performed against dark controls.

For irradiated samples, extractability of residues identified as phosphonate decreased from 4.7 mg/kg soil by day zero to 1.0 mg/kg by day 45.
Extractability of residues identified as phosphonate decreased from 4.7 mg/kg soil by day zero to 2.6 mg/kg after 45 days for dark controls.
The dissipation of the test substance could be affected by at least three factors, i.e. a decrease of extractability from soil in general, due to the influence of irradiation and, to some extent, due to microbial transformation as indicated by the dark controls investigated.

Phosphonate could therefore be subject to slow photo-degradation at soil surfaces caused by indirect photolytic processes influenced by soil components.
As supplemental information the study demonstrated that photo-transformation of phosphonate in soil was a potential mechanism for the elimination of phosphonates from the soil environment. The contribution is expected to be rather limited considering the slow photolysis process and residues transported after application to the soil surface in the following to deeper soil layers after rainfall under field conditions.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material
Analytical grade phosphonic acid was used, batch EA5152SD2.

2. Soil
The test soil originated from [redacted], France. The soil was air-dried and sieved to a particle size ≤ 2 mm. The soil characteristics were summarized in Table 7.1.1.3- 2.

Table 7.1.1.3- 2: Physico-chemical properties of test soil

Parameter		Soil
Soil Designation		[redacted]
Geographic Location		
City		[redacted]
Country		France
Textural Class (USDA)		Loam
Coarse sand [200 µm – 2 mm]	(%)	23.2
Fine sand [50 µm – 200 µm]	(%)	19.8
Coarse silt [20 µm – 50 µm]	(%)	23.1
Fine silt [2 µm – 20 µm]	(%)	21.1
Clay [< 2 µm]	(%)	12.8
pH (water)		6.8
pH (1 M KCl)		6.6
Total phosphorus (P_2O_5) (g/kg)		0.129
Organic Matter (g/kg)		9.9
Organic carbon (g/kg)*		5.8
Cation Exchange Capacity (meq/100 g)		6.4

* Calculated by division using a factor of 1.72

B. STUDY DESIGN

1. Experimental Conditions

The test was performed in 'static' systems consisting of stainless steel dishes each covered to a depth of approximately 1 cm with moistened soil to result in 50 g soil per sample.

The test was performed at a concentration of 4 mg/kg via drop wise application of the aqueous solution of the test material to the soil surface.

Samples were irradiated with a xenon burner (Hanau Suntest) simulating natural sunlight at an intensity of 490 W/m². Soil samples were cooled during irradiation to maintain a temperature of 22 °C at the soil surface. Additional samples were incubated in the dark in parallel.

Loss of soil moisture was compensated for by daily weighing and appropriate addition of deionised water.

2. Sampling

Duplicates of irradiated samples and dark controls were removed for analysis by day zero and after 7, 15, 21, 30 and 45 days of incubation.

3. Analytical Procedures

Soil samples were extracted with aqueous ammonia buffer solution at ambient temperature for one hour followed by rinsing of extracted soil twice with isopropanol. Combined extract and rinses were filled up to the mark with isopropanol followed by de-cationisation of an aliquot by use of a cation exchange resin. Following addition of trimethylsilyl diazomethane as derivatizing reagent the aliquot was concentrated to a final volume of approx. 2 mL and filled up to the mark with isopropanol.

The purified, derivatised and concentrated aliquots were analysed for the phosphonic acid dimethyl ester derivative by gas chromatography (GC) and the use of a photometric flame detector. Phosphonic acid was quantified by use of external standards. The limit of quantification (LOQ) of the analytical method was 0.100 mg phosphonic acid/kg soil.

II. RESULTS AND DISCUSSION

A. DATA

The results of photo-transformation of phosphonic acid onto the surface of [redacted] soil were summarized along with dark controls in Table 7.1.1.3- 3.

Table 7.1.1.3- 3: Photo-transformation of phosphonic acid on [redacted] soil

Component	Irradiated / Dark control	mean SD	Incubation time 0	7	15	21	30	45
Phosphonic acid	irradiated	mean	4.7	3.4	3.0	2.3	1.6	1.0
		SD	0.1	0.1	0.2	0.1	0.1	0.0
	dark	mean	4.7	3.9	3.6	2.7	2.1	2.6
		SD	0.1	0.1	0.2	0.2	0.1	0.1

All values expressed as residues recovered in terms of mg/kg soil
DAT: days after treatment

B. MATERIAL BALANCE

Following use of non-labelled test material no material balance including the determination of non-extractable residues could be established.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

For irradiated samples, extractability of residues decreased from 4.7 mg/kg soil by day zero to 1.0 mg/kg by day 45.
Extractability of residues in dark controls decreased from 4.7 mg/kg soil by day zero to 2.6 mg/kg after 45 days.

D. VOLATILES

Owing to the nature of the test material the formation of volatile components was not expected and thus not determined.

E. TRANSFORMATION OF TEST SUBSTANCE

For irradiated samples, extractability of residues identified as phosphonate decreased from 4.7 mg/kg soil by day zero to 1.0 mg/kg by day 45.
Extractability of residues identified as phosphonate decreased from 4.7 mg/kg soil by day zero to 2.6 mg/kg after 45 days for dark controls.
The data served as an indication that dissipation of phosphonate was faster for irradiated samples.

However, the dissipation of the test substance could be affected by at least three factors, i.e. a decrease of extractability from soil in general, due to the influence of irradiation and, to some extent, due to microbial transformation as indicated by the dark controls investigated.

The exact contribution of each of the potential factors of influence mentioned was thus not clear.

III. CONCLUSIONS

Following irradiation at soil surfaces residues of phosphonate extractable from soil were found to decrease with time.
The dissipation of the test substance could be affected by at least three factors, i.e. a decrease of extractability from soil in general, due to the influence of irradiation and, to some extent, due to microbial transformation as indicated by the dark controls investigated.

In total, it was concluded that phosphonate could be subject to slow photo-degradation at soil surfaces caused by indirect photolytic processes influenced by soil components.

As supplemental information the study demonstrated that photo-transformation of phosphonate in soil was a potential mechanism for the elimination of phosphonates from the soil environment. The contribution is expected to be rather limited considering the slow photolysis process and residues transported after application to the soil surface in the following to deeper soil layers after rainfall under field conditions.

Since the potential for direct absorption of light by phosphonic acid or the active substance fosetyl-Al is very limited (i.e. no significant absorption at wavelengths of more than 290 nm), the actual degradation observed is explained by indirect photolytic effects, i.e. the reaction of singlet oxygen, hydroxyl radicals and peroxy radicals as oxidative species formed in the top 2 mm of soil from irradiation as indicated by publications submitted (see KCA 7.1.1.3/04 and KCA 7.1.1.3/05).

Report:	KCA 7.1.1.3/04 [redacted] L, 1999; M-234789-01-1
Title:	Predicting photoreaction rates in surface waters
Report No.:	C034361
Document No.:	M-234789-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The publication deals with some principles with regard to the estimation of photolysis rates of organic compounds when direct or indirect mechanisms are involved.

Direct photolysis rates can be estimated only for the limiting case of a quantum yield of one using relations shown in the publication to result in estimations for a maximum photolysis rate constant.
Indirect photolysis rates can be estimated using measured or estimated rate constants for each major photo-oxidant (i.e. singlet oxygen, hydroxyl-radicals and peroxy-radicals) toward the chemical of interest.

The hydroxyl-radical is the dominant photo-oxidant in many freshwaters for many classes of organic compounds. Availability of indirect photolysis rate constants along with several good quantity-activity-relationships (QSARs) could ensure that values of the indirect photolysis rate constants could be readily estimated also for new structures.

The publication was submitted as supplemental information that indirect photolysis is a fact to allow, in principle, the estimation of the corresponding photolysis rates and thus transfer to structures for which experimental rates are not known.

I. INTRODUCTION

Environmental photoreactions are driven by sunlight, which has significant photon fluxes only above 295 nm in the near ultraviolet. These reactions occur in surface waters, on soil, and in the atmosphere and are often the dominant environmental transformation processes. Photo-oxidation in the atmosphere, mediated by hydroxyl radical, controls the lifetime of most organic compounds found there.
Environmental photoreactions fall into two broad categories: direct and indirect photoreactions. Direct photolysis can take place only if a photon is absorbed by a compound, leading to bond cleavage or rearrangement to form a new, stable product. Rates of photolysis in dilute solution are the products of the rates of light absorption and the quantum yields (reaction efficiencies).

Indirect environmental photoreactions depend on formation of transient ground or excited state oxidants by insolation of naturally occurring sensitizers, such as dissolved organic matter (DOM), followed by reaction with other compounds present in the same environmental compartment in thermal (dark) reactions. The rates of indirect photolysis follow simple bimolecular kinetics.

II. INDIRECT PHOTOREACTIONS

Photooxidants and Kinetics

Indirect photolysis is more important for compounds that absorb little or no sunlight, where the process usually involves oxidation by transient photooxidants formed by sunlight absorption of natural chromophores such as DOM or NO_3^-. The transient oxidants in surface waters include singlet oxygen, HO radical, and peroxy radicals, all of which are electrophilic, making electron-rich compounds the main targets of indirect photolysis. Many of these same compounds also undergo rapid direct photoreactions. Aqueous HO radical, which oxidizes almost all classes of organic chemicals, is derived mainly from photolysis of nitrate ion. HO appears to be important in degrading synthetic chemicals in a variety of nitrate-bearing freshwaters.

Indirect Photoreaction Estimation Methods

Bimolecular rate constants for oxidations of a wide range of organic compounds by oxyradicals and singlet oxygen have been compiled and used to develop reasonably accurate SARs for photooxidations. Estimating an indirect photoreaction rate constant for a specific compound requires that a reaction profile be developed for each oxidant toward compound C in the form of kox[Ox] in Reaction. The HO radical oxidizes all structural units, each of which is assigned a reactivity value that, when summed over all units, gives the total reactivity of the compound toward HO. Sometimes reactivity of one molecular unit has been measured, but the reactivity of another unit must be estimated from an SAR.

SARs for Environmental Oxidants

Oxyradicals (peroxy or alkoxy radicals), HO radical and singlet oxygen are the most important photooxidants in aqueous environmental reactions with organics. SARs have been developed for reactions of these oxidants in organic solvents. Where comparisons are possible, relative reactivities in water and organic media are similar, although rate constants appear to be 2 to 10 times larger in water. Other photooxidants are not usually important in aqueous environmental reactions with organics. One exception may be superoxide (O_2^-), which forms most of the H_2O_2 in marine systems.

Most HO reaction constants have values around 5×10^9 M^{-1} s^{-1}, and a large data-base of k_{OH} values is available for the gas and aqueous phases. Peroxy radicals react with organic compounds by H-atom transfer or addition to double bonds, with rate constants ranging from < 0.01 to 300 M^{-1} s^{-1} at 25 °C. They are rarely important under environmental conditions because the average concentration of RO_2 in surface waters is 10^{-10} M. Singlet oxygen ($^1O_2$) reactivity, combined with its day-averaged surface water concentrations of about 3×10^{-14} M, limit environmental reactions to compounds like furans, dialkyl sulfides, polycyclic aromatics, pyrroles, and phenolate anions.

Estimation of k_{OX} for Selected Chemicals

Anthracene is used to illustrate the procedure for preparing an indirect photooxidation reactivity profile. Anthracene is a polycyclic, conjugated structure that cannot be fragmented into smaller units for estimation purposes. Different oxidants have different preferred points of oxidation on the conjugated rings, but the 9 and 10 positions are favoured because of symmetry and stabilization of benzylic radicals. Rate constants for oxidation of anthracene by RO_2, $^1O_2$ and HO have been measured in solution or in vapor: $k_{OX}(RO_2)$ is 60 M^{-1} s^{-1} in chlorobenzene at 25 °C; k_{OX} ($^1O_2$) is 5×10^8 M^{-1} s^{-1} for the water soluble 1-sulfonatoanthracene; k_{OX}(HO) is $6 \times 10^{-1°}$ M^{-1} s^{-1}. The total indirect oxidation rate constant for anthracene is controlled equally by HO and $^1O_2$. In most cases, HO radical appears to be the most important species, as it is in the troposphere. One difference in aqueous systems is that HO concentrations in insolated natural waters largely depend on the NO_3^- concentrations, whereas $^1O_2$ and RO_2 appear to depend more on the DOM concentration.

III. CONCLUSIONS

Direct photolysis rates can be estimated only for the limiting case of a quantum yield of one. This maximum photolysis rate constant can be used to evaluate the possible importance of photolysis as an environmental fate process compared with other kinds of degradation processes.
Indirect photolysis rates can be estimated using measured or estimated rate constants for each major photo-oxidant ($^1O_2$, RO_2, HO) toward the chemical of interest. HO is the dominant photo-oxidant in many freshwaters for many classes of organic compounds. Availability of reliable values of k_{HO} along with several good SARs and correlation equations ensures that k_{HO} values for new structures can be readily estimated and used as baseline values for lifetimes of compounds in insolated surface waters. Oxidation kinetics by $^1O_2$ and RO_2 are less well characterized in water, with the result that SARs for these reactions are fewer and less reliable. Nonetheless, a reactivity profile for each chemical can usually be estimated, from which the rate for indirect photolysis can be estimated and compared with the rate for direct photolysis, as well as rates for other transformation and transport processes acting on the compound.

The processes of indirect photo-transformation for compounds that absorb little or no sunlight (e.g. phosphonic acid) discussed in this publication may also be transferred to soil and its soil/pore water. Photo-generated, transient oxidants like singlet oxygen, hydroxyl radicals and peroxy radicals can be the cause for oxidation reactions with such compounds.

Report:	KCA 7.1.1.3/05 [redacted],; [redacted]; 1990; M-234783-01-1
Title:	Depth dependence of direct and indirect photolysis on soil surfaces
Report No.:	C054358
Document No.:	M-234783-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	no

Executive Summary

The publication deals with the influence of soil depth on the direct and indirect photolysis of the two active substances flumetralin (dinitroaniline herbicide) and disulfoton (dialkyl thioether organophosphorus insecticide) as examples. The investigations were performed in four soils with residues of each compound exposed at 28 to 31 °C to simulated sunlight for 8 days under conditions of the laboratory and under outdoor conditions. The tests were performed at a test concentration of 100 mg/kg dry weight of soil. Additional samples were incubated in the dark to serve as dark controls.

Outdoor irradiations were conducted at Reno, US, for 5 days between April and September (1985 and 1986). Laboratory irradiations used fluorescent lamps as light source (Westinghouse FS40 sunlamp).

Samples were analysed at 24 hours intervals over a total period of 8 and 5 days for laboratory and outdoor samples, respectively.

Photo-transformation was for flumetralin via direct photolysis while it was via indirect photolysis for disulfoton, supported by the reaction with singlet oxygen.

Various depths of treated soils (0.4 to 4.0 mm) were exposed to natural sunlight and laboratory lighting until no further degradation of chemical was detected. An estimate for the depth of photolysis was determined by multiplying the soil depth by the percent loss of each chemical. Direct photolysis was found to be restricted to the photic depth of soils (0.2 to 0.4 mm), while the indirect photolysis depth was slightly deeper. Vertical migration of singlet oxygen to depths greater than the depth of light penetration appears likely, although greater chemical movement of the more volatile disulfoton may account, in part, for the enhancement in indirect photolysis. In all cases photolysis was limited to

less than 1.0 mm for laboratory irradiations. Irradiation of the soil in sunlight resulted in greater depths of photolysis (up to 2 mm).
The publication was used as supplemental information that effects of direct and indirect photo-transformation exist in principle. Of course, such effects could be observed only for compounds that were susceptible for these two potential causes of photo-transformation.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

Non-labelled flumetralin (chem. purity 98.8%) and disulfoton (chem. purity > 95%) were used.

2. Test Soils

The study was carried out using four soils as summarized for their characteristics in Table 7.1.1.3- 4. The test soils were air-dried and sieved to a particle size of ≤ 0.425 mm.

Table 7.1.1.3- 4: Physico-chemical characteristics of test soils

Parameter	**Soil**			
Soil Designation	Kracaws	Main Station Farm	Montana Grain	Chico Orchard
Geographic Location				
City	[redacted]	[redacted]	[redacted]	[redacted]
Country	USA	USA	USA	USA
Particle size				
Sand [%]	45	54	50	55
Silt [%]	47	32	28	31
Clay [%]	8	14	22	14
pH	7.5	7.2	7.6	6.5
Organic Matter [%]	0.8	2.0	2.2	6.1

B. STUDY DESIGN

1. Experimental Conditions

Each of the soils was coated with a methylene chloride solution of flumetralin and disulfoton. The solvent was removed slowly from the soil slurry by rotary evaporation at 40 °C. This method gave a uniform pesticide distribution in the soil at 100 mg/kg. For each treated soil, 4, 8, 16, and 32 g portions were evenly spread on the bottom of glass Petri dishes (10 cm diameter), 10 dishes for each of the four soil depths. Five of these dishes were exposed to light and the other five were used as unexposed (dark) controls. Dark control trays were covered with 4 mil black polyethylene film.
Irradiations were conducted in the outdoors in Reno between April and September (1985 and 1986). One sunlight exposed and one dark control tray were removed at 24 hours intervals and placed in cold storage until the end of the 5 day irradiation period.

For laboratory irradiations, Petri dishes were placed on a 400 x 40 cm grid consisting of 40 10 x 10 cm quadrants under eight 4 ft fluorescent FS40 Westinghouse sunlamps. The dark controls were covered with aluminium foil. Electric fans were positioned under the light bank to stabilize temperatures between 28 and 31 °C during irradiation.

2. Sampling

A complete set consisting of four soil depths and their respective aluminium foil covered dark controls were removed at 48 h intervals and placed in cold storage until the end of the 192 h irradiation period.

3. Analytical Procedures

Soil samples were transferred from Petri dishes to 100 mL beakers and homogenized. A 1 g subsample from each beaker was extracted three times with 4 mL of acetone and analysed by using a gas chromatograph equipped with a nitrogen-phosphorus detector.

II. RESULT AND DISCUSSION

A. DEPTH DEPENDENCE OF DIRECT PHOTOLYSIS

In preliminary studies measuring the light transmission on thin layers of soil ultraviolet light was found to be greater than 90% attenuated in the top 0.2 mm in all irradiated soils. Direct photolysis was expected to be similarly restricted to the same vertical region.

The dinitroaniline herbicide flumetralin was selected to estimate the mean depth dependence of direct photolysis.

Table 7.1.1.3- 5: Estimated mean photolysis depths of flumetralin

Soil depth [mm]	Conditions	Soil: Kracaws	Main Station Farm	Montana Grain	Chico Orchard
0.4-0.5	outdoor	0.2	0.1	0.1	0.2
	indoor	0.1	0.1	0.1	0.1
0.8-1.0	outdoor	0.3	0.1	0.1	0.3
	indoor	0.2	0.2	0.1	0.2
1.6-2.0	outdoor	0.6	0.2	0.2	0.7
	indoor	0.2	0.2	0.2	0.5
3.1-4.0	outdoor	0.8	0.4	0.1	1.2
	indoor	0.2	0.2	0.2	1.0

On all irradiated soils, the loss of flumetralin was significantly slower than solution photolysis rates. In most instances, greater than 50% of the original concentration was recovered after 5 days of sunlight irradiation. A rapid initial loss of flumetralin was observed, but generally from day 3 to the termination of the experiment, no further significant loss was evident.

Temperatures measured at the surface of sunlight exposed soils typically exceeded 40 °C at noon. At these temperatures, pesticide movement at depths below the soil optical zone may have accounted for greater photochemical availability at the exposed surface of the deeper soils. Although the soils used in this study were air-dried, convective transport to the soil-atmosphere interface has been previously reported to be a significant process.

Pesticide sorption on natural surfaces has been reported to suppress various fate processes including photolysis. It was reported earlier that photolysis rates of polynuclear aromatic hydrocarbons (PAHs) are appreciably slowed on coal fly ashes that are relatively high in carbon and iron content. The role organic matter plays in direct photolysis of surface-exposed soils is not clear.

The averages of the mean photolysis depth values for all soils and at all soil depths were 0.32 and 0.23 nm for outdoor and laboratory irradiations, respectively. The higher direct photolysis depth estimates for outdoor exposures were not surprising in view of possibly greater photochemical availability of the flumetralin from surface disturbances caused by wind and greater surface temperatures that could possibly increase chemical transport to the exposed surface.

Flumetralin absorbs sunlight over a wider wavelength range (300 to 500 nm) than most pesticides. Since humic substances have higher extinction coefficients in the shorter wavelengths, the penetration of light into soils is likely greater for the longer sunlight wavelengths. Therefore, the mean photolysis depths determined for flumetralin may be greater than for compounds absorbing only the short-ultraviolet sunlight wavelengths.

B. DEPTH DEPENDENCE OF INDIRECT PHOTOLYSIS

The thioether pesticide disulfoton was selected to evaluate the depth dependence of indirect photolysis at the soil surface. Disulfoton does not absorb or undergo direct photolysis in the sunlight spectrum. On soils, however, photosensitized oxidation to its corresponding sulfoxide is rapid.

Table 7.1.1.3- 6: Estimated mean photolysis depths for disulfoton

Soil depth [mm]	Conditions	Soil			
		Kracaws	**Main Station Farm**	**Montana Grain**	**Chico Orchard**
0.4-0.5	outdoor	0.2	0.2	0.3	0.3
	indoor	0.2	0.1	0.2	0.2
0.8-1.0	outdoor	0.3	0.4	0.4	0.6
	indoor	0.2	0.3	0.3	0.2
1.6-2.0	outdoor	0.5	0.7	0.6	1.2
	indoor	0.2	0.2	0.2	0.4
3.1-4.0	outdoor	0.6	0.7	0.8	2.1
	indoor	0.4	0.4	0.4	0.6

For the four sunlight-exposed soils containing disulfoton, the mean depths for photosensitized oxidations were consistently greater than the simultaneously measured mean depths of photolysis for flumetralin. The averages of the mean estimated photolysis depth among the four soils were 0.28 and 0.72 mm, for laboratory and sunlight-exposed samples, respectively.

The photo-oxidation of disulfoton was found to occur appreciably deeper than the optical depth. Mean indirect photolysis depths were reported to be greater than 0.7 mm for outdoor exposures. This observed depth value is conservative when compared to calculated values of mean singlet oxygen diffusion in the vapour phase. In the aerated, unsaturated soil environment, penetration of singlet oxygen to soil depths greater than 2 mm is possible. The depth to which this oxidant vertically diffuses under environmental conditions will depend on moisture content, soil porosity, and steepness of thermal gradients on the sunlight-exposed soil interface. The reported differences in direct and indirect photolysis depths may also, to a certain degree, reflect differences in chemical volatility of the two pesticides used in this study.

The observed enhancement of indirect photolysis depths in relation to direct photolysis may also be attributable to differences in chemical volatility of pesticides used in this study; disulfoton is substantially more volatile than flumetralin. Although loss in dark controls was negligible among all soils in this study, greater disulfoton availability in relation to flumetralin on the exposed surface could be considerable and, in part, account for the observed enhancement of indirect photolysis to greater soil depths.

Mass balances for dark controls varied from 87 to 104%.

III. CONCLUSIONS

Direct photolysis was found to be restricted to the photic depth of soils (0.2 to 0.4 mm), while the indirect photolysis depth was slightly deeper. Vertical migration of singlet oxygen to depths greater than the depth of light penetration appears likely, although greater chemical movement of the more volatile disulfoton may account, in part, for the enhancement in indirect photolysis.
For all cases photolysis was limited to less than 1.0 mm for laboratory irradiations. Irradiation of the soil in sunlight resulted in greater depths of photolysis (up to 2 mm).

The publication provided supplemental information on principles of the effect of soil depth on phototransformation.

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

Report:	KCA 7.1.2.1.1/01 [redacted]; [redacted]; [redacted]; 1978; M-163672-01-1
Title:	Aluminium ethylphosphite - Degradation in the soil.
Report No.:	R002963
Document No.:	M-163672-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.2.1.1/02 [redacted]; [redacted]; 1982; M-159391-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil metabolism study
Report No.:	R000825
Document No.:	M-159391-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.2.1.1/03 [redacted]; [redacted]; 1999; M-184329-01-1
Title:	The rate of degradation of (14C)-fosetyl-Al in three soils under aerobic conditions at 20 degree Celsius
Report No.:	R011664
Document No.:	M-184329-01-1
Guideline(s):	EU (=EEC): 95/36/EC, (1995); SETAC: (1995); Equivalent to US EPA OPPTS Guideline No. 835.4100
Guideline deviation(s):	none
GLP/GEP:	**yes**

For the active substance fosetyl-aluminium (fosetyl-Al), information on the rate of degradation in aerobic soil in the laboratory could be derived, in principle, from studies performed under the following conditions:

- three soils (20 and 12 °C, moisture at 70% of water retention capacity for one soils and at 50% for two soils) after application of 1-^{14}C-labeled and ^{32}P-labeled fosetyl-Al (KCA 7.1.2.1.1/01);
- four soils (20 °C, moisture at 75% of water capacity at 0.33 bar) after application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.2.1.1/02);
- three soils under standard conditions (20 °C, moisture at 40% of the maximum water holding capacity (MWHC) after application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.2.1.1/03).

This data requirement had been addressed under Point 7.1.1.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

Study KCA 7.1.2.1.1/01 had been excluded from existing risk assessment. No analysis of soil extracts was performed and consequently, this did not allow for distinguishing between active substance and metabolites. Moreover, reporting was unclear about the basis of soil moisture determination and its maintenance during incubation.

Following latest guidance on kinetic evaluation the data from existing studies KCA 7.1.2.1.1/02 and KCA 7.1.2.1.1/03 have been re-evaluated and therefore superseding the existing kinetic evaluations.

The evaluations were performed according to FOCUS Guidance in order to derive values for the half-lives and the DT_{90} for comparison with trigger endpoints and half-lives for modeling endpoints for input into environmental risk assessments.

Report:	KCA 7.1.2.1.1/04[redacted].; 2015; M-528985-01-1
Title:	Fosetyl-Al and Ethanol - Kinetic evaluation of aerobic degradation in soil according to FOCUS guidance
Report No.:	EnSa-15-0443
Document No.:	M-528985-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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

For the active substance fosetyl-aluminium (fosetyl-Al) aerobic soil degradation data as referenced under KCA 7.1.2.1.1/02 and KCA 7.1.2.1.1/03 were kinetically evaluated according to actual guidance [FOCUS, 2015] to derive values for the half-life and the DT_{90} in for modelling and trigger endpoints. Following application of 1-^{14}C-labelled fosetyl-Al and incubation under conditions of the laboratory data were considered from two studies performed in seven soils in total.

The kinetic evaluation followed a stepwise approach. The first step consisted of identification of best fits to measured data starting with the SFO kinetic model. Tests with the bi-phasic model FOMC did not result in better fits thus best fit half-lives for comparison against trigger endpoints were derived from use of the SFO model. Finally, values for the DT_{50} were normalised to reference conditions (20 °C, pF2 moisture).

Trigger endpoints:

Non-normalised values of the DT_{50} and the DT_{90} were derived from SFO best fits in six soils with results summarized in Table 7.1.2.1.1- 1. No reliable half-life could be estimated for the sandy soil of study KCA 7.1.2.1.1/03.

Non-normalised half-lives of fosetyl-Al from tests at 20 °C ranged from less than 0.01 days (0.2 hours) for a sandy loam soil to 0.06 days (1.5 hours) for clay loam soil 4 while values for the DT_{90} were from 0.03 days (0.7 hours hours) to 0.2 days (5.0 hours) in the same soils.

For estimation of the trigger half-life at 10 °C, a Q_{10} factor of 2.58 was applied to result in a maximum value of the DT_{50} of 0.15 days and a DT_{90} of 0.51 days as observed in clay loam soil 4 (study KCA 7.1.2.1.1/02).

Table 7.1.2.1.1- 1: Summary of results of kinetic evaluation of degradation for fosetyl-Al in aerobic soil in the laboratory for comparison against EU triggers

Parameter	**Fosetyl-Al**
20 °C, Non-normalised DT_{50}, range (days)	0.01 – 0.06
Worst case DT_{50} (days)	**0.06**
20 °C, Non-normalised DT_{90}, range (days)	0.03 – 0.2
Worst case DT_{90} (days)	**0.02**
10 °C, Non-normalised DT_{50} (days)	0.15
10 °C, Non-normalised DT_{90} (days)	0.51

Modelling endpoints:
Values of the DT_{50} and DT_{90} in aerobic soil following normalization to reference conditions (20 °C, pF2 moisture) were summarized in Table 7.1.2.1.1- 2.
For use as modelling endpoint, the overall geometric mean of normalised half-lives of fosetyl-Al was calculated to 0.0161 days.

Table 7.1.2.1.1- 2: Normalised laboratory DT_{50}-values for fosetyl-Al in aerobic soil for use as modelling input parameters in environmental exposure assessments

Compound	Fosetyl-Al
Normalised DT_{50} (20 °C, pF2), range (days)	0.0054 - 0.456
Geometric mean	**0.0161**

I. Material and Methods

For the parent compound fosetyl-Al details on study conduct and its results have been summarised in Section CA 7.1.1.1. The degradation data were evaluated following actual kinetic guidance [FOCUS, 2006, amended 2015] with the software KinGUI2.
The measured values were taken into account as reported and thus treated as individual replicates. All sets along with their data points were weighted equally. Time zero residues for fosetyl-Al were set to the recovered amount.
Following the recommended procedure for determining modelling endpoints by FOCUS, all datasets were evaluated using the simple first order (SFO) kinetic model with free optimisation of parameters.
FOCUS kinetic evaluation rules aimed at deriving DT_{50} values for use as model and trigger inputs and were performed according to the respective decision flowchart. The kinetic evaluations including statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-square (IRLS) optimisation.

II. Results and Discussion

Trigger endpoint determination:
Following the flowchart, the kinetic model FOMC showed no improvement over SFO, thus evaluations using DFOP were not conducted. SFO kinetics was determined to be the best-fit for all soils, but for the sandy soil of study KCA 7.1.2.1.1/03. No reliable kinetic endpoint could be derived for this soil.
The resulting non-normalised values for the DT_{50} and the DT_{90} derived are summarised in Table 7.1.2.1.1- 3.

Modelling endpoint determination:
For use in environmental modelling degradation half-lives were normalised to reference conditions regarding soil moisture (100% field capacity) and temperature (20 °C). The parameters used in the laboratory tests and the respective correction factors calculated were summarised in Table 7.1.2.1.1- 4.
The half-lives resulting from normalisation were summarised in Table 7.1.2.1.1- 5.

Table 7.1.2.1.1- 3: Trigger evaluation: Non-normalised DT_{50}-values for fosetyl-Al in aerobic soils under laboratory conditions

Soil	Label position	Model	DT_{50} (days)	DT_{90} (days)	Chi^2 (%)	Parameter	Visual[a)]
Soil 1 sandy loam, 20 °C (Study 1)	1-^{14}C	SFO	0.012 (0.3 h)	0.040 (1.0 h)	2.3	k = 57.66	+
Soil 2 loamy sand, 20 °C (Study 1)	1-^{14}C	SFO	0.049 (1.2 h)	0.162 (4.0 h)	0.6	k = 14.22	+
Soil 3 silt loam, 20 °C (Study 1)	1-^{14}C	SFO	0.051 (1.2 h)	0.170 (4.0 h)	12.2	k = 13.53	O
Soil 4 clay loam, 20 °C (Study 1)	1-^{14}C	SFO	0.060 (1.5 h)	0.20 (5.0 h)	4.1	k = 11.47	+
Clay loam, 20 °C (Study 2)	1-^{14}C	SFO	0.014 (0.3 h)	0.047 (1.0 h)	11.4	k = 2.04	
Sand, 20 °C (Study 2)	1-^{14}C	-	-	-	-	-	-
Sandy loam, 20 °C (Study 2)	1-^{14}C	SFO	0.008 (0.2 h)	0.027 (0.7 h)	3.1	k = 3.61	

Study 1: KCA 7.1.1.1/02, KCA 7.1.2.1.1/02 and KCA 7.1.2.1.2/02
Study 2: KCA 7.1.1.1/03, KCA 7.1.2.1.1/03 and KCA 7.1.2.1.2/03
[a)] Visual assessment: + = good, O = moderate, - = poor

Table 7.1.2.1.1- 4: Correction factors for soil temperature and moisture content

Soil	Label position	Temperature (°C)	Incubation moisture (%w/w)	pF2 moisture (%w/w)	Correction factor
Soil 1 sandy loam, 20 °C (Study 1)	1-^{14}C	20	11.3	19	0.693
Soil 2 loamy sand, 20 °C (Study 1)	1-^{14}C	20	6.8	14	0.600
Soil 3 silt loam, 20 °C (Study 1)	1-^{14}C	20	15.8	26	0.704
Soil 4 clay loam, 20 °C (Study 1)	1-^{14}C	20	18.8	28	0.755
Clay loam, 20 °C (Study 2)	1-^{14}C	20	12.8	28	0.578
Sand, 20 °C (Study 2)	1-^{14}C	-	-	-	-
Sandy loam, 20 °C (Study 2)	1-^{14}C	20	10.8	19	0.673

Study 1: KCA 7.1.1.1/02, KCA 7.1.2.1.1/02 and KCA 7.1.2.1.2/02
Study 2: KCA 7.1.1.1/03, KCA 7.1.2.1.1/03 and KCA 7.1.2.1.2/03

Table 7.1.2.1.1- 5: Normalised (20 °C and pF2) DT_{50} values for fosetyl-Al as modelling endpoints

Soil	Kinetics	DT_{50} (days)	DT_{90} (days)	Non-normalised DT_{50} estimate for modelling (days)	Normalised DT_{50} [20°C and pF2] (days)
Soil 1 sandy loam, 20°C (Study 1)	SFO	0.012 (0.3 h)	0.040 (1.0 h)	0.012 (0.3 h)	0.0083 (0.2 h)
Soil 2 loamy sand, 20°C (Study 1)	SFO	0.049 (1.2 h)	0.162 (4.0 h)	0.049 (1.2 h)	0.0293 (0.7 h)
Soil 3 silt loam, 20°C (Study 1)	SFO	0.051 (1.2 h)	0.170 (4.0 h)	0.051 (1.2 h)	0.0361 (0.9)
Soil 4 clay loam, 20°C (Study 1)	SFO	0.060 (1.5 h)	0.20 (5.0 h)	0.60 (1.5 h)	0.0456 (1.1)
Clay loam, 20°C (Study 2)	SFO	0.014 (0.3 h)	0.047 (1.0 h)	0.014 (0.3 h)	0.0082 (0.2 h)
Sand, 20°C (Study 2)	-	-	-	-	-
Sandy loam, 20°C (Study 2)	SFO	0.008 (0.2 h)	0.027 (0.7 h)	0.008 (0.2 h)	0.0054 (0.1 h)
Geometric mean					**0.0161** (0.4 h)

Study 1: KCA 7.1.1.1/02, KCA 7.1.2.1.1/02 and KCA 7.1.2.1.2/02
Study 2: KCA 7.1.1.1/03, KCA 7.1.2.1.1/03 and KCA 7.1.2.1.2/03

III. Conclusion

The kinetic evaluation according to FOCUS kinetic guidance resulted in the use of the monophasic model SFO to derive reliable values for the half-lives and the DT_{90} of the active substance fosetyl-Al from five soils in total.
For comparison with EU trigger endpoints non-normalised half-lives of fosetyl-Al from tests at 20 °C ranged from less than 0.01 days (0.2 hours) for a sandy loam soil to 0.06 days (1.5 hours) for clay loam soil 4 while values for the DT_{90} were from 0.03 days (0.7 hours) to 0.2 days (5.0 hours) in the same soils.
For estimation of the trigger half-life at 10 °C, a Q_{10} factor of 2.58 was applied to result in a maximum value of the DT_{50} of 0.15 days and a DT_{90} of 0.51 days as observed in clay loam soil 4.

For use as modelling input parameters in environmental risk assessments the evaluation resulted in a geometric mean half-life normalised for moisture (pF2) and temperature (20 °C) of 0.0161 days.

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

Request from the RMS:
In the kinetic assessment by [redacted] (2015, KCA 7.1.2.1.1/04), the default humidity values as provided by FOCUS Kinetic Guidance (2014) were used in the normalization process for the soils from [redacted] and [redacted] (1982, KCA 7.1.2.1.1/02). However, according to FOCUS Kinetic Guidance (2014), the humidity actually measured during the study should be taken into account in the normalization process when available. In this respect, additional normalization calculations should be provided.

Response from BCS:

For moisture normalization according to FOCUS (2014) two sets of values are necessary: soil moisture under study conditions and soil moisture under reference conditions (pF2). In the study from [redacted] and [redacted] (1982, KCA 7.1.2.1.1/02) only the moisture content under study conditions (75% of 0.33 bar) and under non-FOCUS reference conditions (0.33 bar / pF 2.5) are provided. Thus, direct normalisation to pF2 is not possible. Mixing of moisture data from lab studies and the FOCUS default values should be avoided, because this would compare soil physical data for structured soil (field situation from FOCUS default values) and disturbed soil (laboratory), which are not comparable regarding the water holding capacity. Therefore, the default FOCUS values for both study and reference conditions were used for normalization, which provides consistent and realistic normalization factors.

If longer degradation half-lives (and hence lower reference moisture) is regarded more conservative for the risk assessment, the moisture content at pF 2.5 can be used as a conservative estimate for the moisture content at pF 2, because it is clear that the moisture content is lower at higher suction pressure. With this approach the water content under study conditions is 75% of the water content under reference conditions and a normalization factor of 0.818 results for all four soils.

Soil	Texture class (USDA)	MWHC [%] [3]	Moist. at 0.33bar [%]	Incubation moisture [%MWHC/0.33bar]	θ [%]	$θ_{ref}$ (10kPa) [%]	$f_θ$
Soil 1 [1]	sandy loam		24	75	18.0	24 [4]	0.818
Soil 2 [1]	loamy sand		16	75	12.0	16 [4]	0.818
Soil 3 [1]	silt loam		26	75	19.5	26 [4]	0.818
Soil 4 [1]	clay loam		26	75	19.5	26 [4]	0.818
S 261 [2]	clay loam	32		40	12.8	28 [3]	0.578
S 263 [2]	sandy loam	27		40	10.8	19 [3]	0.673

[1] [redacted], [redacted] et al. (1982, KCA 7.1.2.1.1/02)
[2] [redacted], [redacted] (1999, KCA 7.1.2.1.1/03)
[3] from Table 2.2 of FOCUS (2014)
[4] The moisture content at 0.33 bar was used as a conservative estimate.

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

Report:	KCA 7.1.2.1.2/01 [redacted]; [redacted]; 1982; M-159391-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil metabolism study
Report No.:	R000825
Document No.:	M-159391-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.2.1.2/02 [redacted]; [redacted]; 1999; M-184329-01-1
Title:	The rate of degradation of (14C)-fosetyl-Al in three soils under aerobic conditions at 20 degree Celsius
Report No.:	R011664
Document No.:	M-184329-01-1
Guideline(s):	EU (=EEC): 95/36/EC, (1995); SETAC: (1995); Equivalent to US EPA OPPTS Guideline No. 835.4100
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.1.2.1.2/03 [redacted]; [redacted]; 1953; M-234773-01-1
Title:	Transition of phosphite to phosphate in soils
Report No.:	C034350
Document No.:	M-234773-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.2.1.2/04 [redacted]; [redacted]; 1999; M-184316-01-1
Title:	Aerobic metabolism of (33P)-phosphorous acid in two soils.
Report No.:	R011658
Document No.:	M-184316-01-1
Guideline(s):	USEPA (=EPA): N, 163-1 (1982)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.1.2.1.2/05 [redacted]; [redacted]; [redacted]; 2001; M-203498-01-1
Title:	Fosetyl-Al Investigation of the potential for phosphorous acid residues in succeeding crops
Report No.:	C019853
Document No.:	M-203498-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.2.1.2/06 [redacted] F; 2015; M-528985-01-1
Title:	Fosetyl-Al and Ethanol - Kinetic evaluation of aerobic degradation in soil according to FOCUS guidance
Report No.:	EnSa-15-0443
Document No.:	M-528985-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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**

Report:	KCA 7.1.2.1.2/07 [redacted],; 2015; M-532341-01-1
Title:	Phosphonic acid - Rate of degradation in four soils under aerobic conditions
Report No.:	M-532341-01-1
Document No.:	M-532341-01-1
Guideline(s):	OECD Guidelines for Testing Chemicals: Aerobic and Anaerobic Transformation in Soil, Guideline 307 (Adopted 24th April 2002)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.1.2.1.2/08 [redacted],; 2015; M-531799-01-1
Title:	Phosphonic Acid (H3PO3) - Kinetic Evaluation of Aerobic Transformation in Soil According to FOCUS Kinetics Guidance
Report No.:	EnSa-15-0632
Document No.:	M-531799-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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**

For metabolite ethanol data on the rate of degradation in aerobic soil can be derived from existing laboratory studies performed with the active substance fosetyl-aluminium (fosetyl-Al) and from separate dosing of ethanol to soil under the following conditions:

- four soils (20 °C, moisture at 75% of water capacity at 0.33 bar) after application of 1-^{14}C-labeled active substance. In addition and for comparison, investigations were also performed with 1-^{14}C-labeled ethanol separately dosed to two soils and incubated under the same conditions as for the active substance (KCA 7.1.2.1.2/01);
- three soils under standard conditions (20 °C, moisture at 40% of the maximum water holding capacity (MWHC) after application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.2.1.2/02)

For metabolite phosphonic acid data on rate of degradation in aerobic soil were additionally derived from the following existing information:

- one soil incubated at 28 °C and moisture at field capacity (FC) following application of non-labeled disodium phosphonate (KCA 7.1.2.1.2/03);
- two soils incubated under standard conditions (20 °C, moisture at 45% MWHC for the first soil and at 75% of the field capacity at 0.33 bar for the second) following application of ^{33}P-labelled phosphonic acid (KCA 7.1.2.1.2/04);
- one soil incubated under variable semi-outdoor conditions of temperature and moisture following application of non-labelled phosphonic acid (KCA 7.1.2.1.2/05).

For metabolite phosphonic acid this data requirement had been addressed under Point 7.1.1.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The existing soil degradation data were re-evaluated against requirements in design and conduct of OECD Guideline 307 and, in view of latest guidance on kinetic evaluation. For studies KCA 7.1.2.1.2/03 and KCA 7.1.2.1.2/05, the design, conduct and reporting was significantly different from standards defined by OECD 307 and, consequently, the data were excluded. Studies KCA 7.1.2.1.2/03 and KCA 7.1.2.1.2/05 are therefore regarded as supplemental information with no consideration in environmental risk assessment.

In view of the potential data gap on information on rate of in aerobic soil, a new study was initiated investigating the degradation of non-labelled phosphonic acid in four soils as summarized under KCA 7.1.2.1.2/07.
The kinetic evaluation of study KCA 7.1.2.1.2/04 and KCA 7.1.2.1.2/07 was performed in KCA 7.1.2.1.2/08 in order to derive values for the comparison with trigger and modelling endpoints for input into environmental risk assessments.

For metabolite ethanol, the data from existing study KCA 7.1.2.1.2/02 were evaluated following latest guidance on kinetic evaluation as reported under KCA 7.1.2.1.2/06.

New information: New kinetic evaluations and rate of degradation study in soil for metabolites

The existing data for the active substance data were new evaluated following actual requirements in kinetic assessment of the rate of degradation.

Report:	KCA 7.1.2.1.2/06 [redacted],; 2015; M-528985-01-1
Title:	Fosetyl-Al and Ethanol - Kinetic evaluation of aerobic degradation in soil according to FOCUS guidance
Report No.:	EnSa-15-0443
Document No.:	M-528985-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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

For metabolite ethanol degradation data could be derived from tests with the active substance fosetyl-aluminium (fosetyl-Al) as referenced under KCA 7.1.2.1.2/02. The study also included tests performed with ^{14}C-labelled ethanol dosed separately to soils. The data were kinetically evaluated according to actual guidance [FOCUS, 2015] to derive values for the half-life and the DT_{90} in aerobic soil for modelling and trigger endpoints.

Following application of 1-^{14}C-labelled fosetyl-Al degradation data were available from four soils in total. From application of 1-^{14}C-labelled ethanol to two soils tested with the active substance another two data sets were available for the metabolite.

The kinetic evaluation followed a stepwise approach. The first step consisted of identification of best fits to measured data starting with the SFO kinetic model. Tests with the bi-phasic model FOMC did not result in better fits thus best fit half-lives for comparison against trigger endpoints were derived from use of the SFO model. Finally, values for the DT_{50} were normalised to reference conditions (20°C, pF2 moisture).

<u>Trigger endpoints:</u>

Non-normalised values of the DT_{50} and the DT_{90} were derived from SFO best fits in four soils with results summarized in Table 7.1.2.1.2- 1.

Non-normalised half-lives of fosetyl-aluminium from tests at 20 °C ranged from less than 0.01 days (0.2 hours) for a sandy loam soil to 0.06 days (1.5 hours) for clay loam soil 4 while values for the DT_{90} were from 0.03 days (0.7 hours hours) to 0.2 days (5.0 hours) in the same soils.

Table 7.1.2.1.2- 1: EU trigger endpoint: Non-normalised DT_{50}- and DT_{90}-values for ethanol in aerobic soil

Parameter	Ethanol
Non-normalised DT_{50}, range, 20 °C (days)	0.086 – 0.176
Worst case DT_{50} (days)	**0.176**
Non-normalised DT_{90}, range, 20 °C (days)	0.32 – 0.58
Worst case DT_{90} (days)	**0.58**

Modelling endpoints:
Values of the DT_{50} and DT_{90} in aerobic soil following normalization to reference conditions (20 °C, pF2 moisture) were summarized in Table 7.1.2.1.2- 2.
For use as modelling endpoint, the overall geometric mean of normalised half-lives of ethanol was calculated to 0.091 days.

Table 7.1.2.1.2- 2: Modelling input parameter: Normalised DT_{50}-values for ethanol in aerobic soil

Compound	**Ethanol**
Normalised (20 °C, pF2) DT_{50}, range (days)	0.065 - 0.124
Geometric mean	**0.091**

I. Material and Methods

For the parent compound fosetyl-Al details on study conduct and its results have been summarised in Section CA 7.1.1.1. The degradation data were evaluated following actual kinetic guidance [FOCUS, 2006, amended 2015] with the software KinGUI2.
The measured values were taken into account as reported and thus treated as individual replicates. All sets along with their data points were weighted equally. Time zero residues for fosetyl-Al were set to the recovered amount.
Following the recommended procedure for determining modelling endpoints by FOCUS, all datasets were evaluated using the simple first order (SFO) kinetic model with free optimisation of parameters.
FOCUS kinetic evaluation rules aimed at deriving DT_{50} values for use as model and trigger inputs and were performed according to the respective decision flowchart. The kinetic evaluations including statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-square (IRLS) optimisation.

II. Results and Discussion

Trigger endpoint determination:
Following the FOCUS flowchart, the kinetic model FOMC showed no improvement over SFO, thus evaluations using DFOP were not conducted. The SFO kinetic model was to result in best fits for all soils of study KCA 7.1.2.1.1/02. No reliable kinetic endpoint could be derived for ethanol in soils of study KCA 7.1.2.1.1/03. The resulting non-normalised values for the DT_{50} and the DT_{90} derived are summarised in Table 7.1.2.1.2- 3.

Modelling endpoint determination:
For use in environmental modelling degradation half-lives were normalised to reference conditions regarding soil moisture (100% field capacity) and temperature (20 °C). The parameters used in the laboratory tests and the respective correction factors calculated were summarised in Table 7.1.2.1.2- 4.
The half-lives resulting from normalisation were summarised in Table 7.1.2.1.2- 5.

Table 7.1.2.1.2- 3: Trigger evaluation: Non-normalised DT_{50}-values for ethanol in aerobic soils under laboratory conditions

Soil	Label position	Kinetic model	DT_{50} (days)	DT_{90} (days)	Chi^2 (%)	Parameter	Visual[a)]
Soil 1 sandy loam, 20 °C (Study 1)	1-^{14}C	SFO	0.162 (3.9 h)	0.54 (12.9 h)	9.6 (9.6)[b)]	k = 7.15	+
Soil 1 sandy loam, 20 °C (Study 1)	1-^{14}C-ethanol	SFO	0.171 (4.1 h)	0.57 (13.6 h)	8.3 (8.0)[c)]	k = 7.64	+
Soil 2 loamy sand, 20 °C (Study 1)	1-^{14}C	SFO	0.123 (3.0 h)	0.41 (10.0 h)	4.8 (3.0) [b)]	k = 9.01	+
Soil 3 silt loam, 20 °C (Study 1)	1-^{14}C	SFO	0.176 (4.2 h)	0.58 (13.9 h)	4.3 (11.1) [b)]	k = 6.31	+
Soil 4 clay loam, 20 °C (Study 1)	1-^{14}C	SFO	0.086 (2.1 h)	0.29 (7.0 h)	20.0 (11.2) [b)]	k = 10.50	O
Soil 4 clay loam, 20° C (Study 1)	1-^{14}C-ethanol	SFO	0.095 (2.3 h)	0.32 (7.6 h)	15.5 (14.0)[c)]	k = 12.1	O

Study 1: KCA 7.1.1.1/02, KCA 7.1.2.1.1/02 and KCA 7.1.2.1.2/02
Study 2: KCA 7.1.1.1/03, KCA 7.1.2.1.1/03 and KCA 7.1.2.1.2/03
[a)] Visual assessment: + = good, O = moderate, - = poor
[b)] For system in combined evaluation with active substance
[c)] For system in combined evaluation with volatile fraction

Table 7.1.2.1.2- 4: Correction factors for soil temperature and moisture content

Soil	Label position	Temperature (°C)	Incubation moisture (%w/w)	pF2 moisture (%w/w)	Correction factor
Soil 1 sandy loam, 20 °C (Study 1)	1-^{14}C	20	11.3	19	0.693
Soil 1 sandy loam, 20 °C (Study 1)	1-^{14}C-ethanol	20	11.3	19	0.693
Soil 2 loamy sand, 20 °C (Study 1)	1-^{14}C	20	6.8	14	0.600
Soil 3 silt loam, 20 °C (Study 1)	1-^{14}C	20	15.8	26	0.704
Soil 4 clay loam, 20 °C (Study 1)	1-^{14}C	20	18.8	28	0.755
Soil 4 clay loam, 20 °C (Study 1)	1-^{14}C-ethanol	20	18.8	28	0.755

Study 1: KCA 7.1.1.1/02, KCA 7.1.2.1.1/02 and KCA 7.1.2.1.2/02
Study 2: KCA 7.1.1.1/03, KCA 7.1.2.1.1/03 and KCA 7.1.2.1.2/03

Table 7.1.2.1.2- 5: Modelling endpoints: Normalised (20 °C and pF2) DT50 values for ethanol

Soil	Kinetic model	DT_{50} (days)	DT_{90} (days)	Non-normalised DT_{50} estimate for modelling (days)	Normalised DT_{50} [20°C and pF2] (days)
Soil 1 sandy loam, 20 °C (Study 1)	SFO	0.162 (3.9 h)	0.54 (12.9 h)	0.162 (3.9 h)	0.112 (2.7 h)
Soil 1 sandy loam, 20 °C (Study 1)	SFO	0.171 (4.1 h)	0.57 (13.6 h)	0.171 (4.1 h)	0.119 (2.9 h)
Soil 2 loamy sand, 20 °C (Study 1)	SFO	0.123 (3.0 h)	0.41 (10.0 h)	0.123 (3.0 h)	0.074 (1.8 h)
Soil 3 silt loam, 20 °C (Study 1)	SFO	0.176 (4.2 h)	0.58 (13.9 h)	0.176 (4.2 h)	0.124 (3.0 h)
Soil 4 clay loam, 20 °C (Study 1)	SFO	0.086 (2.1 h)	0.29 (7.0 h)	0.086 (2.1 h)	0.065 (1.6 h)
Soil 4 clay loam, 20 °C (Study 1)	SFO	0.095 (2.3 h)	0.32 (7.6 h)	0.095 (2.3 h)	0.072 (1.7 h)
Geometric mean					**0.091** (2.2 hours)

Study 1: KCA 7.1.1.1/02, KCA 7.1.2.1.1/02 and KCA 7.1.2.1.2/02
Study 2: KCA 7.1.1.1/03, KCA 7.1.2.1.1/03 and KCA 7.1.2.1.2/03

III. Conclusion

The kinetic evaluation according to FOCUS kinetic guidance resulted in the use of the monophasic model SFO for all data sets to derive reliable values for the half-lives and the DT_{90} of metabolite ethanol from four soils in total.
For comparison with EU trigger endpoints non-normalised half-lives of ethanol from tests at 20 °C ranged from less than 0.086 days (2.1 hours) for clay loam soil 4 to 0.176 days (4.2 hours) for silt loam soil 3 while values for the DT_{90} were from 0.29 days (7.0 hours) to 0.58 days (13.9 hours) in the same soils.
For use as modelling input parameters in environmental risk assessments the evaluation resulted in a geometric mean half-life normalised for moisture (pF2) and temperature (20 °C) of 0.091 days.

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

Report:	KCA 7.1.2.1.2/07 [redacted],; 2015; M-532341-01-1
Title:	Phosphonic acid - Rate of degradation in four soils under aerobic conditions
Report No.:	M-532341-01-1
Document No.:	M-532341-01-1
Guideline(s):	OECD Guidelines for Testing Chemicals: Aerobic and Anaerobic Transformation in Soil, Guideline 307 (Adopted 24th April 2002)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The degradation rate of metabolite phosphonic acid was investigated in the four soils [redacted] (silt loam), [redacted] (clay loam), [redacted] (sandy loam) and [redacted] (sandy loam) under aerobic conditions at 20 °C and moisture of 50% of the maximum water holding capacity in the dark. The study was performed with non-labelled test material for a maximum incubation period of 117 days.

The nominal application rate was 15 mg phosphonic acid/kg soil, assuming a maximum occurrence of 100% AR from the active substance fosetyl-aluminium to result in a single treatment rate in the field of 11.25 kg a.s./ha.

Values for phosphonic acid recovered from soil were shown to decrease from 99.4 (day zero) to 49.6% (day 117) in soil [redacted] from 63.5 to 7.2% in soil [redacted], from 96.0 to 66.4% in soil [redacted] and from 93.6 to 2.0% in soil [redacted].

Mean values of recoveries from fresh spiked soil samples (concurrent recoveries) for phosphonic acid were 102.3% ([redacted]), 78.8% ([redacted]), 95.5% ([redacted]) and 98.7% ([redacted]). Processing during work-up of samples till analysis had therefore no significant influence on the detection of phosphonic acid in soil.

The kinetic evaluation applying the SFO model resulted in values for the DT_{50} and DT_{90} of phosphonic acid in aerobic soil as summarised in Table 7.1.2.1.2- 6.

Table 7.1.2.1.2- 6: DT_{50} and DT_{90} values of phosphonic acid in aerobic soil

Soil	Kinetic model	DT_{50} [days]	DT_{90} [days]	Chi² error [%]
[redacted]	SFO	114	380	3.34
[redacted]	SFO	38.9	129	7.17
[redacted]	SFO	219	726	5.75
[redacted]	SFO	27.5	91.4	11.3

I. Material and Methods

A. Materials

1. Test Material: Phosphonic acid (BCS-AT27878, AE 0540099)
Chemical name (IUPAC): Phosphonic acid
Appearance: white, sticky crystals
Batch: 04911DN
Chemical purity: 98.7%
CAS: 13598-36-2

2. Soils:
The test soils originated from the EU and reflected a range of physico-chemical characteristics as summarized in Table 7.1.2.1.2- 7. The soils were collected fresh from the field and passed through a 2 mm sieve.

Table 7.1.2.1.2- 7: Characteristics of test soils

	Soil			
	[redacted]	[redacted]	[redacted]	[redacted]
Geographic location (city / state / country)	[redacted] Germany	[redacted] Germany	[redacted] Germany	[redacted]
GPS Coordinates	[redacted]	[redacted]	[redacted]	[redacted]
Textural class [A]	silt loam	clay loam	sandy loam	sandy loam
Sand (%)[A] Silt (%)[A] Clay (%)[A)]	25 61 14	29 39 32	53 31 16	77 15 8
pH (water) (0.01 M $CaCl_2$) (0.01 M KCl)	6.4 6.0 5.8	7.3 7.2 6.9	5.3 5.0 4.6	6.5 6.1 5.9
Organic matter [%][B]	2.8	7.4	2.8	2.1
Organic carbon [%]	1.6	4.3	1.6	1.2
Microbial biomass (mg C / 100 g soil), - DAT-0	450	1250	537	382
- DAT-117	497	892	436	405
Cation exchange capacity [meq/100 g]	10.3	17.5	9.1	7.1
Water holding capacity at zero bar (pF 0) [%][11]	69	99.6	63.1	49.9
Water holding capacity at 0.33 bar (pF 2.5) (%) at 1/10 bar (pF 2) (%)	 27.0 30.8	 32.9 36.3	 21.2 21.7	 11.9 12.5
Bulk density (disturbed) (g/cm³)	1.11	0.96	1.11	1.25

A USDA classification
B % organic matter = % organic carbon x 1.724

B. Study design

1. Experimental conditions:

Samples of 100 g dry weight of soil each were filled into glass incubation flasks with each sample to receive 1.5 mg test substance/kg soil, a dose representing a field rate of 11.25 kg test substance/ha. Following application the samples were attached to 'flow through' systems and incubated at 20 ± 1 °C and a moisture content of 50% of MWHC in the dark for 117 days in maximum. In addition, untreated soil samples were incubated under the same conditions for determination of soil microbial activity.

2. Sampling:

Duplicate samples were removed for work-up after 0, 3, 7, 14, 30, 61, 90 and 117 days of incubation. The complete samples were immediately processed by extraction. Samples for determination of soil microbial biomass were investigated after 0 and 117 days of incubation.

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

3. Analytical procedures:

The entire soil sample in each test vessel was extracted four times successively with aqueous ammonium hydrogencarbonate buffer solution of pH 9.2 at ambient temperature for 30 min. Ambient extracts were pooled and sub-samples concentrated to dryness (i.e. lyophilized). Residues were re-constituted in 0.1 M aqueous tartaric acid solution of pH 2.0 assisted by ultra-sonication. Analysis of soil extracts from incubated samples and from untreated soil samples freshly fortified with test substance was performed by HPLC coupled with MS/MS detection techniques.

C. Determination of degradation kinetics

Degradation data were kinetically evaluated for SFO fits by use of the software KinGUI, version 2.2014.224.1704.

II. Results and Discussion

A. Verification of extraction procedures

Mean values of recoveries of phosphonic acid in soil extracts at day zero ranged from 93.6 to 99.4% for soils [redacted], [redacted] and [redacted] (see Table 7.1.2.1.2- 8, Table 7.1.2.1.2- 10 and Table 7.1.2.1.2- 11). A quantitative recovery was demonstrated underlining the suitability of the extraction method. For soil [redacted] the mean recovery at day zero was 63.5% presumably owing to the higher calcareous content and an overall lower application of test substance. In addition, lower recoveries at day zero were also observed in a previous study (KCA 7.1.2.1.2/04) therefore demonstrating the potential of phosphonic acid to form, in contact with soil, insoluble residues spontaneously. This assumption is confirmed by mean values for concurrent recoveries to be 102.3% ([redacted]), 78.8% ([redacted]II), 95.5% ([redacted]) and 98.7% ([redacted]) thus indicating no major influence of the soil on the detection of phosphonic acid.

B. Decline of residues of phosphonic acid in soil

Residual concentrations of phosphonic acid in soil in terms of percentages of amount applied recovered are summarized in Table 7.1.2.1.2- 8 to Table 7.1.2.1.2- 11.

Values for the concentration of phosphonic acid showed a decline from 99.4% (soil [redacted]), 63.5% ([redacted]), 96.0% ([redacted]) and 93.6% of applied ([redacted]) after zero hours to 49.6, 7.2, 66.4 and 2.0% after 117 days of incubation, respectively.

Table 7.1.2.1.2- 8: Degradation of phosphonic acid in soil [redacted] under aerobic conditions

Component	Sample	Sampling interval (days)							
		0	3	7	14	30	61	90	117
Phosphonic acid	A	101.5	100.9	92.4	85.1	80.9	68.6	57.5	54.8
	B	97.4	101.0	95.3	80.2	78.5	63.8	58.4	44.5
	Mean	99.4	100.9	93.9	82.6	79.7	66.2	58.0	49.6
	SD	2.9	0.1	20.2	3.4	1.7	3.4	0.7	7.3

Values given as percentages of initially applied test item
SD = standard deviation;

Table 7.1.2.1.2- 9: Degradation of phosphonic acid in soil [redacted] under aerobic conditions

Component	Sample	Sampling interval (days)							
		0	3	7	14	30	61	90	117
Phosphonic acid	A	64.1	57.8	48.2	36.6	31.2	226	15.4	4.6
	B	62.9	54.3	48.8	44.3	32.9	24.2	13.2	7.2
	Mean	63.5	56.0	48.5	40.4	32.1	23.4	13.3	7.2
	SD	0.9	2.5	0.4	5.4	1.2	1.1	0.2	3.7

Values given as percentages of initially applied test item
SD = standard deviation;

Table 7.1.2.1.2- 10: Degradation of phosphonic acid in soil [redacted] under aerobic conditions

Component	Sample	Sampling interval (days)							
		0	3	7	14	30	61	90	117
Phosphonic acid	A	97.8	87.1	90.4	80.8	74.4	62.6	65.6	64.9
	B	94.1	84.5	89.5	78.0	73.4	65.9	69.0	67.9
	Mean	96.0	84.3	90.0	79.4	73.9	64.0	67.3	66.4
	SD	2.6	4.0	0.7	2.0	0.7	2.7	2.4	2.1

Values given as percentages of initially applied test item
SD = standard deviation;

Table 7.1.2.1.2- 11: Degradation of phosphonic acid in soil [redacted] under aerobic conditions

Component	Sample	Sampling interval (days)							
		0	3	7	14	30	61	90	117
Phosphonic acid	A	102.0	82.7	89.4	85.7	51.7	12.7	3.9	2.8
	B	85.1	79.6	83.7	78.6	45.7	14.9	2.6	1.2
	Mean	93.6	81.1	86.6	82.2	48.7	13.8	3.3	2.0
	SD	12.0	2.2	4.0	5.0	4.2	1.6	0.9	1.1

Values given as percentages of initially applied test item
SD = standard deviation;

C. Degradation kinetics

The test was kinetically evaluated following application of simple first order (SFO) to measured data to result in values as provided in Table 7.1.2.1.2- 12.

Table 7.1.2.1.2- 12: Half-lives and DT_{90}-values of phoshonic acid in aerobic soil according to SFO kinetics

Soil	Kinetic Model	DT_{50} [days]	DT_{90} [days]	Chi² error [%]	r^2
[redacted]	SFO	114	380	3.34	0.9497
[redacted]	SFO	38.9	129	7.17	0.9628
[redacted]	SFO	219	726	5.75	0.7240
[redacted]	SFO	27.5	91.4	11.3	0.9551

The kinetic evaluation according to SFO resulted in half-lives of 114 days (soil [redacted]), 38.9 days (soil [redacted]), 219 days (soil [redacted]) and 27.5 days (soil [redacted]).

III. Conclusions

Residues of phosphonic acid in aerobic soil were found to degrade with SFO fit half-lives ranging from 27.5 to 219 days under the conditions of the laboratory. The corresponding DT_{90}-values ranged from 91.4 to 726 days.

Report:	KCA 7.1.2.1.2/08 [redacted]; 2015; M-531799-01-1
Title:	Phosphonic Acid (H3PO3) - Kinetic Evaluation of Aerobic Transformation in Soil According to FOCUS Kinetics Guidance
Report No.:	EnSa-15-0632
Document No.:	M-531799-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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

For metabolite phosphonic acid degradation data could be derived from tests with the metabolite separately dosed to soil as referenced under KCA 7.1.2.1.2/04 and KCA 7.1.2.1.2/07. The studies included tests performed with ^{33}P-labelled- (KCA 7.1.2.1.2/04) or non-labelled phosphonic acid (KCA 7.1.2.1.2/07) dosed separately to soils. The data were kinetically evaluated according to actual guidance [FOCUS, 2015] to derive values for the half-life and the DT_{90} in aerobic soil for modelling and trigger endpoints.
Following application of ^{33}P-labelled-phosphonic acid degradation data were available from two soils in total while from application of non-labelled phosphonic acid another four data sets were available.

The kinetic evaluation resulted in the identification of the SFO kinetic model as the best fits to measured data. Tests with the bi-phasic model FOMC did not result in significantly better fits associated with high standard errors for the parameters α and β. Best fit half-lives for comparison against trigger endpoints were derived from use of the SFO model. For deriving a modelling endpoint for soil [redacted], the four kinetic models SFO, FOMC, DFOP and HS were tested to result in the HS model and the back-calculation from its slow phase to be appropriate for modelling endpoint determination. Finally, values for the DT_{50} were normalised to reference conditions (20 °C, pF2 moisture).
<u>Trigger endpoints</u>:
Non-normalised values of the DT_{50} and the DT_{90} were derived from SFO best fits in six soils with results summarized in Table 7.1.2.1.2- 13.
Non-normalised half-lives of phosphonic acid from tests at 20 °C ranged from 27.5 days for sandy loam soil [redacted] to 219 days for sandy loam soil [redacted] while values for the DT_{90} were from 91.4 days to 726 days in the same soils.

Table 7.1.2.1.2- 13: EU trigger endpoint: Non-normalised DT_{50}- and DT_{90}-values for phosphonic acid in aerobic soil

Parameter	Phosphonic acid
Non-normalised DT_{50}, range, 20°C (days)	27.5 – 219
Worst case DT_{50} (days)	**219**
Non-normalised DT_{90}, range, 20°C (days)	91.4 – 726
Worst case DT_{90} (days)	**726**

Modelling endpoints:

Values of the DT_{50} and DT_{90} in aerobic soil following normalization to reference conditions (20 °C, pF2 moisture) were summarized in Table 7.1.2.1.2- 14.
For use as modelling endpoint, the overall geometric mean of normalised half-lives of phosphonic acid was calculated to 83.8 days.

Table 7.1.2.1.2- 14: Modelling input parameter: Normalised DT_{50}-values for phosphonic acid in aerobic soil

Compound	**Phosphonic acid**
Normalised (20°C, pF2) DT_{50}, range (days)	27.5 - 264
Geometric mean	**83.8**

I. Material and Methods

For the metabolite phosphonic acid details on study conduct and its results have been summarised under KCA 7.1.2.1.2/04 and KCA 7.1.2.1.2/07. The degradation data were evaluated following actual kinetic guidance [FOCUS, 2006, amended 2015] with the software KinGUI2.
The measured values were taken into account as reported and thus treated as individual replicates. All sets along with their data points were weighted equally. Time zero residues for phosphonic acid were set to the recovered amount.
Following the recommended procedure for determining modelling endpoints by FOCUS, all datasets were evaluated using the simple first order (SFO) kinetic model with free optimisation of parameters.
FOCUS kinetic evaluation rules aimed at deriving DT_{50}-values for use as model and trigger inputs and were performed according to the respective decision flowchart. The kinetic evaluations including statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-square (IRLS) optimisation.

II. Results and Discussion

Trigger endpoint determination:

Following the FOCUS flowchart, the kinetic model FOMC showed no improvement over SFO, thus further evaluations were not conducted for the soils 97/24 and 97/25 of study KCA 7.1.2.1.1/04 and for soils [redacted] and [redacted] of study KCA 7.1.2.1.1/07. For soil [redacted], the four kinetic models SFO, FOMC, DFOP and HS (Hockey Stick) were tested to result in the SFO model as best fit for trigger endpoint evaluation. For modelling endpoints and following FOCUS guidance the HS model was identified when being interpreted in its conservative form, i.e. the use of the slow phase of the model to derive values of the DT_{50}. The resulting non-normalised values for the DT_{50} and the DT_{90} derived are summarised in Table 7.1.2.1.2- 15.

Modelling endpoint determination:

For use in environmental modelling degradation half-lives were normalised to reference conditions regarding soil moisture (100% field capacity) and temperature (20 °C). The parameters used in the laboratory tests and the respective correction factors calculated were summarised in Table 7.1.2.1.2- 16. The half-lives resulting from normalisation were summarised in Table 7.1.2.1.2- 17.

Table 7.1.2.1.2- 15: Trigger evaluation: Non-normalised DT_{50}-values for phosphonic acid in aerobic soils under laboratory conditions

Soil	Label position	Model	DT_{50} (days)	DT_{90} (days)	Chi^2 (%)	Parameter	Visual[a)]
Soil 97/24 loam, 20 °C (Study 1)	^{33}P	SFO	190	632	9.21	k = 0.00365	O
Soil 97/25 sandy loam, 20 °C (Study 1)	^{33}P-	SFO	130	432	6.88	k = 0.00533	O
Soil [redacted] silt loam, 20 °C (Study 2)	-	SFO	114	379	3.35	k = 0.00607	+
Soil [redacted] clay loam, 20 °C (Study 2)	-	SFO	38.9	129	7.17	k = 0.01783	+
Soil [redacted] sandy loam, 20 °C (Study 2)	-	SFO	219	726	5.75	k = 0.00317	O
Soil [redacted] sandy loam, 20 °C (Study 2)	-	SFO	27.5	91.4	11.3	k = 0.02519	+

Study 1: KCA 7.1.2.1.2/04
Study 2: KCA 7.1.2.1.2/07
[a)] Visual assessment: + = good, O = moderate, - = poor

Table 7.1.2.1.2- 16: Correction factors for soil temperature and moisture content

Soil	Label position	Temperature (°C)	Incubation moisture (%w/w)	pF2 moisture (%w/w)	Correction factor
Soil 97/24 loam, 20 °C (Study 1)	^{33}P	20	14.0	25	0.666
Soil 97/25 sandy loam, 20 °C (Study 1)	^{33}P	20	11.3	19	0.693
Soil [redacted] silt loam, 20 °C (Study 2)	-	20	27.6	31	1.000
Soil [redacted] clay loam, 20 °C (Study 2)	-	20	39.8	36	1.000
Soil [redacted] sandy loam, 20 °C (Study 2)	-	20	25.2	22	1.000
Soil [redacted] sandy loam, 20 °C (Study 2)	-	20	20.0	13	1.000

Study 1: KCA 7.1.2.1.2/04
Study 2: KCA 7.1.2.1.2/07

Table 7.1.2.1.2- 17: Modelling endpoints: Normalised (20 °C and pF2) DT_{50} values for phosphonic acid

Soil	Kinetics	DT_{50} (days)	DT_{90} (days)	Non-normalised DT_{50} estimate for modelling (days)	Normalised DT_{50} [20°C and pF2] (days)
Soil 97/24 loam, 20 °C (Study 1)	SFO	190	632	190	127
Soil 97/25 sandy loam, 20 °C (Study 1)	SFO	130	432	130	90.1
Soil [redacted] silt loam, 20 °C (Study 2)	SFO	114	379	114	114
Soil [redacted] clay loam, 20 °C (Study 2)	SFO	38.9	129	38.9	38.9
Soil [redacted] sandy loam, 20 °C (Study 2)	HS*	264	876	264	264
Soil [redacted] sandy loam, 20 °C (Study 2)	SFO	27.5	91.4	27.5	27.5
Geometric mean					**83.8**

Study 1: KCA 7.1.2.1.2/04
Study 2: KCA 7.1.2.1.2/07
* Derived from slow phase of Hockey Stick kinetic model

III. Conclusion

The kinetic evaluation according to FOCUS kinetic guidance resulted reliable values for the half-lives and the DT_{90} of metabolite phosphonic acid from six soils in total.

For comparison with EU trigger endpoints non-normalised half-lives of phosphonic acid from tests at 20 °C ranged from 27.5 days for soil [redacted] to 219 days for soil [redacted] while values for the DT_{90} were from 91.4 days to 726 days in the same soils, respectively.
For use as modelling input parameters in environmental risk assessments the evaluation resulted in a geometric mean half-life normalised for moisture (pF2) and temperature (20 °C) of 83.8 days.

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

Request from the RMS:
Concerning the kinetic assessment by [redacted] (2015, KCA 7.1.2.1.2/08), some observations can be made:
- Concerning the [redacted] and [redacted] soils, since both SFO and FOMC are not visually acceptable, a DFOP kinetic fitting should have been performed to verify whether such kinetic would be more suitable to determine trigger endpoints.
- Concerning the [redacted] soil, since FOMC kinetic is visually more acceptable than SFO kinetic, a DFOP kinetic fitting should have been performed to verify whether such kinetic would be suitable to determine trigger endpoints.
- Concerning the [redacted] soil, although the HS and SFO kinetics are statistically acceptable, they are not visually acceptable. In order to take into account the potential of phosphonic acid for accumulation, DFOP kinetic should be preferred to determine trigger and modelling endpoints.

In the table 3 of the study report, θ values for the soils from [redacted] (2015, KCA 7.1.2.1.2/07) seem to be erroneous. A correction should be performed.

Response from BCS:

[redacted] soil

For [redacted] soil, both SFO and FOMC fits are visually acceptable (no systematic deviations) and the chi-square errors are low. Therefore, no further fits are required according to FOCUS Kinetics guidance. For the convenience of the RMS we have carried out all four model fits. It can be seen from the plot that the difference between the models is minor. As SFO is acceptable, it should be chosen for modelling endpoints according to FOCUS Kinetics (2014).

However, DFOP model indeed fits the data better. Parameter uncertainties are not relevant for trigger endpoints, because no extrapolation is involved. Therefore, DFOP can be used to determine trigger endpoints. The DT_{50} and DT_{90} derived from DFOP were listed below in Table 1 together with those calculated from SFO.

Table 1: [redacted] **trigger endpoints based on DFOP in comparison with the endpoints derived from SFO.**

Model	χ^2 error (%)	DT_{50}	DT_{90}
SFO	7.17	38.9	129.1
DFOP	3.37	30.8	143.4

[redacted] soil

For the U?kä゜ (ex グä zJD・_hä soil, SFO fit is acceptable both visually (no systematic deviations) and statistically (very low chi square error). All 4 model fits were plotted together to demonstrate that the difference between the models is minor. SFO should be used for modelling endpoints but DFOP model indeed fits the data better if not considering the parameter uncertainties and can be used to determine trigger endpoints. The DT_{50} and DT_{90} derived from DFOP were listed below in Table 2 together with those from SFO. It should be noted that DT_{90} derived from DFOP model is based on extrapolation.

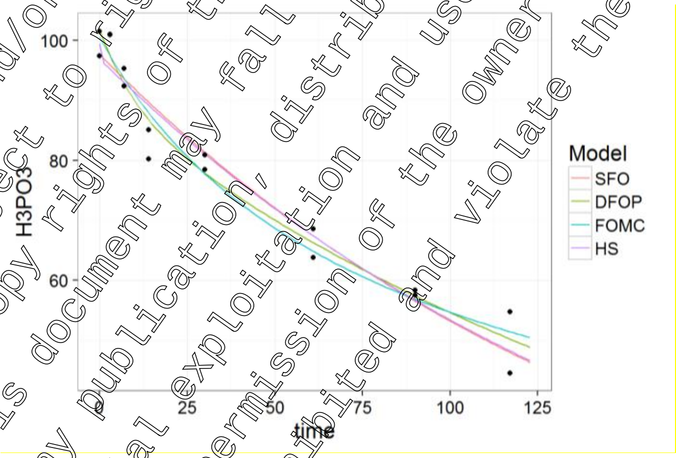


Table 2: [redacted]**: trigger endpoints based on DFOP in comparison with the endpoints derived from SFO.**

Model	χ^2 error (%)	DT_{50}	DT_{90}
SFO	3.348	114.3	379.6
DFOP	2.604	114.5	440.6

[redacted] soil

For [redacted] soil, SFO and HS were assessed visually and listed as moderate fits because there is no clear systematic deviations and error is relatively small compared to observed values. Both models are acceptable according to FOCUS Kinetics criteria.

Regarding the DFOP model the slow phase degradation rate is derived based on only 3 time points (DAT-61, 90, 117) at the end of the study and therefore no reliable estimation can be obtained. It seems that the concentration of phosphonic acid reached a plateau and even increased from DAT 61 to 117. This phenomenon is not consistent with the behaviour observed in the other 5 soils. Moreover, as the concentration did not go below 50%, the DT_{50} and DT_{90} estimations will be based on a lot of extrapolation. DT_{50} based on DFOP would be unrealistically high considering also the behaviour in other soils. FOMC is generally not suitable for extrapolation, especially in the context of long-term soil accumulation calculations (EFSA Scientific Report (2009) 338, 1-32). Therefore, inference based on DFOP or FOMC is not reliable. DFOP was deemed inappropriate for the derivation of both trigger and modelling endpoints.

Error in the θ values in Table 3

There is indeed an error in the θ values in Table 3 f[redacted], 2015; KCA 7.1.2.1.2/08). Thank you for making us aware. The correct values are 34.5, 49.8, 51.6, and 25.0 for soils [redacted], respectively. However, the calculated normalisation factors are correct.

Study summaries of existing studies and publications on rate of aerobic degradation in soil for metabolite phosphonic acid:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.2.1.2/04 [redacted],; [redacted]; 1999; M-184316-01-1
Title:	Aerobic metabolism of (33P)-phosphorous acid in two soils.
Report No.:	R011658
Document No.:	M-184316-01-1
Guideline(s):	USEPA (=EPA): N, 163-1, (1982)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The biotransformation of phosphonate, applied in the form of the free [^{33}P]-phosphonic acid, was investigated under aerobic conditions of the laboratory in two soils UK clay loam and US sandy loam in the dark at 20 °C and soil moisture at 75% of the field capacity at 0.33 bar for 117 days in maximum.

The nominal test concentration was 15 mg phosphonic acid/kg soil was based on an application rate of 15 kg a.s./ha in the field.

Mean material balances of two replicates corrected for isotope half-life of 25.34 days ranged from 90.8 to 107.2% AR for the UK clay loam and from 92.6 to 98.0% AR for the US sandy loam soil. Exceptions were observed for samples of UK clay loam (86.9% AR) and for the US sandy loam (88.4% AR) each by day 3 after application.

Volatile radioactivity was not collected owing to the use of ^{33}P as radioisotope resulting in the conclusion that no formation of volatile components was anticipated.

Total extractable radioactivity decreased from 62.2% AR by day zero to 31.3% AR after 117 days of incubation for the UK clay loam and from 77.2% AR by day zero to 46.6% AR after 117 days for the US sandy loam. Non-extractable residues (NER) ranged from 34.4% AR by day zero to peak at 74.2% AR by day 87 and to decline to 68.5% AR by day 117 for the UK clay loam. For the US sandy loam NER were 19.3% AR by day zero to increase to 49.4% AR after 117 days of incubation.

Values for extractable radioactivity allocated to phosphonate decreased from 62.1% AR by day zero to 25.7% AR after 117 days of incubation for the UK clay loam and from 77.2 to 30.9% AR for the US sandy loam within the same incubation period.

Degradation rates of phosphonic acid in aerobic soil were calculated on the basis of the simple first order kinetic model using Excel (linear regression analysis), the software KIM and the Timme-Frehse approach.

Owing to the character of data to show a fast decline of phosphonic acid in a first phase followed by slower decline at later sampling intervals, this resulted in non-acceptable fits when data of all sampling intervals were used as input.

Fits were acceptable when late sampling intervals were use as input data.

Based on late sampling intervals the calculated half-lives were 108.5 to 116.8 days for the UK clay loam and 124.7 to 136.5 days for the US sandy loam.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

[^{33}P]-phosphonic acid

Sample ID:	PO 10998 A
Specific Activity:	100 mCi/mmole
Radiochemical Purity:	> 98%

Non-radiolabelled phosphorous acid (Batch 10007089, chemical purity of 98%) was used to dilute the radiolabelled compound.

2. Test Soils

The soils had been sieved to ≤ 2 mm. The physico-chemical characteristics were summarized in Table 7.1.2.1.2- 18.

Table 7.1.2.1.2- 18: Physico-chemical properties of test soils

Parameter	**Soil**	
Soil Designation	97/24[a]	97/25[a]
Geographic Location City Country	 [redacted] UK	 Iola, Wisconsin USA
Textural classification (USDA) Sand [63 µm – 2 mm] (%) Silt [2 – 63 µm] (%) Clay [< 2 µm] (%)	Loam 24 52 24	Sandy loam 57 36 7
pH (water)	7.3	6.0
pH (1 M KCl)	7.2	4.8
pH (0.01 M $CaCl_2$)	6.9	5.0
Organic Carbon (%)	2.1	1.3
Organic Matter[1] (%)	3.61	2.24
Cation Exchange Capacity (meq/100 g)	13.8	4.4
Water Holding Capacity @ pF 0 (%)	35.3	47.5
Water Holding Capacity @ 0.33 bar (%)	25.1	14.0
Biomass, initial (µg C/g soil)	566	377
Biomass , study end (µg C/g soil)	199	201

[a] USDA: United States Department of Agriculture
[1] % organic matter = % organic carbon x 1.724

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in flow through systems consisting of glass flasks (250 mL) each containing 100 g of soil. No traps for volatile radioactivity were attached due to the non-volatile character of the test item and its transformation products. Soil moisture during incubation was maintained by passing humidified air through the test samples.

The tests were performed at a concentration of 15 mg phosphonic acid/kg soil, based on a rate of 15 kg a.s./ha in the field. The radiolabelled material (3 mg) was diluted with unlabelled material (87 mg) and dissolved in deionised water to result in a concentration of 1.5 mg/0.5 mL.

The test substance was applied as aqueous solution drop wise onto the soil surface of soil samples. Soil samples were adjusted to 45% of water holding capacity at zero bar (pF 0) for the UK clay loam and to 75% of the water holding capacity at 1/3 bar for the US loamy sand. The samples were incubated at 20 ± 1 °C under aerobic conditions in the dark for 117 days in maximum.

2. Sampling

Duplicate samples were removed for analysis following 0, 3, 7, 14, 28, 56, 87 and 117 days of incubation. Microbial biomass of soil was determined at start and at the end of the study.

3. Analytical Procedures

Volatile radioactivity was not collected since no volatile transformation products were anticipated to originate from application of the ^{33}P radio-labelled test substance.

Soil samples were extracted four times successively with aqueous ammonia buffer (pH 9.3) at ambient temperature for one hour. Soil samples of day zero were additionally extracted with 0.1 M aqueous tartaric acid solution (pH 1.9). Radioactivity in soil extracts was determined by liquid scintillation counting (LSC). After pooling and concentration the soil extracts were analysed by HPLC combined with radio-detection.

Non-extractable radioactive residues were determined for extracted and air-dried soils. Following homogenisation and suspension of aliquots in water and scintillator radioactivity was determined by LSC.

Extracted soils of samples of day 117 were subject to organic matter fractionation of soil into fulvic acid, humic acid and humins following a standard procedure involving dissolution in alkaline solution and precipitation by adjustment of pH.

Soil extracts of day 7 and the following were subject to analysis by GC to confirm the identity in particular of phosphonic acid after derivatisation to the corresponding dimethyl ester.

4. Determination of degradation kinetics

The kinetic evaluation of data was performed *via* the three approaches in total, i.e. use of an EXCEL spreadsheet (SFO model via linear regression function), the software KIM and, a non-specified software as tool for the approach by Timme and Frehse to obtain fits to measured data.

II. RESULTS AND DISCUSSION

The results of aerobic biotransformation of [^{33}P]-phosphonic acid following incubation in soils UK clay loam and US sandy loam were summarized in Table 7.1.2.1.2- 19 and Table 7.1.2.1.2- 20.

A. DATA

Table 7.1.2.1.2- 19: Degradation of [^{33}P]-phosphonic acid in UK clay loam soil under aerobic conditions .

Component	Replicate	Incubation time (days)							
		0	3	7	14	28	56	87	117
Phosphonic acid (rrt = 1)	mean	62.1	39.4	26.5	35.3	41.3	40.6	28.8	25.7
	SD	1.0	0.5	1.7	1.5	0.4	0.3	0.0	0.3
Unknown 1 (rrt = 0.45)	mean	-	-	-	-	-	-	-	-
	SD	-	-	-	-	-	-	-	-
Unknown 2 (rrt = 0.50)	mean	-	-	-	-	-	-	-	-
	SD	-	-	-	-	-	-	-	-
Unknown 3 (rrt = 0.64)	mean	-	-	-	-	-	-	0.8	-
	SD	-	-	-	-	-	-	0.2	-
Unknown 4 (rrt = 0.74)	mean	-	-	-	-	-	-	1.4	-
	SD	-	-	-	-	-	-	1.4	-
Unknown 5 (rrt = 0.87)	mean	-	-	-	-	-	-	1.3	3.3
	SD	-	-	-	-	-	-	1.3	0.4
Region 6 (rrt = 1.45)	mean	-	-	-	-	-	-	-	1.6
	SD	-	-	-	-	-	-	-	0.4
Region 7 (rrt = 1.75)	mean	-	-	-	-	-	-	0.7	-
	SD	-	-	-	-	-	-	0.7	-
Region 8 (rrt = 1.96)	mean	-	-	-	-	-	-	-	0.6
	SD	-	-	-	-	-	-	-	0.1
Total Extractable Radioactivity	mean	62.2	39.4	26.5	35.3	41.3	40.6	33.1	31.3
	SD	1.1	0.5	1.7	1.5	0.4	0.3	0.8	1.1
Non-extractable Residues	mean	34.4	47.6	64.3	62.9	56.6	56.0	74.2	68.5
	SD	1.9	0.3	2.7	1.4	1.4	0.6	0.3	5.7
Total radioactivity	mean	96.5	86.9	90.8	98.2	97.8	96.6	107.2	99.8
	SD	0.9	0.9	0.9	2.9	1.0	0.3	0.4	4.6

Values given as percentage of total applied radioactivity, corrected for isotope half-life of 25.34 days
rrt = relative retention time
Unknowns to consist of polar (rrt <than test substance) and 'unpolar'(rrt > than test substance) components
SD = standard deviation

Table 7.1.2.1.2- 20: Degradation of [^{33}P]-phosphonic acid in US sandy loam soil under aerobic conditions

Component	Replicate	Incubation time (days)							
		0	3	7	14	28	56	87	117
Phosphonic acid (rrt = 1)	mean	77.2	55.4	55.9	54.8	55.1	54.1	37.9	30.9
	SD	0.7	4.4	0.9	1.0	1.4	0.5	5.9	11.3
Unknown 1 (rrt = 0.45)	mean	-	-	-	-	-	-	1.0	8.2
	SD	-	-	-	-	-	-	1.0	8.2
Unknown 2 (rrt = 0.50)	mean	-	-	-	-	-	-	-	3.3
	SD	-	-	-	-	-	-	-	3.3
Unknown 3 (rrt = 0.64)	mean	-	-	-	-	-	-	4.1	1.4
	SD	-	-	-	-	-	-	3.8	1.4
Unknown 4 (rrt = 0.74)	mean	-	-	-	-	-	-	1.1	0.6
	SD	-	-	-	-	-	-	1.1	0.6
Unknown 5 (rrt = 0.87)	mean	-	-	-	-	-	-	1.7	-
	SD	-	-	-	-	-	-	1.7	-
Region 6 (rrt = 1.45)	mean	-	-	-	-	-	-	2.4	0.5
	SD	-	-	-	-	-	-	0.3	0.5
Region 7 (rrt = 1.75)	mean	-	-	-	-	-	-	0.4	1.1
	SD	-	-	-	-	-	-	0.4	1.1
Region 8 (rrt = 1.96)	mean	-	-	-	-	-	-	1.4	0.6
	SD	-	-	-	-	-	-	1.4	0.3
Total Extractable Radioactivity	mean	77.2	55.5	56.0	54.8	55.1	54.1	49.8	46.6
	SD	0.7	4.4	0.8	1.1	1.4	0.5	0.2	0.7
Non-extractable Residues	mean	19.3	33.1	38.6	41.7	42.9	38.5	44.8	49.4
	SD	1.7	0.8	2.2	0.3	3.4	1.4	0.0	0.4
Total radioactivity	mean	96.4	88.4	94.8	96.4	98.0	92.6	94.6	96.0
	SD	2.3	3.6	1.1	0.8	2.1	0.9	0.3	1.1

Values given as percentage of total applied radioactivity, corrected for isotope half-life of 25.34 days
rrt = relative retention time
Unknowns to consist of polar (rrt < than test substance) and 'unpolar'(rrt > than test substance) components
SD = standard deviation

B. MATERIAL BALANCE

Material balances were corrected for isotope half-life.

Mean material balances of two replicates per sampling interval ranged from 90.8 to 107.2% AR for the UK clay loam and from 92.6 to 98.0% AR for the US sandy loam. Exceptions were observed for samples after 3 days of incubation for both soils to result in mean material balances of 86.9 and 88.4% AR, respectively. While this applied for both replicates of soil clay loam (86.0 and 87.8% AR for single replicates), it was just one replicate of soil sandy loam (84.9 and 92.0% AR for single replicates). No explanations were given for the lack of material balance in the samples. Since fully acceptable balances were found at the other sampling intervals and since there were no general trends for lowered recoveries with time, this finding was regarded to have no impact on the overall outcome of the study.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable radioactivity decreased from 62.2% AR by day zero to 31.3% AR after 117 days of incubation in UK clay loam and from 77.2% AR by day zero to 46.6% AR by day 117 in the US sandy loam.

Non-extractable residues (NER) ranged from 34.4% AR by day zero to peak at 74.2% AR by day 87 and to decline to 68.5% AR by day 117 for the UK clay loam. For the US sandy loam NER were 19.3% AR by day zero to increase to 49.4% AR after 117 days of incubation.
Organic matter fractionation of extracted soils showed that the remaining radioactivity was strongly associated with the fraction of fulvic acids to account for 32.6% AR (fulvic acids), 1.0% AR (humic acids) and 14.4% AR (humins) for the UK clay loam. For the US sandy loam distribution was 33% AR for fulvic acids, 1.0% AR humic acids and 0.0% AR in humins.

D. VOLATILES

Volatile radioactivity was not collected since no volatile transformation products were anticipated to originate from application of the ^{33}P radio-labelled test substance.

E. TRANSFORMATION OF TEST SUBSTANCE

Values for extractable radioactivity allocated to phosphonate decreased from 62.1% AR by day zero to 25.7% AR after 117 days of incubation for the UK clay loam and from 77.2 to 30.9% AR for the US sandy loam within the same incubation period.
The degradation of phosphonate was accompanied by the formation of a number of minor components and regions all observed clearly below 5% AR in the course of the experiment.
An exception was reported for a single replicate of US sandy loam soil of day 117. A component reported as Unknown 1 was detected at 8.2% AR as the mean of two replicates while it was found in one of the two replicates at 16.4% AR. The component was thus observed in just one of the two replicates and at the last sampling interval only. There were indications for the artificial character of this component twhen considering the following: It was not observed in the UK clay loam soil and it occurred it was hardly observed at any time point before, i.e. at 1.9% AR in one of the two replicates of the previous sampling interval, day 87. Unknown 1 had a relative retention time (rrt) of 0.45 thus showing up in the very polar region of the HPLC chromatographic system. It is a more general problem in the analysis of soil extracts, in particular those of late sampling intervals, that extracts have to be concentrated causing high matrix loads for the sample to be analysed, in particular, when sensitive methods such as ion pair chromatography have to be used.
Another factor of influence contributing was the character of the ^{33}P-phosphorus isotope as test item with a half-life of 25.35 days only. The late sampling intervals of days 87 and 117 were already by more than a factor of three beyond the isotope half-life, i.e. total radioactivity available had decreased already to less than 12.5% of the value initially applied after more than 75 days of incubation.
In addition, phosphorus compounds serve as potential nutrients being therefore subject for uptake into organisms including soil microbes.
Higher matrix load combined with lowered total radioactivity and the progress in phosphorus digestion and uptake into microbes thus were factors of influence to impact on chromatographic results in particular for late sampling intervals.

F. DEGRADATION KINETICS

Degradation rates of phosphonic acid in aerobic soil were calculated using the Timme-Frehse approach, the software KIM and linear regression analysis. The results were summarized in Table 7.1.2.1.2- 21.

Owing to the character of data to show a fast decline of phosphonic acid in a first phase followed by slower decline at later sampling intervals, this resulted in non-acceptable fits when data of all sampling intervals were used as input.
Fits were acceptable when late sampling intervals were use as input data.

Based on late sampling intervals the calculated half-lives were 108.5 to 116.8 days for the UK clay loam and 124.7 to 136.5 days for the US sandy loam.

Table 7.1.2.1.2- 21: Rate of degradation of phosphonic acid in two soils under aerobic conditions

Soil	Approach	DT_{50} [days]	Quality of fit [1]	Kinetic model
UK clay loam	Excel/all sampling intervals	120.9	0.327	SFO
	KIM/all sampling intervals	8.7	0.906	SFO
	Timme Frehse/all sampling intervals	89.2	0.388	SFO
	Excel/late sampling intervals	116.8	0.906	SFO
	KIM/late sampling intervals	108.5	0.996	SFO
	Timme Frehse/ late sampling intervals	116.8	0.880	SFO
US sandy loam	Excel/all sampling intervals	102.8	0.730	SFO
	KIM/all sampling intervals	70.6	0.960	SFO
	Timme Frehse/all sampling intervals	37.4	0.759	SFO
	Excel/late sampling intervals	136.5	0.864	SFO
	KIM/late sampling intervals	133.3	0.985	SFO
	Timme Frehse/late sampling intervals	124.7	0.617	SFO

[1] r squared for Excel, 'modified r squared' for Timme-Frehse and 'fit criterion' (modification of r squared) for KIM.
KIM: kinetic modelling

III. CONCLUSIONS

The degradation of phosphonic acid in aerobic soil under the conditions of the laboratory was moderate to result in values of the DT_{50} of 108.5 to 116.8 days for the UK clay loam and 124.7 to 136.5 days for the US sandy loam.

Report:	KCA 7.1.2.1.2/05 [redacted], [redacted]; [redacted]; 2001; M-203498-01-1
Title:	Fosetyl-Al Investigation of the potential for phosphorous acid residues in succeeding crops
Report No.:	C012853
Document No.:	M-203498-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	no

Executive Summary

The potential for phosphonate residues for uptake into plants of succeeding crops was studied. Following treatment of bare soil at a rate equivalent to 15 kg test substance/ha (4.9 mg/kg soil) plants representing root crops (radish), leafy crops (lettuce) and grain crops (barley) were grown.

The test was performed in plant pots containing 6.4 kg of soil. Before sowing, the soil pots (treated and untreated) were left in incubation during 32 days (additionally 182 days for one experiment with radish), outdoors but sheltered from rain. Water was added as appropriate to maintain moisture without drainage.

Duplicate or quadruple samples were taken for analysis before and immediately after treatment with phosphonic acid, and then after 32 days (sowing time), 69 days (lettuce-radish harvest) and 182 days (barley harvest).

Phosphonic acid was extracted from soil with ammonia buffer solution and from plants with a mixture of water and acetonitrile.

Soil and plant extracts were quantified by gas chromatography on a semi-capillary column, using a flame photometric detector (phosphorus mode).

In the soil, no appreciable decline of phosphonic acid was observed during the ageing period of one month following treatment. However, significant degradation (or irreversible binding) was observed afterwards. The depletion of phosphorus was faster in cropped soil than in bare soil.

Data obtained on plants, although in some cases not very accurate, showed that for barley (grain and straw) sown one month after soil treatment, and for radish (roots and leaves) sown 6 months after treatment of the soil, differences between treated and untreated samples were not significant (residues clearly below 0.5 mg/kg) whereas in radish (roots and leaves) and in lettuce (leaves) sown/planted one month after treatment, residues in treated samples were observed at levels significantly higher than in untreated samples, however not exceeding 1 mg/kg.

As such residues were observed in plants installed only one month after application to the soil, at once, of phosphorous acid in amounts equivalent to the total of active substance which is normally applied over several months, it can be concluded from the results of these experiments that uses of fosetyl are not likely to result in significant residues in succeeding crops.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

phosphonic acid	
Sample ID:	not reported
Chemical Purity:	not reported

The phosphonate test substance was applied as aqueous solution prepared by neutralization of the free phosphonic acid with potassium hydroxide.

2. Test Soils

The physico-chemical characteristics of the test soil were summarized in Table CA 7.1.2.1.2-22.

Table 7.1.2.1.2- 22: Physico-chemical characteristic of soil

Parameter		Soil
Soil Designation		[redacted]
Geographic Location		
City		[redacted],
Country		France
Textural class		Loamy sand
Coarse sand	[200 - 2000 µm]	5.4%
Fine sand	[50 - 200 µm]	31.9%
Coarse silt	[20 - 50 µm]	25.7%
Fine silt	[2 - 20 µm]	23.3%
Clay	[< 2 µm]	13.8%
pH (water)		6.5
pH (KCl)		5.34
Organic Matter		1.9%
Cation Exchange Capacity [meq/100 g]		Not reported
Water Holding Capacity		Not reported

B. STUDY DESIGN

1. Experimental Conditions

The test was performed in plant pots (20 cm diameter, 15 cm depth) containing 6.4 kg of soil. The soil had been treated at a concentration of 4.9 mg phosphonate test substance /kg soil.

Plants in treated and untreated pots were grown for 32 days under outdoor conditions protected from rain. During growing plants were watered as appropriate.

Two treated and untreated pots each containing barley, radish, lettuce were harvested after 32 days of growing.

2. Sampling

Soil samples were taken for analysis just before and immediately after treatment with phosphonate and then after 32 days (sowing time), 69 days (lettuce-radish harvest) and 182 days (barley harvest) of growing of plants.

3. Analytical Procedures

Phosphonates were extracted from soil with ammonia buffer solution. Extracts were de-cationized by cation exchange resin and evaporated to dryness followed by derivatization with trimethylsilyldiazomethane.

Phosphonate residues were extracted from plants with aqueous acetonitrile by maceration. Plant extracts were cleaned up using an octadecyl cartridge followed by derivatization with trimethylsilyldiazomethane.

Derivatized phosphonate residues were quantified by gas chromatography on a semi-capillary column, using a flame photometric detector (phosphorous mode) and the use of external standards. The limit of quantification (LOQ) was 0.2 mg/kg soil for samples analysed at time of treatment and 0.1 mg/kg in the following. For plants, the LOQ was 0.5 mg/kg. Attempts to lower the LOQ to 0.1 mg/kg (or 0.25 mg/kg for barley straw) were not successful owing to inconsistent recoveries for low residue levels.

II. RESULT AND DISCUSSION

The results of determination of residues of phosphonic acid in soil and plants of succeeding crops at various sampling intervals were summarised in Table 7.1.2.1.2- 23 and Table 7.1.2.1.2- 24.

A. DATA

Table 7.1.2.1.2- 23: Residues of phosphonic acid in soil

Sample	Sampling interval				
	T_0	T_1	DAT 32	DAT 69	DAT 182
Soil, treated	-	3.5	3.9	1.3	0.1
Soil, lettuce pots	-	-	-	0.3	-
Soil, radish pots	-	-	-	0.1	-
Soil, barley pots	-	-	-	-	< 0.1

Mean values, expressed as mg phosphonic acid equivalents/kg soil
T_0 = Untreated; T_1 = directly after treatment, i.e. Day zero
DAT = Days after treatment

Table 7.1.2.1.2- 24: Residues of phosphonic acid in plants of succeeding crops

Crop	Sample	Treatment	Time (days) to harvest 69	Time (days) to harvest 182	Time (days) to harvest 182/222
Radish	leaves	untreated	0.04	-	-
		treated	0.35	-	0.09
	roots	untreated	0.10	-	-
		treated	0.80	-	0.03
Lettuce	leaves	untreated	0.04	-	-
		treated	0.76	-	-
Barley	grain	untreated	-	0.10	-
		treated	-	0.14	-
	straw	untreated	-	0.19	-
		treated	-	0.42	-

Mean values, expressed as mg phosphonic acid equivalents/kg plant
Sowing was 32 days after treatment of soil for lettuce and barley and 182 days for radish

B. Residues in Soil and Plants

No significant decline of residues of phosphonic acid was observed following sampling of soil one month after treatment. The decline of residue concentration was faster for cropped than for bare soils, however, the exact cause was unclear since direct uptake by plants was minimal.
Residues were low and variable for untreated soil samples as well as for treated soils at later sampling intervals.

Residues of phosphonic acid in radish were 0.35 mg/kg for roots and 0.80 mg/kg for leaves for plants sown 32 days after treatment and harvested after 69 days of growing. For comparison, residues were 0.76 mg/kg for lettuce plants sown 32 days after treatment and harvested after 69 days of growing. Residues were significantly lower for barley grain and straw sown one month after soil treatment and harvested after 6 months of growing.

III. CONCLUSIONS

The results indicated little uptake of phosphonic acid residues to plants of succeeding crops.

By their design, the data did not contribute to a better understanding of the rate of degradation of phosphonate residues in aerobic soil. The results were therefore regarded as supplementary information with no use in environmental risk assessment.

CA 7.1.2.1.3 Anaerobic degradation of the active substance

Report:	KCA 7.1.2.1.3/01 [redacted]; 1984; M-159549-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Anaerobic aquatic metabolism study.
Report No.:	R000917
Document No.:	M-159549-01-1
Guideline(s):	USEPA (=EPA): D, 162-3
Guideline deviation(s):	none
GLP/GEP:	**no**

The rate of degradation of the active substance fosetyl-aluminium (fosetyl-Al) was calculated within the respective study on route of degradation in anaerobic soil (KCA 7.1.1.2/01).

The data requirement had been addressed under Point 7.1.1.2.1.4 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The evaluation revealed that fosetyl-Al was rapidly degraded under the conditions of the test to result in half-lives of 40 hours (1.67 days) for a silty clay loam and of 14 hours (0.58 days) for a sandy loam soil.

The study was summarized under CA 7.1.1.2 in detail including information on rate of degradation for the active substance in anaerobic soil.

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

Report:	KCA 7.1.2.1.4/01 [redacted]; 1984; M-159549-01-1
Title:	Fosetyl-AP (aluminium tris-O-ethylphosphonate): Anaerobic aquatic metabolism study.
Report No.:	R000917
Document No.:	M-159549-01-1
Guideline(s):	USEPA (=EPA): D, 162-3
Guideline deviation(s):	none
GLP/GEP:	**no**

The data requirement had been addressed under Point 7.1.1.2.1.5 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The evaluation revealed that, besides the transformation products observed in aerobic soil, no metabolites were found that were specifically formed under anaerobic conditions.
Moreover, the intended use of fosetyl-aluminium is for crops where anaerobic conditions in soil are not prevalent.
No specific study is therefore required.

The study was summarized under CA 7.1.1.2 in detail including information on rate of degradation for transformation products in anaerobic soil.

CA 7.1.2.2 Field studies

CA 7.1.2.2.1 Soil dissipation studies

This data requirement had been addressed under Point 7.1.1.2.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

The evaluation revealed that the values for the DT_{50} and the DT_{90} of fosetyl-aluminium resulting from laboratory tests performed were all significantly below the current triggers set to investigate the degradation behaviour additionally under outdoor conditions of the field.

Values of the $DegT_{50}$ of metabolite phosphonic acid in aerobic soil in the laboratory were higher than the specified trigger values in the EU.
Following data requirements of Commission Regulation 283/2013 this triggers the generation of dissipation data for estimation of a $DisT_{50}$ of the metabolite in the field. If possible, the time required for degradation ($DegT_{50}$/$DegT_{90}$) of the active substance shall be estimated. Where relevant, information on metabolites, breakdown and reaction products shall be provided.
For the conduct of field studies, Commission Notice 2013/C 95/01 to Commission Regulation 283/2013 specified US EPA OCSPP 835.6100 as the corresponding 'test method', i.e. there is currently no agreed or accepted test design available at OECD or EU level addressing the investigation of dissipation in the field.

In view of the more general context described, no particular field studies were performed investigating the dissipation of metabolite phosphonic acid. Moreover and considering regulatory practise in the past and actually, the data requirement can be regarded as a higher tier option when considering the following context:

1. With regard to the former use of data in regulatory practise and the risk assessment in the environment, laboratory data are lowest tier to estimate the potential of residues for persistence in the soil environment. In contrast, field data are used as higher tier to investigate the behaviour under the more realistic and practical conditions of use.
   The background is that laboratory tests in the dark triggering field studies allow to investigate the contribution of microbial degradation only. Filed dissipation tests were a common higher tier to demonstrate study experimentally the behaviour of residues when allowing additional potential factors of influence to microbial degradation, dissipation by volatilisation and photolytic processes at soil surfaces and uptake by plants. These parameters were therefore finally taken into account for risk assessment mostly focused on the active substance.
   Resulting field $DisT_{50}$ triggered field accumulation data in case on being higher than 1 year. The set of dissipation data served as a basis to identify two sites of highest persistence to perform field accumulation tests. The potential for accumulation was determined to derive the plateau concentration in soil after repeated application for several successive years.

2. With regard to actual regulatory practise the assessment of persistence of a compound in soil is meanwhile based on laboratory degradation data as Tier 1. This approach allows for the risk assessment and reflects the most conservative approach. In turn, higher tier field data allowing for additional dissipation processes must be less conservative. However, such more realistic approach does not find regulatory acceptance as indicated by a number of EFSA publications in the form of Opinions, Guidelines and Guidances for evaluation, interpretation and use of field data in the recent past. Again, it should be noted that the major portions of changes in interpretation of data and requirements were published when preparations for the AIR3 process were at a late stage thus not allowing for their consideration in testing and dossier preparation.

Overall, the determination of field half-lives in soil for the active substance or metabolites, breakdown and reaction products would therefore not result in a more conservative assessment of the behaviour of residues in soil.
It should be noted that the same applies for the assessment of the long term behaviour in soil, i.e. the estimation of accumulation. Based on worst case laboratory values of the DT_{50} the plateau concentration in aerobic soil can be reliably calculated conservatively from the existing laboratory data rather than to be determined in the field experimentally.
Considering current regulatory practise in assessment of residues in soil, field $DisT_{50}$ data do not contribute to an improvement of risk assessments neither do such experimental data contribute to an overall better understanding of degradation or dissipation processes in soil.
Conclusively, data requirements resulting from formal fulfilment of EU persistence triggers can be adequately addressed by laboratory data for active substances as well as metabolites, breakdown and reaction products as the most conservative Tier.
No particular field dissipation or degradation tests are thus regarded as necessary as higher tier option for metabolite phosphonic acid.
Moreover, there is still a lack of agreed or accepted field test designs at OECD or EU level to adequately address the data requirements of Commission Regulation 283/2013. The same applies for the use and interpretation of field data in the context of risk assessment in soil.
Also in view of more general issues and inconsistencies in data requirements and its interpretation, the non-availability of field data for metabolite phosphonic acid should not be interpreted as a data gap.

CA 7.1.2.2.2 Soil accumulation studies

This data requirement had been addressed under Point 7.1.1.2.1.3 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

The evaluation revealed that the values for the DT_{90} of fosetyl-aluminium from laboratory and field tests performed were all significantly less than one year thus with no indication for accumulation of the active substance in the soil environment.

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

Report:	KCA 7.1.3.1.1/01 [redacted]; [redacted]; 1982; M-159330-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil sorption studies
Report No.:	R000784
Document No.:	M-159330-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.3.1.1/02 [redacted]; [redacted]; 1986; M-159778-01-1
Title:	Adsorption of fosetyl ammonium salt onto ditch-bottom sludge
Report No.:	R001033
Document No.:	M-159778-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Attempts to investigate the adsorption of the active substance fosetyl-aluminium (fosetyl-Al) to soil under conditions of the laboratory were made in:

- three soils under conditions similar to batch equilibrium tests following application of non-labeled active substance (KCA 7.1.3.1.1/01);
- bottom sludge of two ditches under conditions similar to batch equilibrium tests following application of 1-^{14}C-labeled fosetyl-Al (KCA 7.1.3.1.1/02).

The data requirement had been addressed under Point 7.1.2.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

For study KCA 7.1.3.1.1/01 the evaluation for the Annex I inclusion of fosetyl under Directive 91/414/EEC revealed that the active substance fosetyl-Al was either not adsorbed (loamy sand and silt loam soil) or some decrease from the water phase was observed suggesting some adsorption to soil (sandy loam). Since the apparent adsorption was accompanied by degradation no measurable value for adsorption could be determined.

For study KCA 7.1.3.1.1/02 no investigations had been performed to demonstrate the stability of fosetyl-Al under the conditions of the test to differentiate between effects of adsorption and degradation as observed for study KCA 7.1.3.1.1/01. In addition, sediments were used thus being not regarded to be representative for ‘soil’ in the EU. The study was therefore excluded from use in risk assessment.

Conclusively the value describing the adsorption to soil (Kf,oc) for environmental risk assessment was set near to zero, i.e. to 0.1 mL/g.

New information: New adsorption study to soil for the active substance

In view of the existing non-GLP and non-guideline data available for the active substance new data were generated in order to fulfil the requirements as set by Commission Regulation (EC) No 283/2013 amending Regulation (EC) No 1107/2009.

Report:	KCA 7.1.3.1.1/03 [redacted]; 2015; M-532010-01-1
Title:	[ethyl-2-14C]fosetyl-aluminium: Adsorption/desorption on five soils
Report No.:	S15-03004
Document No.:	M-532010-01-1
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

Tests to investigate the adsorption/desorption characteristics of [ethyl-2-^{14}C]fosetyl-aluminium were performed under conditions of batch equilibrium experiments in five soils.
No definitive phase was performed due to insufficient stability of the test compound under the conditions of the test.

Recoveries of the preliminary phase were in the acceptable range of 96.0 to 106.1% AR for all soils investigated. However and dependent on soil-to-water-ratio the recoveries of the test item were 60.2 to 87.1% AR and thus outside an acceptable range.

No values for the Freundlich adsorption coefficient ($K_{F, ads}$) or the Freundlich coefficient 1/n in soil were therefore determined.

I. Material and Methods

A. Materials

1. Test Material: [ethyl-2-^{14}C]fosetyl-aluminium

Specific radioactivity:	2.22 MBq/mg (60.0 µCi/mg)
Batch:	8710AXU003-5
Radiochemical purity:	100% (HPLC)

2. Soil:

Sorption tests were performed with four soils covering a range of pH, organic carbon content and texture. The characteristics of soils originating from the UK and the US are summarised in Table 7.1.3.1.1- 1.

Table 7.1.3.1.1- 1: Characteristics of test soils

Soil	[redacted] **(AX)**	[redacted] **(DD)**	[redacted] **(HH)**	[redacted] **(HN)**	[redacted] **(WW)**
Geographic Location (City/State/Country)	[redacted], Germany	[redacted], Germany	[redacted], Germany	[redacted], Germany	[redacted], Germany
GPS coordinates	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Textural Class (USDA)	sandy loam	loam	silt loam	loam	sandy loam
Sand (%) [A] Silt (%)[A] Clay (%)[A]	72 19 9	29 44 27	19 66 15	31 50 19	50 32 18
pH (0.01 M $CaCl_2$) pH (Water)	6.3 6.5	7.3 7.4	6.1 6.3	5.1 5.4	5.1 5.5
Org. Matter [B] (%)	3.4	8.8	4.8	5.3	3.4
Org. Carbon (%)	2.0	5.1	2.1	3.1	2.0
CEC (meq/100 g)	9.0	21.5	11.3	9.9	10.4

[A] According to USDA classification; [B] % Organic matter = % organic carbon x 1.72
CEC: Cation exchange capacity

B. Study design

1. Experimental conditions:

Preliminary tests included the determination of the adequate soil-to-solution ratio (30 min, 1 h and 3 hrs) and the 'adequate times needed to reach adsorption equilibrium' at two test concentrations of 0.3 mg/L and 1 mg/L for all soils (two replicates). Supernatants after centrifugation and soil extracts were analysed for radioactivity (mass balance) and for test item (parental mass balance). In view of the rapid degradability of the test item in the contact with soil, most of the tests including those on stability were performed in sterilized (i.e. gamma-irradiated) soils. However, significant degradation of the test item was observed for all sampling points investigated.

No definitive tests on adsorption or desorption to soil were therefore performed due to a lack of stability of the test item.

For work-up the aqueous supernatant was separated from soil by decantation and centrifugation. Radioactivity in water and soil extracts was determined by liquid scintillation counting (LSC) and analysed for the test item by HPLC-MS/MS.

2. Analytical procedures:

Radioactivity was determined by liquid scintillation counting (LSC). The purity and stability of the test item was investigated by HPLC analysis using mass spectroscopic detection techniques (ESI, m/z of 108.9/110.9 and m/z of 81.0 detected as test item ions).

II. Results and Discussion

A. Mass balance and results of preliminary tests

Pre-tests on adsorption to the walls of test vessels by shaking an aqueous solution of the test substance in the absence of soil showed no adsorption. The tests also confirmed the solubility and stability of the test item in aqueous calcium chloride solution. The test item was known to be degraded in the presence of microbially active soil (see also KCA 7.1.2.1.2) and thus sterilized soils were used in preliminary tests. The tests on determination of the adequate soil-to-solution ratio (30 min, 1 h and 3 hrs) and the 'adequate times needed to reach adsorption equilibrium' were accompanied by investigations for stability of the test item in supernatants after centrifugation and soil extracts.
Analysis for radioactivity (mass balance) indicated recoveries to range from 92.1 to 94.7% for all soils and test concentrations.

B. Transformation of test substance

Following adsorption phases of 30 min, 1 hour or 3 hours to sterilized soil and HPLC analysis of water and soil extracts the stability of the test substance was significantly below 90% for the soil-to-solution ratio of interest. Analysis for test item (parental mass balance) indicated recoveries of 81.5% (0.5 hours, soil [redacted]) or significantly below for all soils and test concentrations (see Table 7.1.3.1.1- 2).

Table 7.1.3.1.1- 2: Preliminary test: Total recovery of ^{14}C-fosetyl-Al in samples after adsorption phase

Soil/Test conc./Ads. time **0.3 mg/mL, 0.5h**	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Total recovery of radioactivity*	94.3	94.3	92.7	92.1	93.3
Total recovery of test item*	81.5	56.8	75.2	59.6	70.3
0.3 mg/mL, 1 hour					
Total recovery of radioactivity*	93.6	92.4	93.8	92.6	92.1
Total recovery of test item*	78.3	50.3	84.0	51.5	55.7
0.3 mg/mL, 3 hours					
Total recovery of radioactivity*	94.6	89.6	91.8	91.2	93.0
Total recovery of test item*	72.4	41.1	72.0	37.2	69.8
1.0 mg/mL, 0.5 h					
Total recovery of radioactivity*	94.0	94.7	93.9	94.0	93.8
Total recovery of test item*	65.9	45.4	60.3	53.9	57.7
1.0 mg/mL, 1 hour					
Total recovery of radioactivity*	94.9	95.3	93.6	92.7	94.0
Total recovery of test item*	56.1	41.1	59.2	44.2	45.3
1.0 mg/mL, 3 hours					
Total recovery of radioactivity*	93.7	87.2	93.5	93.6	93.4
Total recovery of test item*	50.3	33.0	48.3	30.6	42.8

* Mean values in terms of radioactivity applied in supernatants and soil extracts from two replicates

C. Findings

Following the results on tests on stability, no definitive phase on adsorption or desorption to soil was performed due to a lack of stability of the test item. This finding is well in line with the fast degradation observed in aerobic soil (see Section CA 7.1.2.1.2).

Consequently, no adsorption constants $K_{F, ads}$ have been determined.

The adsorption behaviour of [^{14}C]fosetyl-Al cannot be described reliably by batch equilibrium tests according to OECD Guideline 106 although precautionary measures were taken like a minimization of contact time with soil and the use of sterilized soils.

III. Conclusion

No adsorption constants $K_{F,\ ads}$ have been determined in five sterilized soils due to instability of fosetyl-Al under the conditions of the test.

Study summaries of existing studies and publications on adsorption of the active substance to soil:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.3.1.1/01 [redacted]; [redacted]; 1982; M-159330-01-1
Title:	Fosetyl-Al (aluminium tris-O-ethylphosphonate): Soil sorption studies
Report No.:	R000784
Document No.:	M-159330-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.3.1.1/02 [redacted] W; [redacted]; 1986; M-159778-01-1
Title:	Adsorption of fosetyl ammonium salt onto ditch-bottom sludge
Report No.:	R001033
Document No.:	M-159778-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

For study KCA 7.1.3.1.1/01 the evaluation for the Annex I inclusion of fosetyl under Directive 91/414/EEC revealed that the active substance fosetyl-Al was either not adsorbed (loamy sand and silt loam soil) or some decrease from the water phase was observed suggesting some adsorption to soil (sandy loam). Since the apparent adsorption was accompanied by degradation no measurable value for adsorption could be determined.

Study KCA 7.1.3.1.1/01 served as supplemental information and it was therefore replaced by new information as submitted under KCA 7.1.3.1.1/03.
In this context, it is noted that study KCA 7.1.3.1.1/02 was also excluded from use in risk assessment since the use of adsorption values from sediments was not regarded to be representative for 'soil' in the EU. Finally and as can be expected from the very fast degradation of fosetyl-Al in contact with soil stability of fosetyl-Al under the conditions of the test was not demonstrated. It was thus not possible to differentiate between effects of adsorption and degradation as observed for study KCA 7.1.3.1.1/01.
Again, the new information submitted under KCA 7.1.3.1.1/03 was well in line with the existing data in KCA 7.1.3.1.1/01 and KCA 7.1.3.1.1/02.

In view of the fact that KCA 7.1.3.1.1/01 and KCA 7.1.3.1.1/02 were considered for risk assessment during Annex I inclusion and being replaced by new data in EU approval renewal, no detailed summary of this obsolete data was given.

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

Report:	KCA 7.1.3.1.2/01 [redacted]; [redacted]; 2000; M-189213-01-1
Title:	Phosphorous acid: Adsorption on three soils
Report No.:	R014228
Document No.:	M-189213-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Attempts to investigate the adsorption of metabolite phosphonic acid to soil were reported in study KCA 7.1.3.1.2/01 using:

- three soils under conditions similar to batch equilibrium tests following application of non-labeled phosphonic acid as test substance.

The point had been addressed under Point 7.1.2.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The evaluation revealed that the study may be used for evaluation but results should be considered as indicative, i.e. as supplemental information with no use in risk assessment. It should also be noted that by its design the data resulted in values for the desorption of phosphonic acid (i.e. Kd) rather than values of adsorption that would result from batch equilibrium tests according to OECD 106. Values of Kd were determined to be 8.5, 30.1 and 139 mL/g for the three soils loam, silt loam and loam, respectively. The results were well in line with those described in the next section for KCA 7.1.3.2/01.

As an overall conclusion, sorption data for the metabolite phosphonic acid in terms of values of Kd were derived from soil column leaching experiments performed in two soils as summarized under KCA 7.1.4.1.2/01 and its evaluation under KCA 7.1.4.1.2/02.

Study summaries of existing studies and publications on adsorption of metabolites, i.e. phosphonic acid, to soil:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.3.1.2/01 [redacted]; [redacted]; 2000; M-189213-01-1
Title:	Phosphorous acid: Adsorption on three soils
Report No.:	R014228
Document No.:	M-189213-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary
The adsorption behaviour of phosphonate was studied following application of phosphonic acid at a test concentration of 2 mg/L to three French soils [redacted] and [redacted] and incubation for 24 hours.

Values of adsorption constants in terms of $K_{d,ads}$ were 8.55 mL/g ([redacted]), 30.15 mL/g ([redacted]) and 139.05 mL/g ([redacted]). The corresponding values referenced to organic carbon content of soil ($K_{oc,ads}$) were 578, 2818 and 3254 mL/g, respectively.

Due to performance at one test concentration no values for the Freundlich adsorption coefficient ($K_{F,ads}$) or the Freundlich coefficient 1/n in soil were determined.

The results of this non-GLP study were evaluated as supplemental information with no use in risk assessment.
Designed as indicative in study conduct and reporting, the study did not follow OECD Guideline 106, for example, regarding pretests to determine adsorption equilibrium and stability of the test substance, the testing at various test concentrations, performance at controlled test temperature or determination of a material balance including the determination of the extent of test substance adsorbed to soil.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material
The origin, purity and identity of the test material was not reported and thus not specified.

2. Test Soils
The study was performed with three soils as characterised in detail in Table 7.1.3.1.2- 1.

Table 7.1.3.1.2- 1: Physico-chemical properties of test soils

Parameter		Soil		
Soil Designation		[redacted]	[redacted]	[redacted]
Geographic Location				
City		[redacted]	[redacted]	[redacted]
Country		France	France	France
Textural Class		Loam	Silt loam	Loam
Coarse sand (%)	[200 µm – 2 mm]	23.9	0.6	16.5
Fine sand (%)	[50 – 200 µm]	14.4	2.7	14.9
Coarse silt (%)	[20 – 50 µm]	21.4	43	22.6
Fine silt (%)	[2 – 20 µm]	21.2	27.2	23.6
Clay (%)		16.6	24.5	20.4
pH (KCl)		6.1	7.1	5.1
Organic Carbon (%)		1.48	1.07	1.2
Organic Matter (%)		2.5	1.8	2.1
Cation Exchange Capacity (meq/100 g)		14	17.4	7.7

B. STUDY DESIGN

1. Experimental Conditions

Details of experimental conditions were only briefly reported.

The test was performed by incubation of 20 g soil samples with 100 mL aqueous solution of phosphonic acid at a concentration of 2 mg/L at unknown temperature for 24 hours.

2. Sampling

An unknown number of soil samples were removed for analysis after 24 hours of incubation.

3. Analytical Procedures

Following centrifugation, soil and supernatant were separated and the supernatant filtered on GF/A filters.

The concentration of phosphonates in the supernatant was determined by derivatization with trimethylsilyl diazomethane (TMSD) to form the methyl derivative followed by gas chromatographic (GC) analysis and the use of a flame photometric detector (FPD). The determination followed method AR154-97 not reported in detail. No method limit of quantification (LOQ) was reported.

II. RESULTS AND DISCUSSION

A. DATA

The results of adsorption tests of phosphonic acid onto three French soils were summarized in Table 7.1.3.1.2- 2.

Table 7.1.3.1.2- 2: Adsorption of phosphonic acid to soil

Soil	$K_{d, ads}$ [mL/g]	$K_{oc, ads}$ [mL/g]
[redacted]	8.55	578
[redacted]	30.15	2818
[redacted]	139.05	3254

The adsorption of phosphonate to soil in terms of values for the adsorption constant $K_{d,ads}$ ranged from 8.55 and 139.05 mL/g. The corresponding values of adsorption constants based on organic carbon of soil ($K_{oc,ads}$) ranged from 578 to 3254 mL/g.

B. MATERIAL BALANCE

Following use of non-labelled test material no material balances including the determination of non-extractable residues could be established.

C. TRANSFORMATION OF TEST SUBSTANCE

The decrease of the concentration of phosphonate in the water phase was followed. Consequently, the degradation of the test item was not investigated.

III. CONCLUSIONS

Following application of phosphonic acid, values of adsorption constants of phosphonate in terms of $K_{d,ads}$ were 8.55 mL/g ([redacted]), 30.15 mL/g ([redacted]) and 139.05 mL/g ([redacted]). The corresponding values referenced to organic carbon content of soil ($K_{oc,ads}$) were 578, 2818 and 3254 mL/g, respectively.

Due to performance at one test concentration no values for the Freundlich adsorption coefficient ($K_{F,ads}$) or the Freundlich coefficient 1/n in soil were determined.

No correlation of adsorption was found for organic carbon content, cation exchange capacity or pH of the soils.

The results of this non-GLP study were evaluated as supplemental information with no use in risk assessment.

Designed as indicative in study conduct and reporting, the study did not follow OECD Guideline 106, for example, regarding pretests to determine adsorption equilibrium and stability of the test substance, the testing at various test concentrations, performance at controlled test temperature or determination of a material balance including the determination of the extent of test substance adsorbed to soil.

CA 7.1.3.2 Aged sorption

Report:	KCA 7.1.3.2/01 [redacted], [redacted], 2001; M-204613-01-1
Title:	Simplified sorption study of phosphorous acid on different soils
Report No.:	C013437
Document No.:	M-204613-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	yes

Following ageing of phosphonic acid residues by incubation in aerobic soil desorption from soil had been investigated under conditions of the laboratory in study KCA 7.1.3.2/01 using:

- five soils incubated at ambient temperature and 70% of MWHC under aerobic conditions of the laboratory following application of non-labeled phosphonic acid.

The point had been addressed under Point 7.1.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The evaluation for the Annex I inclusion of fosetyl under Directive 91/414/EEC revealed that residues of phosphonic acid were found to undergo ageing in aerobic soil as indicated by increasing time-dependent sorption. From results of extraction with water the RMS France calculated values of Kd for phosphonic acid after 1 day and 34 days of equilibration as summarized in Table 7.1.3.2- 1.

Table 7.1.3.2- 1: Values of soil-water distribution coefficient (Kd) estimated for phosphonic acid

Soil	Kd	
	Ageing time of 1 d	Ageing time of 34 d
Soil A, Loam	3.3	7.1
Soil B, Sand	2.3	5.7
Soil C, Clay	6.7	48
Soil D, Loam	8.0	65
Soil E, Silty clay	65	65

Values derived from mean values of duplicate samples

The data were considered to be indicative, i.e. supplemental information, since the strong adsorption of phosphonic acid to soil observed was regarded as a complex phenomenon that cannot be readily characterized by batch equilibrium data. It was also questioned that the sorption of phosphonic acid to soil could be described by use of Koc as input into environmental risk assessment.

Study summaries of existing studies and publications on aged sorption of metabolites, i.e. phosphonic acid, to soil:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.3.2/01 [redacted],; [redacted]; 2001; M-204613-01-1
Title:	Simplified sorption study of phosphorous acid on different soils
Report No.:	C013437
Document No.:	M-204613-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	yes

Executive Summary

A simplified sorption study was performed by application of phosphonic acid to five French soils at a concentration of 4 mg/kg and ageing of residues by incubation in the dark under conditions of the laboratory (20 °C, 70% of max. WHC) for 83 days in maximum.

Results from extraction with water in comparison with aqueous ammonia buffer demonstrated that the latter was significantly more efficient.

In conclusion, extraction of phosphonate residues was more exhaustive when using aqueous ammonia buffer solution than for water. Following ageing under aerobic conditions extractability of phosphonate residues decreased significantly with time. Among other potential factors of influence (i.e. microbial transformation) there were indications that the extent of extractability was dependent on soil characteristics such as the clay and organic carbon content

Being a non-guideline study in its design, the data were considered as indicative, i.e. supplementary information.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Analytical grade phosphonic acid was used (batch EA5152SD2, chemical purity: 98.3%).

2. Test Soils

Five soils originating from France were used as characterised in detail in Table 7.1.3.2- 2. The soils had been sieved to a particle size ≤ 2 mm.

Table 7.1.3.2- 2: Physico-chemical characteristics of test soils

Parameter		Soil				
Soil Designation		A	B	C	D	E
Geographic Location						
City		[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Country		France	France	France	France	France
Textural Class (USDA)		Loam	Sand	Clay	Loam	Silty clay
Coarse sand (%)	[2000 µm – 2 mm]	23.2	91.3	0.7	40.4	0.2
Fine sand (%)	[50 µm – 2000 µm]	19.8	4.8	3.6	3.6	1.0
Coarse silt (%)	[20 µm – 50 µm]	23.1	0.9	10.4	8.7	17.3
Fine silt (%)	[2 µm – 20 µm]	21.1	1.5	22.6	22.5	32.0
Clay (%)	[< 2 µm]	12.8	1.5	55.7	24.8	49.5
pH (water)		6.8	5.2	8.1	8.3	6.8
pH (1 M KCl)		6.6	4.9	7.5	8.0	6.1
Phosphorous (H_2O_5) (g/kg)		0.129	0.137	0.168	0.259	0.027
Organic Carbon (%)		0.573	1.534	3.166	1.391	3.588
Organic Matter (%)		0.99	0.264	5.45	2.39	6.17
Cation Exchange Capacity (meq/100 g)		6.4	4.2	26.3	8.7	25.0
Water Holding Capacity (%)		29.8	21.7	56.3	48.8	53.6

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in glass flasks (250 mL) each containing 50 g dry weight of soil and the samples adjusted to soil moisture of 70% of the maximum water holding capacity (MWHC).
The test substance was applied as aqueous solution drop wise to the surface of soil samples to result in a test concentration of 4 mg/kg soil. The samples were incubated at ambient temperature in the dark for 83 days in maximum.

2. Sampling

Duplicate samples were removed for analysis after 1, 34 and 77 days of incubation by using water and, after 1, 34 and 83 days of incubation by using aqueous ammonia buffer as solvent for extraction.

3. Analytical Procedures

Soil samples were extracted with water or aqueous ammonia buffer solution at ambient temperature for one hour. The extracted soil was rinsed twice with isopropanol. Combined extract and rinses were filled up to the mark with isopropanol. An aliquot of the combined solution was subject to de-cationisation using a cation exchange resin. An aliquot was concentrated and phosphonate residues were derivatized with trimethylsilyl diazomethane and the methyl ester derivate quantified by gas chromatographic (GC) analysis on semi-capillary column using a flame photometric detector and the use of external standards (method AR 214-99). The method limit of quantification (LOQ) was 0.100 mg phosphonic acid/kg soil.

II. RESULTS AND DISCUSSION

A. DATA

The results of extraction of phosphonate residues from soil after ageing of residues under aerobic incubation conditions were summarized in Table 7.1.3.2- 3 (extraction with water) and in Table 7.1.3.2- 4 (extraction with aqueous ammonia buffer solution).

Table 7.1.3.2- 3: Phosphonate residues extracted with water from five soils following ageing at various incubation intervals

Soil	Mean SD	Incubation time (days)		
		1	**34**	**77**
A	mean	38.1	22.3	11.4
	SD	±0.9	±2.8	±3.4
B	mean	60.3	25.5	9.6
	SD	±3.0	±1.8	±3.1
C	mean	22.8	3.5	<5%
	SD	±0.5	±0.0	n.a.
D	mean	20.0	3.1	<5%
	SD	±16.5	±1.1	n.a.
E	mean	3.4	2.6	<5%
	SD	±0.1	±0.4	n.a.

All values expressed as percentage of phosphonate recovered
DAT: days after treatment, SD: standard deviation; n.a. = not applicable due to low residues

Table 7.1.3.2- 4: Phosphonate residues extracted with aqueous ammonia buffer from five soils following ageing at various incubation intervals

Soil	Mean SD	Incubation time (days) 1	34	83
A	mean	89.0	78.3 [1]	25.6
	SD	±1.8	-	±6.1
B	mean	81.4	73.1	33.6
	SD	±0.9	±9.9	±0.1
C	mean	66.9	22.4	19.5 [1]
	SD	±3.9	±2.4	-
D	mean	75.3	33.1	19.0
	SD	±3.5	±1.9	±8.8
E	mean	54.8	33.6	30.8
	SD	±4.3	±1.1	±1.0

All values expressed as percentage of phosphonate recovered
DAT: days after treatment, SD: standard deviation
[1] value for single replicate

B. MATERIAL BALANCE

Following use of non-labelled test material, no material balance including the determination of non-extractable residues could be established.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

The results demonstrated aqueous ammonia buffer to be a significantly more efficient extraction solvent than water.
Recoveries of phosphonate residues from soil were 89.0% (soil A), 81.4% (soil B), 66.9% (soil C) , 75.3% (soil D) and 54.8% (soil E) for aqueous ammonia buffer after one day in comparison to 38.1% (soil A), 60.3% (soil B), 22.8% (soil C), 20.0% (soil D) and 3.4% (soil E) for water after the same time of incubation.
Recoveries of phosphonate residues from soil decreased steadily to 25.6% (soil A), 33.6% (soil B), 19.5% (soil C), 19.0% (soil D) and 30.8% (soil E) for aqueous ammonia buffer after 83 days in comparison to 11.4% (soil A), 9.6% (soil B), < 5% (soil C), < 5% (soil D) and < 5% (soil E) for water after 77 days of incubation.

There were therefore indications that the difference in extraction efficiency for the two solvents was due to the clay content and the organic carbon content of soil.

D. VOLATILES

Owing to the nature of the test material the formation of volatile components was not anticipated and thus not determined.

E. TRANSFORMATION OF TEST SUBSTANCE

The study was designed to characterize the behavior of phosphonate residues under conditions of desorption following various time intervals of ageing. It was therefore not the objective of the study to derive a rate of degradation for phosphonate residues in aerobic soil.

III. CONCLUSIONS

In conclusion, extraction of phosphonate residues was more exhaustive when using aqueous ammonia buffer solution than for water. Following ageing under aerobic conditions extractability of phosphonate residues decreased significantly with time. Among other potential factors of influence (i.e. microbial transformation) there were indications that the extent of extractability was dependent on soil characteristics such as the clay and organic carbon content.

Being a non-guideline study in its design, the data were considered as indicative, i.e. supplementary information within the EU Annex I inclusion process.

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

Report:	KCA 7.1.4.1.1/01 [redacted]; [redacted]; [redacted], 1982; M-159329-01-1
Title:	Fosetyl-Al (aluminium tris-O-etyhlphosphonate): Soil leaching studies
Report No.:	R000781
Document No.:	M-159329-01-1
Guideline(s):	US Federal Register, 1978, 43, 132, p 29718 – equivalent to US EPA OPPTS 835.1230 and 835.1240
Guideline deviation(s):	none
GLP/GEP:	**no**

Report:	KCA 7.1.4.1.1/02 [redacted], 1989; M-163677-01-1
Title:	Fosetyl: Soil leaching studies - Addendum to report AG/CRLD/AN/025.82 dated Jan. 15, 1982
Report No.:	R002966
Document No.:	M-163677-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.4.1.1/03 [redacted], 1990; M-163681-01-1
Title:	Fosetyl-Al: Soil leaching studies Addendum to report AG/CRLD-AN no.025/82
Report No.:	R002968
Document No.:	M-163681-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

The mobility of residues of fosetyl-aluminium (fosetyl-Al) in soil had been investigated under conditions of column leaching in the laboratory in:

- soil columns of four test soils eluted at ambient temperature with 200 mm rainfall-equivalent of water under conditions of the laboratory following application of 1-^{14}C-labeled active substance (KCA 7.1.4.1.1/01, amended by KCA 7.1.4.1.1/02 and KCA 7.1.4.1.1/03).

This data requirement had been addressed under Point 7.1.3.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

Column leaching studies were thus performed with the active substance fosetyl-Al and evaluated, however, resulted in view of the significant non-stability of fosetyl-Al in difficulties in interpretation of data. Conclusively there was no use of the information since no reliable estimation could be made regarding the potential for mobility in soil.

The observed non-stability under the conditions of column leaching was well in line with existing and actual results in adsorption tests to soil (KCA 7.1.3.1.1/01 and KCA 7.1.3.1.1/03) or as indicated by tests on aerobic soil degradation.

The evaluation revealed that the mobility in soil was assessed conservatively by assuming no significant adsorption to soil as indicated by a value of Kfoc set to 0.1 mL/g for use in environmental risk assessments.

Considering the non-stability of fosetyl-Al a new column leaching study would not contribute to a better understanding of the mobility of the compound in soil therefore being regarded as not necessary.

Study summaries of existing studies and publications on column leaching of the active substance:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.4.1.1/01 [redacted]; [redacted]; [redacted]; 1982; M-159329-01-1
Title:	Fosetyl-Al (aluminium tris-O-etylphosphonate): Soil leaching studies
Report No.:	R000781
Document No.:	M-159329-01-1
Guideline(s):	US Federal Register, 1978, 43, 132 p 29718 – equivalent to US EPA OPPTS 835.1230 and 835.1240
Guideline deviation(s):	none
GLP/GEP:	**no**

Executive Summary

The potential for leaching of non-aged and aged residues of [^{14}C]-fosetyl-Al was investigated under laboratory conditions for the four soils sandy loam, loamy sand, silt loam and clay loam by soil column leaching and by soil thin layer chromatography (soil-TLC).

Non-aged column leaching: Investigations were performed with soil columns of 30 cm in height. Following application of fosetyl-Al at a rate equivalent to 80 kg/ha columns were irrigated drop wise with in total 1190 mL of water equivalent to 200 mm rainfall for approx. 14 hours. Soil segments and leachate were analysed.

Aged column leaching: Samples of soil sandy loam were treated with fosetyl-Al at an application rate equivalent to 80 kg a.s./ha (500 mg/kg soil) and incubated at 21 °C and 72% moisture of water capacity at 0.33 bar in the dark for 30 days. Radioactive residues were determined after 30 days for duplicate samples followed by placement of subsamples (representing 80% of the total sample each) on top of the soil columns. The leaching phase was conducted in the dark at 21 °C for 45 days. Soil segments and leachate were analysed.

Soil thin layer chromatography: Soil-TLC was performed on both sterilized and biologically active soils. The elution behaviour of fosetyl-Al was investigated against 2,4-dichlorophenoxy acetic acid as a reference compound. Soil was segmented and radioactivity determined by combustion.

Extensive transformation of fosetyl-Al was observed in microbial active soil under conditions of non-aged and aged soil column leaching in the laboratory.
The transformation under formation of volatile radioactivity resulted in significant losses in the total material balance, in particular when microbial active soil was used.
Results of investigations via soil-TLC using sterilised soil indicated a potential for mobility of fosetyl-Al in soil in case other factors of influence like degradation can be excluded.

In view of the rapid transformation of fosetyl-Al and its residues under the conditions of the test the results can be used as indicative information on the potential for mobility in soil only.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

[ethyl-1-^{14}C]-fosetyl-Al	
Sample ID:	KWC 1025
Specific Activity:	1.2 mBq (33.5 µCi/mg)
Radiochemical Purity:	95%

The specific activity of the test substance was diluted by addition of non-labelled fosetyl-Al (batch EA-1167-1).

2. Test Soils

The study was performed by using three soils sieved to a particle size ≤ 2 mm and as characterized in Table 7.1.4.1.1- 1. For preparation of soil-TLC plates, the soil was sieved to 0.5 mm.

Table 7.1.4.1.1- 1: Physico-chemical properties of test soils

Parameter		**Soil**			
Soil ID		Sandy loam	Clay loam	Loamy sand	Silt loam
Geographic Location		not reported			
Textural Classification		Sandy loam	Clay loam	Loamy sand	Silt loam
Sand (%)	[50 -2000 µm]	62.3	34.0	81.2	15.2
Silt (%)	[2 µm – 50 µm]	20.2	27.6	13.8	55.3
Clay (%)	[< 2 µm]	13.6	37.5	3.1	23.0
pH		5.3	7.6	6.6	6.6
Organic Material (%)		3.6	2.6	1.3	2.3
Cation Exchange Capacity [meq/100 g]		13	21	5	14
Water Capacity @ 0.33 bar (%)		24	26	16	26

B. STUDY DESIGN

1. Non-aged column leaching

The sieved soils were packed up to 30 cm height into a column (8.7 cm in diameter), assembled from 5 cm height glass cylinders. The soil columns were topped with a glass fibre filter, on which 12 mL of an aqueous solution containing 47.5 mg of fosetyl-Al (specific activity of 151 kBq/mg) were dripped.

The application rate was 80 kg/ha, which is equivalent to the highest recommended rate of fosetyl-Al assuming a treated area of 59.4 cm².

After treatment, each column was eluted with 1.19 L of water equivalent to 200 mm rainfall, of which 25 mL were delivered first with a pipette and the remainder being applied at a flow-rate of 8 mL/min using a pump. After complete elution of the water after approx. 14 hours, the soil columns were allowed to drip for an additional 24 hours period. The soil column was then disassembled to afford six 5 cm height segments.

The percolates were analysed by liquid scintillation counting (LSC) for total radioactivity and its contents were characterized by GLC and HPLC. Radioactivity in the soil was determined by combustion/LSC.

2. Aged column leaching

The test was performed using duplicate samples of soil sandy loam. The incubation phase was performed under flow-through conditions consisting of glass flasks each containing soil samples of 98 g dry weight. Volatile radioactivity was collected each by two successive traps containing sodium hydroxide and sulfuric acid, respectively. Fosetyl-Al was applied at a concentration of 500 mg/kg soil equivalent to an application rate of 80 kg a.s./ha in the field.
The soil water content was. The samples were incubated under flow-through conditions at 21 ± 4 °C and 72% moisture of water capacity at 0.33 bar in the dark for 30 days.
Volatile radioactivity was collected and determined after 3, 8, 15 and 30 days of incubation.

Following 30 days of incubation, the total radioactivity of homogenised soil was determined. The portion extractable with water was determined for a sub-sample of 5 g by extraction twice with 50 mL of water for 30 minutes (magnetical stirring).
A sub-sample (80% of the total residual radioactivity, equivalent to 47.7 mg fosteyl-Al) each was placed on top of a soil column containing the same type of untreated soil.

The soil columns were irrigated with water in the dark at 21 ± 4 C at a daily rate of 29 mL (i.e. 4.9 mm height) for 45 days. Water started to drip from the soil columns after six days of irrigation to result in the collection of eleven successive leachate fractions of about 100 mL.
After irrigation, the soil in the columns was segmented into the originally treated layer and six layers of 5 cm. The radioactivity was determined by LSC in leachates and in soil by combustion/LSC.
Test item and transformation products in percolates were quantified by HPLC/radio-detection. Following derivatization fosetyl and phosphonic acid were determined in percolates by gas chromatography (GC) and the use of a phosphorus specific flame photometric detector.

3. Soil thin-layer chromatography

Following sieving to 0.5 mm two soil thin layer plates were prepared per test soil. One plate consisting of biologically active soil was developed while the other was sterilized by heating overnight at 120 °C. ^{14}C-Fosetyl-Al and ^{14}C-2,4-D as reference were spotted as aqueous solution onto the plates. The air-dried plates were developed at 10 °C horizontally with distilled water. Following development the radioactive spots were located on the air-dried plates and scraped off for determination of total radioactivity by combustion/LSC.

II. RESULTS AND DISCUSSION

Results of tests using biologically active soils indicated significant transformation of fosetyl-Al. It was therefore not possible to provide conclusive information on the mobility of the active substance fosetyl-Al in soil.
Transformation of fosetyl-Al was insignificant following application to sterile soil-TLC plates. The results can be used as indicative information to evaluate the mobility of fosetyl-Al in soil.

1. Non-aged column leaching

The data representing the results of non-aged column leaching of fosetyl-Al in soil were summarized in Table 7.1.4.1.1- 2 to Table 7.1.4.1.1- 5.

Total material balances were 82.8% AR for soil sandy loam, 89.2% AR for clay loam, 81.6% AR for loamy sand and 84.4% AR for the silt loam.

In this context it should be noted that the total runtime of the leaching phase was at least about 38 hours. In addition, the soil columns were an 'open system' with no traps to collect volatiles. In view of the spontaneous transformation of fosetyl residues in contact with biologically active soil (see, for example, Section CA 7.1.1.1), the losses can be explained by formation of the volatile components like ethanol and carbon dioxide that escaped from the test system.

The radioactivity retained in the soil was nearly uniformly distributed within the entire soil column for soils loamy sand and the silt loam. For soils sandy loam and clay loam some gradient was observed for the distribution of radioactive residues along the soil columns resulting in decreasing concentrations from the top to the bottom.

Total radioactive residues in column percolates were 0.4% AR for the sandy loam, 15.2% AR for the clay loam, 43.8% AR for the loamy sand and 14.0% AR for the silt loam.

Radioactive residues in percolates of the sandy loam soil were thus negligible. Total radioactive residues in percolates distributed into fosetyl (3.4% AR), ethanol (≤ 2% AR) and an unknown component (7.5% AR) for soil clay loam, into fosetyl (≤ 2% AR), ethanol (36% AR) and an unknown component (≤ 2% AR) for soil loamy sand and into fosetyl (≤ 2% AR), ethanol (≤ 2% AR) and an unknown component (10% AR) for soil silt loam.

It should be considered that the situation of non-aged soil column leaching testing was not comparable to those of standard degradation tests in aerobic soil. While the soil columns and the percolates contained biologically active soil and its organisms on one hand there were limitations on aeration of soil due to the 'flooded' situation on the other hand. In the absence of detailed information about the conditions of collection, storage and handling of the samples in the following, this is likely to be the cause of artifact formation for test substances rapidly transformed like fosetyl and its rapidly formed residues.

Table 7.1.4.1.1- 2: Non-aged column leaching of [^{14}C]-fosetyl-Al residues in sandy loam soil

Compartment		Recovery (%)
Soil	Segment 1 (top 5 cm)	6.3
	Segment 2 (5- 10 cm)	17.3
	Segment 3 (10-15 cm)	19.9
	Segment 4 (15-20 cm)	19.3
	Segment 5 (20-25 cm)	13.9
	Segment 6 (25-30 cm)	5.7
	Total radioactivity in soil segments	82.4
Water	Fosetyl-Al (GC/phosphorus detection, FPD)	≤ 1
	Fosetyl-Al (HPLC/radio-detection)	n.a.
	Phosphonic acid (GC/phosphorus detection, FPD)	≤ 1
	Phosphonic acid (HPLC/radio-detection)	n.a.
	Ethanol (GC/phosphorus detection, FPD)	n.a.
	Ethanol (HPLC/radio-detection)	n.a.
	Unknown (GC/phosphorus detection, FPD)	n.a.
	Unknown (HPLC/radio-detection)	n.a.
	Total radioactivity in percolates	0.4
Total radioactivity recovered		82.8

n.a.: not analyzed/not applicable
All values expressed as percentage of applied dose

Table 7.1.4.1.1- 3: Non-aged column leaching of [^{14}C]-fosetyl-Al residues in clay loam soil

Compartment		Recovery (%)
Soil	Segment 1 (top 5 cm)	17.4
	Segment 2 (5- 10 cm)	13.4
	Segment 3 (10-15 cm)	13.7
	Segment 4 (15-20 cm)	11.9
	Segment 5 (20-25 cm)	11.4
	Segment 6 (25-30 cm)	6.2
	Total radioactivity in soil segments	74.0
Water	Fosetyl-Al (GC/phosphorus detection, FPD)	2.6
	Fosetyl-Al (HPLC/radio-detection)	3.4
	Phosphonic acid (GC/phosphorus detection, FPD)	5.5
	Phosphonic acid (HPLC/radio-detection)	n.a.
	Ethanol (GC/phosphorus detection, FPD)	n.a.
	Ethanol (HPLC/radio-detection)	≤ 2
	Unknown (GC/phosphorus detection, FPD)	n.a.
	Unknown (HPLC/radio-detection)	7.5
	Total radioactivity in percolates	15.2
Total radioactivity recovered		89.2

n.a.: not analyzed/not applicable
All values expressed as percentage of applied dose

Table 7.1.4.1.1- 4: Non-aged column leaching of [^{14}C]-fosetyl-Al residues in loamy sand soil

Compartment		Recovery (%)
Soil	Segment 1 (top 5 cm)	-
	Segment 2 (5- 10 cm)	7.4
	Segment 3 (10-15 cm)	6.6
	Segment 4 (15-20 cm)	7.2
	Segment 5 (20-25 cm)	8.4
	Segment 6 (25-30 cm)	8.2
	Total radioactivity in soil segments	37.8
Water	Fosetyl-Al (GC/phosphorus detection, FPD)	≤ 1
	Fosetyl-Al (HPLC/radio-detection)	≤ 2
	Phosphonic acid (GC/phosphorus detection, FPD)	12.6
	Phosphonic acid (HPLC/radio-detection)	n.a.
	Ethanol (GC/phosphorus detection, FPD)	n.a.
	Ethanol (HPLC/radio-detection)	36
	Unknown (GC/phosphorus detection, FPD)	n.a.
	Unknown (HPLC/radio-detection)	≤ 2
	Total radioactivity in percolates	43.8
Total radioactivity recovered		81.6

n.a.: not analyzed/not applicable
All values expressed as percentage of applied dose

Table 7.1.4.1.1- 5: Non-aged column leaching of [^{14}C]-fosetyl-Al residues in silt loam soil

Compartment		Recovery (%)
Soil	Segment 1 (top 5 cm)	-
	Segment 2 (5-10 cm)	8.6
	Segment 3 (10-15 cm)	14.1
	Segment 4 (15-20 cm)	18.0
	Segment 5 (20-25 cm)	16.6
	Segment 6 (25-30 cm)	13.1
	Total radioactivity in soil segments	70.4
Water	Fosetyl-Al (GC/phosphorus detection, FPD)	≤ 1
	Fosetyl-Al (HPLC/radio-detection)	≤ 2
	Phosphonic acid (GC/phosphorus detection, FPD)	≤ 0.1
	Phosphonic acid (HPLC/radio-detection)	n.a.
	Ethanol (GC/phosphorus detection, FPD)	n.a.
	Ethanol (HPLC/radio-detection)	≤ 2
	Unknown (GC/phosphorus detection, FPD)	n.a.
	Unknown (HPLC/radio-detection)	10
	Total radioactivity in percolates	14.0
Total radioactivity recovered		84.4

n.a.: not analyzed/not applicable
All values expressed as percentage of applied dose

2. Aged column leaching

Following an aerobic aging period of 30 days in soil sandy loam the results of the column leaching phase were summarized in Table 7.1.4.1.1- 6.

Following 30 days of aging and a leaching phase of 45 days the mean material balance of two replicates was 71.5% AR.

During the leaching phase, the soil columns were an 'open system' with no traps to collect volatiles. In view of the spontaneous transformation of fosetyl residues in contact with biologically active soil (see, for example, Section CA 7.1.1.1), the losses can be explained by formation of the volatile components that escaped from the test system.

The radioactive residues of fosetyl in soil after aerobic aging were predominantly retained in the soil segment applied to the column (68.9% AR).

Radioactivity in other soil column segments was minor and nearly uniformly distributed. Since total radioactive residues in column percolates were below 0.1% AR, percolates were not subject to HPLC analysis. Following derivatization, GC analysis of percolates was performed in order to investigate the leaching potential of phosphonic acid. Phosphonic acid was absent in any of the eluate fractions (detection limit: 0.5 mg/kg, i.e. 0.5 mg total phosphonic acid in the entire eluate).

Table 7.1.4.1.1- 6: Column leaching of [^{14}C]-fosetyl-Al residues aged for 30 days in sandy loam soil

Compartment		Recovery (%)
Soil	Radioactive residues in treated soil	68.9
	Segment 1 (top 5 cm)	0.7
	Segment 2 (5-10 cm)	0.2
	Segment 3 (10-15 cm)	0.1
	Segment 4 (15-20 cm)	0.1
	Segment 5 (20-25 cm)	0.1
	Segment 6 (25-30 cm)	0.1
	Total radioactivity in soil segments	1.3
Water	Total radioactivity in percolates	0.0
Total radioactivity recovered		71.8

All values expressed as percentage of applied dose
Mean values of two replicates

3. Soil thin-layer chromatography

In view of the extensive degradation of fosetyl under conditions of soil column leaching, additional tests were performed by using soil-TLC. Soil-TLC is faster and readily applicable to sterile soil to separate factors of leaching and degradation. The results of tests under conditions of soil-TLC were summarized in Table 7.1.4.1.1- 7.

The total radioactivity recovered as fosetyl-Al and for 2,4-D from the elution lane of sterilized soil was about 90%. In a preliminary experiment, the radioactivity recovered from soil of the chromatographic lane had been shown to be extractable with water (80% of the radioactivity recovered in aqueous extract). HPLC analysis of the extract indicated the presence of parent compound fosetyl only. Conclusively, the predominant portion of fosetyl remained unchanged under conditions of soil-TLC using sterilised soil layers. An R_f of 1 was determined for the four soils thus to indicate higher mobility than the reference compound 2,4-D.

For biologically active soil results in terms of R_f-values in soil-TLC were similar as for sterilised soils. However, radioactivity recovered as fosetyl-Al was about 15 to 50% of the radioactivity applied to the lane of the plate.

Table 7.1.4.1.1- 7: Recovery of [^{14}C]-fosetyl-Al in Soil-TLC

Soil	2 µg spot applied to lane		12 µg spot applied to lane	
	Non-Sterile	Sterile	Non-Sterile	Sterile
Sandy loam	18	86	13	91
Loamy sand	21	90	23	90
Silt loam	41	87	48	94
Clay loam	48	92	54	94

R_f of fosetyl = 1
All values expressed as percentage of total radioactivity recovered per lane

III. CONCLUSIONS

Extensive transformation of fosetyl-Al was observed in microbial active soil under conditions of non-aged and aged soil column leaching in the laboratory.
The transformation under formation of volatile radioactivity resulted in significant losses in the total material balance, in particular when microbial active soil was used.
Results of investigations via soil-TLC using sterilised soil indicated a potential for mobility of fosetyl-Al in soil in case other factors of influence like degradation can be excluded.

In view of the rapid transformation of fosteyl-Al and its residues under the conditions of the test the results can be used as indicative information on the potential for mobility in soil only.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

Report:	KCA 7.1.4.1.2/01 [redacted]; [redacted]; 1998; M-158753-01-1
Title:	Leaching of (33P)-phosphorous acid in two soils
Report No.:	R000500
Document No.:	M-158753-01-1
Guideline(s):	USEPA (=EPA) N, 163-1, (1982)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.1.4.1.2/02 [redacted]; 2004; M-236511-01-1
Title:	Predicted environmental concentrations in groundwater (PECgw) for the fosetyl-Al main metabolite phosphorous acid following a repeated foliar use under european conditions Code: AE F053616
Report No.:	C044834
Document No.:	M-236511-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.1.4.1.2/03 [redacted]; 2015; M-532553-01-1
Title:	Phosphonic acid - Soil column leaching in three soils
Report No.:	20140226
Document No.:	M-532553-01-1
Guideline(s):	EPA Pesticide Assessment Guidelines (1982), Subdivision N, Paragraph 163-1 with modifications; OECD Guidelines for the testing of chemicals: Leaching in Soil Columns Guideline 312 (Adopted 13th April 2004)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.1.4.1.2/04 [redacted]; [redacted]; 2015; M-531831-01-1
Title:	Phosphonic Acid - Evaluation of Soil Column Leaching Data for Sorption Parameters for Use in Environmental Modelling
Report No.:	EnSa-15-0633
Document No.:	M-531831-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

The mobility of residues of phosphonic acid in soil had been investigated under conditions of column leaching in the laboratory in:

- soil columns of two test soils eluted at ambient temperature with 508 mm rainfall-equivalent of water under conditions of the laboratory following application of ^{33}P-labeled phosphonic acid (KCA 7.1.4.1.2/01).

In the absence of other reliable information characterising sorption and mobility of phosphonic acid residues in soil this data requirement had been addressed under Point 7.1.3.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

Designs by OECD Guideline 312 follow existing guidelines, i.e. US EPA Subdivision N, as of 1982, given as reference in the study KCA 7.1.4.1.2/01. The test design is also in line with new soil column leaching data submitted to be fully consistent for the whole data package.
In summary this allows for the conclusion that the study KCA 7.1.4.1.2/01 had no major deviation from designs according to OECD 312.

The evaluation revealed that the results of the column leaching test indicated very low mobility of phosphonic acid in soil. In the following the data of study KCA 7.1.4.1.2/01 were evaluated as submitted in document KCA 7.1.4.1.2/02 in order to derive sorption parameters for use as input in environmental risk assessment.
Sorption values in terms of Kd for phosphonic acid were derived from application of chromatographic theory to describe the relation between mobility observed in column leaching and the transfer into sorption data as published by Lambert (1965) to result in values of Kd of 44 mL/g for the sandy soil Fengate Farm and 46.3 mL/g for the sandy loam [redacted].
Calculations were also performed according to publications by Hamaker (1975) and MacCall (1981) as cited in OECD Guideline 312 (April 2004) to result in sorption values in terms of Kd for phosphonic acid of 48 mL/g for the sandy soil Fengate Farm and 47.1 mL/g for the sandy loam [redacted].
The value of Kd of 44 mL/g from sandy soil Fengate Farm along with a value of 1 for the adsorption coefficient 1/n was finally chosen to reflect a worst case to describe the sorption behaviour of phosphonic acid in soil in environmental risk assessments.

New information: Sorption data to soil for metabolite phosphonic acid from additional soil column leaching study

For the Annex I inclusion of fosetyl under Directive 91/414/EEC, sorption data to soil were available for phosphonic acid from two soils.
In order to fully fulfil data requirements set by Commission Regulation (EC) No 283/2013 amending Regulation (EC) 1107/2009, additional sorption data to soil are submitted in the following in order to serve as a robust data set as input for environmental risk assessment.

Report:	KCA 7.1.4.1.2/03 [redacted].; 2015; M-532553-01-1
Title:	Phosphonic acid - Soil column leaching in three soils
Report No.:	20140226
Document No.:	M-532553-01-1
Guideline(s):	EPA Pesticide Assessment Guidelines (1982), Subdivision N, Paragraph 163-1 with modifications; OECD Guidelines for the testing of chemicals: Leaching in Soil Columns Guideline 312 (Adopted 13th April 2004)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The mobility and sorption characteristics of phosphonic acid to soil were determined by column leaching tests on three soils [redacted], [redacted], [redacted].
Phosphonic acid had been applied to the top of pre-equilibrated soil columns at a test concentration of 3 mg per column, equivalent to a field application rate of 15 kg/ha. The soil columns were irrigated under saturated flow conditions of the laboratory at a temperature of 23.8 ± 1°C in the dark by allowing 525 ± 5 mm aqueous of 0.01 M $CaCl_2$ solution to pass as artificial rainfall the columns for five successive days.

Average total recoveries of phosphonic acid were 46.7% of the applied amount for columns of soil [redacted] II, 77.1% for soil [redacted] and 66.0% for soil [redacted]. No phosphonic acid was found in the leachates of any soil column.

Phosphonic acid was mainly located in the top soil segments (0 to 3 cm) of columns to amount to 24.7%, 69.1% and 35.8% of applied in average from two columns for the three soils, respectively.

I. Material and Methods

A. Materials

1. Test Material: Phosphonic acid
Purity: 98.7% (w/w)
Sample ID: 04911DN

2. Soil: Tests were performed with sieved (2 mm) soils. The three soils amended the range of pH, organic carbon content and texture of soils of study KCA 7.1.4.1.2/01. The soil characteristics are summarised in Table 7.1.4.1.2- 1.

Table 7.1.4.1.2- 1: Characteristics of test soils

Soil	[redacted] ([redacted])	[redacted] ([redacted])	[redacted]
Geographic Location (City/State/Country)	[redacted], Germany	[redacted], Germany	[redacted], Germany
GPS coordinates	[redacted]	[redacted]	[redacted]
Textural Class (USDA)	clay loam	sandy loam	sandy loam
Sand (%) [A] Silt (%)[A] Clay (%)[A]	29 39 32	53 31 16	77 15 8
pH (0.01 M $CaCl_2$) pH (Water)	7.2 7.3	5.0 5.3	6.1 6.5
Org. Matter [B] (%)	7.4	2.8	2.1
Org. Carbon (%)	4.3	1.6	1.2
CEC (meq/100 g)	17.5	9.1	7.1

[A] According to USDA classification; [B] % Organic matter =% organic carbon x 1.72
CEC: Cation exchange capacity; N/A = Not available

B. Study design

1. Experimental conditions:
The test systems consisted of three soil columns for each soil of ca. 30 cm in length and 5 cm in diameter. Duplicates were worked up and analysed following the irrigation phase while one column per soil serving as reserve with no further work up in the course of the study. The columns consisted of PVC material with a glass wool plug at the bottom, followed by a layer of 5 cm silica sand. The columns were packed with air-dried soil (2 mm-sieved) to result in a total height of approx. 31 cm. The columns were saturated with aqueous 0.01 M $CaCl_2$ solution overnight thus avoiding enclosure of air into the soil pores. Following this phase the surplus of $CaCl_2$ solution was allowed to drain and volumes of drained water (dripping volume) were determined. For final pre-equilibration the soil columns were re-watered from the bottom till the $CaCl_2$ solution just covered the top soil layer of the column.

A solution of phosphonic acid was applied on top of each columns to result in a total amount of 3 mg test item applied per column equivalent to a field application rate of 15 kg/ha.

The soil columns were irrigated with aqueous 0.01 M $CaCl_2$ solution equivalent nominally to 50.8 cm/m^2 or 508 mm (actual: 525 ± 5 mm) simulated rainfall for five days. The $CaCl_2$ solution percolated through the columns at a flow rate of approximately 8 to 9 mL/h while maintaining a constant aqueous layer at the top of the soil columns during the irrigation phase (saturated flow). The tests were performed at temperature of 23.8 ± 1 °C in the dark.
It should be noted that the study setup was not intended to represent a realistic leaching scenario, but was designed to provide mobility parameters (sorption characteristics) of phosphonic acid under worst case to extreme conditions of leaching. The set-up allowed for a constant flow of water through the soil columns thus enabling conditions of saturated flow and the latter being the prerequisite for an estimation of Kd values according to the mathematical relationships derived from the theory of chromatographic flow (for evaluation, see KCA 7.1.4.1.2/04).

2. Sampling:
Following irrigation the soil columns were frozen and cut into segments of 1 to 2.5 cm in height (i.e. five 1 cm segments from top to 5 cm, ten 2.5 cm segments for the following per column). Each soil segment was extracted four times successively at ambient temperature with 50 mL aqueous ammonium buffer (pH 9.2, ammonium hydrogen carbonate/ammonia) by shaking for 30 min. An aliquot (30 mL) of the combined extracts was lyophilized to dryness and the residue re-constituted in 30 mL 0.1 M aqueous tartaric acid.

Column leachates were sampled at five successive days during the irrigation period to result in about 200 mL leachates per column and day. The total amount of $CaCl_2$ solution percolated per column was 1043 and 1038 mL for columns 1 and 2 (soil [redacted]), 1028 and 1018 mL for columns 4 and 5 (soil [redacted]) and 1022 and 1047 mL for columns 7 and 8 (soil [redacted]), respectively.

3. Analytical procedures:
Residues of phosphonic acid in soil extracts and column leachates were determined by LC-MS/MS analysis (LOQ = 0.1% of applied for soil extracts and leachates) including the confirmation of stability of the test item in aqueous $CaCl_2$ solution.

In parallel to soil segments, the extraction efficiency and sensitivity of the analytical method was confirmed by fresh fortification of untreated soil samples with phosphonic acid and work up according to the same procedure to result in mean recoveries of 86.9% of applied for soil [redacted], 103.9% for soil [redacted] and 107.2% for soil [redacted].

II. Results and Discussion

A. Recovery of test item

Overall mean recoveries of test item from duplicates were 46.7% of applied for columns of soil [redacted], 77.1% for soil [redacted] and 66.0% for soil [redacted] (see Table 7.1.4.1.2-2). The results indicated a fast and tight adsorption of phosphonic acid to soil particles thus reducing the potential for mobility in soil significantly. The results were well in line with observations made in existing and new studies including tests performed with ^{33}P-labelled phosphonic acid (KCA 7.1.2.1.2/04, KCA 7.1.2.1.2/07 and KCA 7.1.4.1.2/01).

B. Findings

The predominant portion of phosphonic acid was found in the top five cm segments of the soil columns (see Table 7.1.4.1.2- 2) to account for 35.2 and 38.5% for columns 1 and 3 (soil [redacted] II), 73.0 and 74.1% for columns 4 and 5 (soil [redacted]) and 54.5 and 51.3% for columns 7 and 8 (soil [redacted]), respectively. No test item was found in the leachates of soil columns thus there was no contribution of leachates to the total recovery of phosphonic acid in the test systems.

The results of the study were further evaluated to derive sorption values (Kd) by use mathematical relationships based on the theory of chromatographic flow (KCA 7.1.2.1.2/04).

Table 7.1.4.1.2- 2: Total recovery of phosphonic acid in soil columns following irrigation

Soil	[redacted]		[redacted]		[redacted] **XXa**	
Column	**1**	**3**	**4**	**5**	**7**	**8**
Segment 0-1 cm (%)	6.8	4.5	39.3	35.5	11.7	10.0
Segment 1-2 cm (%)	11.4	9.2	21.3	23.5	13.6	12.2
Segment 2-3 cm (%)	7.0	10.4	8.2	10.3	11.6	12.4
Segment 3-4 cm (%)	5.6	8.6	3.6	2.6	10.4	9.6
Segment 4-5 cm (%)	4.4	8.6	1.6	2.2	7.2	7.1
Segment 5-7.5 cm (%)	5.0	5.8	2.1	1.9	5.7	8.2
Segment 7.5-10 cm (%)	3.3	6.3	0.4	0.8	2.7	3.7
Segment 10-12.5 cm (%)	0.8	1.5	0.4	0.5	0.7	2.5
Segment 12.5-15 cm (%)	0.5	1.5	-*	-*	0.4	1.3
Segment 15-17.5 cm (%)	0.3	0.6	-*	-*	0.4	0.3
Segment 17.5-20 cm (%)	-*	-*	-*	-*	-*	-*
Segment 20-22.5 cm (%)	-*	-*	-*	-*	-*	-*
Segment 22.5-25 cm (%)	-*	-*	-*	-*	-*	-*
Segment 25-27.5cm (%)	-*	-*	-*	-*	-*	-*
Segment 27.5-30 cm (%)	-*	-*	-*	-*	-*	-*
Leachates (%)	-*	-*	-*	-*	-*	-*
Total recovery (%)	45.2	48.2	76.9	77.3	64.5	67.4
Mean total recovery (%)	46.7		77.1		66.0	

All values given as percentage of applied test item. *Below LOQ of 0.1% of applied

III. Conclusion

The results of the study demonstrate that the predominant portion of phosphonic acid was found in the top three cm layer of each soil column. No phosphonic acid was observed in the column leachates despite the simulation of extreme irrigation conditions equivalent to more than 500 mm rainfall in five successive days.

Phosphonic acid was therefore shown to be, in fact, immobile in soil when transferring to the situation of outdoor environmental conditions.

The results of the test allowed for the calculation of sorption constants Kd presented under KCA 7.1.4.1.2/04. From distribution of phosphonic acid in soil columns, Kd-values were calculated using mathematical relationships derived from the theory of chromatographic flow following the approaches published by Hamaker and McCall.

Report:	KCA 7.1.4.1.2/04[redacted],;[redacted]; 2015; M-531831-01-1
Title:	Phosphonic Acid - Evaluation of Soil Column Leaching Data for Sorption Parameters for Use in Environmental Modelling
Report No.:	EnSa-15-0633
Document No.:	M-531831-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The sorption characteristics of phosphonic acid to soil in terms of the sorption constants Kd were determined from column leaching tests performed in two studies KCA 7.1.4.1.2/01 and KCA 7.1.4.1.2/03 on five soils in total.
Phosphonic acid had been applied to the top of pre-equilibrated soil columns at a test concentration equivalent to a field application rate of 15 kg/ha. The soil columns were irrigated under saturated flow conditions of the laboratory at ambient temperature in the dark by allowing in total approximately 500 mm artificial rainfall to pass the columns for fifteen (KCA 7.1.4.1.2/01) or five successive days (KCA 7.1.4.1.2/03).

Following the distribution of phosphonic acid in soil columns the linear sorption distribution constants Kd were derived by applying the theory of chromatographic flow and its mathematical relationships according to approaches published by Lambert et al. and Hamaker/McCall.

Linear sorption distribution constants Kd were found to range from 19.2 mL/g for soil [redacted] to 86.9 mL/g for soil [redacted] when following the conservative approach of Lambert. A geometric mean value for Kd of 39.1 mL/g was derived for the range of five soils investigated.

Since the evaluation was based on linear sorption the value for the Freundlich adsorption coefficient 1/n was set of 0 mL/g.

I. Material and Methods

The sorption characteristics of phosphonic acid to soil in terms of the linear distribution constants Kd for sorption were determined from column leaching tests performed in two studies KCA 7.1.4.1.2/01 and KCA 7.1.4.1.2/03 on five soils in total.
Phosphonic acid had been applied to the top of pre-equilibrated soil columns at a test concentration equivalent to a field application rate of 15 kg/ha. The soil columns were irrigated under saturated flow conditions of the laboratory at ambient temperature in the dark by allowing in total approximately 500 mm artificial rainfall to pass the columns for fifteen (KCA 7.1.4.1.2/01) or five successive days (KCA 7.1.4.1.2/03). Within the tests phosphonic acid was mainly located in the top soil segments (0 to 3 cm) of soil columns. No phosphonic acid was found in the leachates.

The results of study KCA 7.1.4.1.2/01 had been evaluated in the process for the Annex I inclusion of fosetyl under Directive 91/414/EEC in document KCA 7.1.4.1.2/02. The evaluation was accepted by RMS France to result in two values of sorption coefficient Kd to characterize the mobility in soil and quantify the extent of adsorption for use in environmental risk assessment. Kd-values were calculated from distribution of phosphonic acid in layers of soil columns. The evaluation followed the approaches published by Lambert[12], Hamaker[13] and McCall et al.[14] based on principles of the theory of

[12] Lambert, S.M.; Porter, I.J.; Pease, H.L. (1965). Movement and sorption of chemicals applied to the soil. Weeds 13, pp 185-190
[13] Hamaker, J. W. (1975). The interpretation of soil leaching experiments, in: Environmental dynamics of pesticides (Eds. R. Haque & V. H. Freed, Plenum Press, New York), pp 115-132
[14] McCall, P. J., Laskowski, D. A., Swann, R. L. & Dishburger, H. J. (1981). Measurement of sorption coefficients of organic chemicals and their use in environmental fate analysis, in: Test protocols for

chromatographic flow and its mathematical relationships. The results of study KCA 7.1.4.1.2/03 have been evaluated for determination of values of Kd the same way in KCA 7.1.4.1.2/04.

For evaluation of study KCA 7.1.4.1.2/03 the two approaches (Lambert versus Hamaker/McCall) were transferred to an Excel-based following the corresponding basic mathematical equations and relations finally allowing for the calculation of Kd on the basis of various soil and column-specific input parameters.

The description of columns included the total irrigation volume, the saturation and dripping excess volume, dry and wet soil weights, column diameter, surface area and length, the number of segments and the segment with maximum concentration. For soils used their organic carbon content, total volume of water in the column and void volume. For details, it is referenced to document KCA 7.1.4.1.2/04.

II. Results and Discussion

The evaluation of study KCA 7.1.4.1.2/03 resulted in values of Kd for soils [redacted], [redacted] and [redacted] as summarized in Table 7.1.4.1.2- 3 along with the values derived earlier within KCA 7.1.4.1.2/02 for soils Fengate and Aldhams farm.

Table 7.1.4.1.2- 3: Values of Kd and Koc of phosphonic acid resulting from soil column leaching experiments

Soil	[redacted] (sand)	[redacted] (sandy loam)	[redacted] (clay loam)	[redacted] (sandy loam)	[redacted] (sandy loam)
Values according to Lambert et al.					
K_d	43.9	46.3	28	87	20
K_{oc}	1829	1543	650	5429	1650
Values according to Hamaker/McCall et al.					
K_d	48.0	47.1	37	114	26
K_{oc}	1998	1570	857	7129	2163
Worst case of Kd (Lambert) taken for input in environmental risk assessment					
K_d	43.9	46.3	28	87	20
K_{oc}	1829	1543	650	5429	1650
Geometric mean of Kd derived for risk assessment:			39.1		

All values given as mL/g.

The approaches were derived on the basis of linear sorption. The distribution constants Kd for sorption should therefore be used accordingly when it comes to the description of concentration dependency (i.e. value for the Freundlich exponent 1/n to be set to zero).

III. Conclusion

The evaluation of two soil column leaching studies performed allowed for the calculation of linear sorption distribution constants Kd for five soils.

Phosphonic acid was strongly bound to soil as indicated by values of Kd of 20 to 87 mL/g when following the approach by Lambert. The approach by Hamaker/McCall resulted in a range of values of

environmental fate and movement of toxicants; Proceedings of AOAC Symposium, AOAC, Washington, DC, pp 89-109

26 to 114 mL/g. When following the more conservative approach by Lambert, this resulted in a mean value of 39.1 mL/g to serve as modelling endpoint from five soils in total.

Since the evaluation was based on linear sorption the value for the Freundlich adsorption coefficient 1/n was set to 1.

Request from the RMS:
In the study by [redacted] and [redacted] (2015, KCA 7.1.4.1.2/04), the calculation of the "ds" parameter seems to be performed with the "dry soil weight per column" for the Fengate and Aldhams soils and with the "wet soil weight per column" for the other soils. An explanation should be provided to state on the reliability of the results.

Response from BCS:
For all soils, the parameter "ds" was calculated from the bulk density of the soil divided by (1-θ), as stated in Section 9.5, Table 13 ([redacted], S.; [redacted], G.; 2015; M-531831-01-1; KCA 7.1.4.1.2/04). In the case of soils [redacted] the soil bulk density was calculated from the dry soil weight (Ms) divided by the total volume of the column. The soil weight was, however, not reported explicitly by [redacted], P.; [redacted], A. M.; 1998; M-158753-01-1 (KCA 7.1.4.1.2/01) for soils Fengate and Aldhams. Instead, a procedure was described to prepare columns with constant soil density, for which values of 1.10 g/cm³ (Fengate) and 1.12 g/cm³ (Aldhams) were reported. These bulk densities were employed for the calculation of ds, in consistency with the evaluation by [redacted], G.; 2004; M-236511-01-1 (KCA 7.1.4.1.2/02). However, it might be the case that the reported density refers to the wet soil where the dry soil density would be appropriate for calculation of ds. If ds is recalculated based on dry soil, K_d values of 57.6 and 60.7 mL/g result from the Hamaker/McCall equation for soils Fengate and Aldhams, respectively. These K_d values are higher than the reported values and would not be used in the exposure calculations, which were based only on the lower K_d values derived from the equation by Lambert.

Study summaries of existing studies and publications on column leaching of metabolites, i.e. phosphonic acid:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.1.4.1.2/01 [redacted],; [redacted]; 1998; M-158753-01-1
Title:	Leaching of (33P)-phosphorous acid in two soils
Report No.:	R000500
Document No.:	M-158753-01-1
Guideline(s):	USEPA (=EPA): N 163-1, (1982)
Guideline deviation(s):	none
GLP/GEP:	yes

Executive Summary
The potential for leaching of non-aged residues of [^{33}P]-phosphonic acid was investigated at 20 C in two UK soils sand and loamy sand under laboratory conditions for 16 days in maximum. Based on a rate of 15 kg/ha, 3 mg of phosphonic acid were applied to each column.

Mean material balances were 96.9 and 94.4% AR for soil columns of the sand and the sandy loam, respectively.

Phosphonic acid was found at 63.2% AR (sand) and 54.0% AR (sandy loam) each in the top zero to 2.5 cm segments of the soil columns with no findings in lower soil column segments.

Phosphonic acid and associated radioactive residues were therefore located predominantly in the top 2.5 cm segment of soil columns while no radioactivity was found in the percolates after approximately 15 days of irrigation simulating heavy rainfall of 508 mm.
It was therefore concluded that phosphonic acid was immobile under conditions of non-aged soil column leaching performed for two contrasting soil types.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

[^{33}P]phosphorous acid
Sample ID: P33C4897
Specific Activity: 3700 MBq/mmole (100 mCi/mmole)
Radiochemical Purity: > 98%

Non-radiolabelled phosphorous acid (Batch 10007089, chemical purity of 98%) was used to dilute the radiolabelled compound.

2. Test Soils

The study was performed by using two soils sieved to a particle size ≤2 mm and as characterized in Table 7.1.4.1.2- 4.

Table 7.1.4.1.2- 4: Physico-chemical characteristics of test soils

Parameter		Results / Units	
Soil Designation		97/04[a]	97/23[a]
Geographic Location			
City		[redacted]	[redacted]
Country		UK	UK
Textural class (USDA)		Sand	Sandy loam
Sand	[63 µm – 2 mm]	89.38%	57.30%
Silt	[2 – 63 µm]	5.49%	33.81%
Clay	[< 2 µm]	5.13%	8.90%
pH (water)		6.9	5.4
pH (1 M KCl)		6.3	4.4
pH (0.01 M CaCl$_2$)		6.2	4.6
Organic Carbon		2.4%	3.0%
Organic Matter [1]		4.1%	5.2%
Cation Exchange Capacity [meq/100 g]		13.2	7.2
Water Holding Capacity (max)		61.03%	59.67%
Water Holding Capacity (0.33 bar)		16.81%	22.43%
Biomass at start of study [µg C/g soil]		647	515

USDA: United States Department of Agriculture
[1] % organic matter = % organic carbon x 1.72

B. STUDY DESIGN

1. Experimental Conditions

The test was performed with soil columns of 30 cm in height consisting of glass segments (each 5 x 5.1 cm in diameter) packed with the soil. At the bottom of each column a funnel shaped segment in addition allowed for the collection of percolates whilst supporting the soil column. Soil columns were prepared in duplicate for each of the two soils investigated. Following packing of columns, the columns were pre-wetted by submerging in aqueous calcium chloride (0.01 M) solution.

A dose equivalent to 3 mg phosphonic acid was applied to each soil column based on field rate of 15 kg/ha and the cross sectional area of each column of 20.43 cm². For preparation of the aqueous application solution the radiolabelled material was diluted with non-labelled material at a ratio of 1:9 with deionised water.

Following application, soil columns were irrigated drop wise with aqueous calcium chloride (0.01 M) solution at a flow rate of 2.9 to 4.0 mL/h to simulate rainfall equivalent of 508 mm of 'rainfall', equivalent to a total volume of 1040 mL for each column. The irrigation phase was performed at a temperature of 20 ± 1 °C for approximately 15 days.

2. Sampling

During the irrigation phase percolates were collected at a daily basis and the volume of each percolate was recorded. At the end of the irrigation phase the soil columns were allowed to stand and drain. Following draining, the soil columns were separated into seven sections, i.e. six soil segments and including the sand section used to support the soil column as section 7.

3. Analytical Procedures

Volatile radioactivity was not collected due to the nature of the ^{33}P-radio-labelled test material. A formation of volatile components was therefore not anticipated.

The soil segments resulting from separation of the columns were extracted with aqueous ammonia buffer and/or up to three times with tartaric acid and ultra-sonication at ambient temperature (sand soil) and additionally by Soxhlet extraction as alternative to ultra-sonication for the sandy loam soil. The extent of extraction procedures for each segment was dependent on the total radioactivity extracted and detected after combustion.

The extracted soils were dried, homogenized and suspended in water and scintillation fluid. The non-extractable residues were then determined by LSC. Organic matter fractionation into fulvic acid, humic acid and humins was performed with post-extraction residues from the top 2.5 cm segment of one column of each soil.

Radioactivity in leachates and extracts was determined by liquid scintillation counting (LSC). After concentration the extracts were analysed by HPLC/^{33}P-radio-detection. The identity of phosphonic acid was confirmed by gas chromatography (GC) after derivatization with diazomethane. Due to the low radioactivity determined for lower soil column segments, only soil extracts of the first two column segments (i.e. zero to 2.5 cm and 2.5 to 5 cm) were analysed.

II. RESULTS AND DISCUSSION

A. DATA

The data representing the results of non-aged column leaching of phosphonic acid in a sand and a sandy loam soil were summarized in Table 7.1.4.1.2- 5 and Table 7.1.4.1.2- 6.

Table 7.1.4.1.2- 5: Leaching of non-aged [^{33}P]phosphonic acid in sand soil Fengate Farm

Component		Segment						
		1 0-2.5 cm	2 2.5-5 cm	3 5-10 cm	4 10-15 cm	5 15-20 cm	6 20-25 cm	7 25-30 cm
Phosphonic acid	Mean	63.2	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	±1.0	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
Unknown 1 (RRT = 0.65 - 0.83)	Mean	n.d.	6.8	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	n.d.	±1.8	n.a.	n.a.	n.a.	n.a.	n.a.
Unknown 2 (RRT = 1.41 - 1.57)	Mean	n.d.	2.2	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	n.d.	±1.4	n.a.	n.a.	n.a.	n.a.	n.a.
Total extractable residues from soil	Mean	62.7	7.9	0.03	0.07	n.d.	n.d.	n.d.
	SD	±1.5	±2.1	±0.0	±0.1	n.d.	n.d.	n.d.
Non-extractable residues in soil	Mean	20.7	5.5	0.03	0.05	0.00	0.00	0.00
	SD	±3.1	±1.7	±0.0	±0.1	±0.0	±0.0	±0.0
Total recovered radioactivity in soil	Mean	83.4	13.4	0.05	0.11	0.00	0.00	0.00
	SD	±4.6	±3.8	±0.0	±0.1	±0.0	±0.0	±0.0
Total radioactivity in percolates	Mean				0.00			
	SD				±0.00			
Total recovered radioactivity	Mean				96.9			
	SD				±0.9			

n.d.: not detected; n.a.: not analysed; Mean values of two replicates; SD = standard deviation
All values expressed as percentage of total applied radioactivity

Table 7.1.4.1.2- 6: Leaching of non-aged [33P]phosphonic acid in sandy loam soil [redacted]

Component		Segment						
		1 0-2.5 cm	2 2.5-5 cm	3 5-10 cm	4 10-15 cm	5 15-20 cm	6 20-25 cm	7 25-30 cm
Phosphonic acid	Mean	54.0	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	±0.8	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
Unknown 1 (RRT = 0.65 - 0.83)	Mean	4.0	2.8	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	±0.0	±0.1	n.a.	n.a.	n.a.	n.a.	n.a.
Unknown 2 (RRT = 1.41 - 1.57)	Mean	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
	SD	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
Total extractable residues from soil	Mean	57.9	2.8	0.00	0.07	n.d.	n.d.	n.d.
	SD	±0.8	±0.1	±0.0	±0.1	n.d.	n.d.	n.d.
Non-extractable residues in soil	Mean	30.8	2.9	0.01	0.00	0.00	0.00	0.00
	SD	±1.4	±0.2	±0.0	±0.0	±0.0	±0.0	±0.0
Total recovered radioactivity in soil	Mean	88.7	5.7	0.01	0.00	0.00	0.00	0.00
	SD	±2.1	±0.1	±0.0	±0.0	±0.0	±0.0	±0.0
Total radioactivity in percolates	Mean				0.00			
	SD				±0.0			
Total recovered radioactivity	Mean				94.4			
	SD				±2.2			

n.d.: not detected; n.a.: not analysed; Mean values of two replicates; SD = standard deviation
All values expressed as percentage of total applied radioactivity

B. MATERIAL BALANCE

Mean material balances of radioactivity of the soil columns including the percolates were 96.9% AR for the sand and 94.4% AR for the sandy loam.

C. RESIDUES IN PERCOLATES

No radioactive residues were detected in the percolates of the soil columns.

D. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Values of extractable radioactivity in the top segment (0 to 2.5 cm) of soil columns were 62.7% AR for the sand and 57.9% AR for the sandy loam soil. For Segment 2 (2.5 to 5 cm) extractable residues were 7.9 and 2.8% AR for the sand and the sandy loam, respectively. Extractable residues were below 0.1% AR for any of the other soil column segments.

Non-extractable radioactivity in the top segment (0 to 2.5 cm) of soil columns was 20.7% AR for the sand and 30.8% AR for the sandy loam soil. For Segment 2 (2.5 to 5 cm) extractable residues were 5.5 and 2.9% AR for the sand and the sandy loam, respectively. Non-extractable residues were at or below 0.1% AR for any of the other soil column segments.

Non-extractable residues of the top soil column segment were subject to organic matter fractionation to result in values of 13.0, 8.0 and 3.0% AR for humic acids, fulvic acids and humins fractions of the sand soil, respectively. The corresponding values were 13.0, 14.0 and 5.0% AR for the sandy loam, respectively.

E. VOLATILES

Volatile radioactivity was not collected due to the nature of the ^{33}P-radio-labelled test material. A formation of volatile components was therefore not anticipated.

F. TRANSFORMATION OF TEST MATERIAL

Phosphonic acid as recovered by extraction of soil was observed in the top segment of columns at 63.2 and 54.0% AR for the sand and the sandy loam soil, respectively. Phosphonic acid was not detected in the other soil column segments.
Two unknown components were observed each in soil extracts of the second segment of the columns while none of the components exceeded 6.8% AR.

III. CONCLUSIONS

Phosphonic acid and associated radioactive residues were found located predominantly in the top 2.5 cm segment of soil columns while no radioactivity was found in the percolates after approximately 15 days of irrigation simulating heavy rainfall of 508 mm.
It was therefore concluded that phosphonic acid immobile under conditions of non-aged soil column leaching performed for two contrasting soil types.

CA 7.1.4.2 Lysimeter studies

This data requirement had been addressed under Point 7.1.3.3.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

The evaluation revealed that the potential for mobility of fosetyl-aluminium residues to ground water can be adequately assessed by the simulation of vulnerable scenarios representative for the EU along with the specific input parameters of the active substance under assessment. The simulations are able to cover a range of worse cases rather than to be limited to soil and climatic conditions reflected by lysimeter studies.

Separate lysimeter studies with fosetyl-aluminium are therefore regarded as not necessary.

CA 7.1.4.3 Field leaching studies

This data requirement had been addressed under Point 7.1.3.3.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

The evaluation revealed that the potential for mobility of fosetyl-aluminium residues to ground water can be adequately assessed by the simulation of vulnerable scenarios representative for the EU along with the specific input parameters of the active substance under assessment. The simulations are able to cover a range of worse cases rather than to be limited to soil and climatic conditions reflected by field leaching studies.

Separate field leaching studies with fosetyl-aluminium are therefore regarded as not necessary.

CA 7.2 Fate and behaviour in water and sediment

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

CA 7.2.1.1 Hydrolytic degradation

Report:	KCA 7.2.1.1/01 [redacted]; [redacted]; [redacted]; 1981; M-159693-01-1
Title:	Fosetyl-Al (Aluminium tris-O-ethylphosphonate): Hydrolysis study
Report No.:	R000987
Document No.:	M-159693-01-1
Guideline(s):	USEPA Federal Register, Vol. 43, #132, 1978
Guideline deviation(s):	none
GLP/GEP:	**no**

Report:	KCA 7.2.1.1/02 [redacted]; 2001; M-203000-01-1
Title:	Hydrolysis under laboratory conditions at pH 4, 7 and 9 Fosetyl-aluminium
Report No.:	C012596
Document No.:	M-203000-01-1
Guideline(s):	European Union Directive 91/414/EEC as amended by European Commission Directive 95/36/EC and OECD Guideline for Testing of Chemicals 111: Hydrolysis as a function of pH; Equivalent to US EPA OPPTS Guideline No. 835.2110
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.2.1.1/03 [redacted]; 1997; M-179049-01-1
Title:	Hydrolysis of phosphorous acid at pH 4, 5, 7 and 9
Report No.:	R009302
Document No.:	M-179049-01-1
Guideline(s):	EU (=EEC): C7; USEPA (=EPA): N, 161-1
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.2.1.1/04 [redacted]; [redacted]; [redacted]; 2000; M-189210-01-1
Title:	Phosphorous acid - Oxidation at pH 4, 7 and 9
Report No.:	R014225
Document No.:	M-189210-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

The hydrolysis of fosetyl-aluminium (fosetyl-Al) was investigated in:

- various non-buffered, non-sterile aqueous solutions at pH ranging from 1 to 13 following application of non-labeled fosetyl-Al at two test concentrations (10 and 200 mg/L) and incubation at 22 and 70 °C (KCA 7.2.1.1/01);
- sterile aqueous buffers at pH 4, 7 and 9 following application of non-labeled active substance and incubation at 50 °C (KCA 7.2.1.1/02).

In addition, the hydrolysis of phosphonic acid was investigated in:

- sterile aqueous buffers at pH 4, 5, 7 and 9 following application of non-labeled test substance and incubation at 25 °C (KCA 7.2.1.1/03);
- sterile aqueous buffers at pH 4, 7 and 9 following application of non-labeled test substance and incubation at approximately 22 °C (KCA 7.2.1.1/04).

The data requirement was addressed under Points 2.9.1 and 7.2.1.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The test designs of studies KCA 7.2.1.1/01 to KCA 7.2.1.1/04 are in line with actual designs in sterile aqueous buffer hydrolysis testing.
In summary this allows for the conclusion that the studies are all consistent with no major deviation from designs according to OECD 111.

The evaluation revealed that fosetyl-Al and its metabolite phosphonic acid were stable to abiotic hydrolysis under the conditions of the test and within the pH relevant for environmental conditions (pH 5 to 9). No half-life was therefore determined for the various values of pH investigated with no hydrolytic pathway proposed.

It is concluded that abiotic hydrolysis is an insignificant process for the elimination of fosetyl-Al or its metabolite phosphonic acid from the natural aquatic environment.
For the active substance fosetyl-Al this is true, in particular, when comparing the result of abiotic sterile hydrolysis with the results of tests in non-sterile natural water systems.

Study summaries of existing studies and publications on hydrolytic degradation of the active substance and metabolites, i.e. phosphonic acid:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.2.1.1/01 [redacted]; [redacted]; [redacted]; 1981; M-159693-01-1
Title:	Fosetyl-Al (Aluminium-tris-O-ethylphosphonate): Hydrolysis study
Report No.:	R000987
Document No.:	M-159693-01-1
Guideline(s):	US EPA Federal Register, Vol. 43, #132, 1978
Guideline deviation(s):	none
GLP/GEP:	no

Executive Summary
The rate of hydrolysis of fosetyl-Al was investigated in aqueous solutions at pH 1, 3, 5, 6, 8, 9 and 13 in the dark at 22 and 70 °C at a nominal test concentration of 200 mg/L.
Another analytical series was performed at pH 3, 6 and 9 and at a nominal test concentration of 10 mg/L. Investigations at pH 1 and 13 and 70 °C were performed for 48 hours, while the other tests were performed for one month (i.e. 33 days) in maximum.

Fosetyl-Al was found to be stable under conditions of aqueous buffer hydrolysis of pH 5, 6, 8 and 9 following 33 days of incubation in maximum at 70 or 22 °C.

Fosetyl-Al was degraded hydrolytically under conditions not representative for the environment in terms of pH and temperature.

The study results were consistent with other data available on the behaviour under conditions of abiotic hydrolysis testing in sterile aqueous buffer.

Being overall scientifically valid, the study was replaced by additional data in line with actual requirements in testing of hydrolysis in sterile aqueous buffer according to OECD 111.
The study was therefore regarded as supplemental information.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Fosetyl-Al	
Sample ID:	DA-67
Chemical Purity:	99%

2. Test Solutions

Aqueous test solutions of pH 1.2 and 13 consisted of aqueous 0.1 N sulfuric acid and 0.1 N sodium hydroxide, respectively. Test solutions of pH 3 to 6 were prepared using citrate buffer, while solutions at pH 8 and 9 consisted of borate buffers.

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in screw-capped glass flasks. The nominal test concentration of fosetyl-Al was 200 mg/L at pH 1.2, 3, 5, 6, 8, 9 and 13. The samples were incubated in the dark at 70 ± 1 °C or at 22 ± 3 °C.
Another analytical series was performed at pH 3, 6 and 9 and at a nominal test concentration of 10 mg/L.
Investigations at pH 1.2 and 13 and 70 °C were performed for 48 hours, while the other tests were performed for one month (i.e. 33 days) in maximum.

2. Sampling

At a nominal test concentration of 200 mg/L, samples of pH 1.2 and 13 were removed for analysis after 0, 2, 4, 6, 8, 24 and 48 hours of incubation at 70 °C.
At a nominal test concentration of 10 mg/L, samples of pH 3 were removed for analysis after 0, 2, 4, 8, 16 and 32 days of incubation at 70 °C.
At a nominal test concentration of 10 mg/L, samples of pH 6 were removed for analysis after 0, 7, 14 and 28 days of incubation at 70 °C.
At a nominal test concentration of 10 mg/L, samples of pH 9 were removed for analysis after 0, 8, 16 and 32 days of incubation at 70 °C.

At a nominal test concentration of 200 mg/L, samples of pH 1.2 and 13 were removed for analysis after 0, 1, 2, 7, 14 21 and 30 days of incubation at 22 °C.
At a nominal test concentration of 200 mg/L, samples of pH 3, 5, 6, 8 and 9 were removed for analysis after 0, 8, 20 and 33 days of incubation at 22 or 70 °C. An additional sampling was made by day 5 for the incubation at 70 °C.
At a nominal test concentration of 10 mg/L, samples of pH 3 and 9 were removed for analysis after 0, 8, 16 and 32 days of incubation at 22 °C.
At a nominal test concentration of 10 mg/L, samples of pH 6 were removed for analysis after 0, 7, 14 and 28 days of incubation at 22 °C.

3. Analytical Procedures

Following removal, the pH was determined.

Analysis for fosetyl-Al and phosphonic acid was by gas chromatography (GC) following derivatization and detection of the derivatives with a phosphorus specific flame photometric detector.

II. RESULTS AND DISCUSSION

A. DATA

Recoveries of fosetyl-Al following incubation in test solutions of pH 1.2, 3, 5, 6, 8, 9 and 13 at 70 °C or 22 °C for 33 days in maximum were summarized in Table 7.2.1.1- 1 to Table 7.2.1.1- 6.

Table 7.2.1.1- 1: Recovery of fosetyl-Al after incubation in aqueous test solutions at pH 1.2 and 13 at 70 °C in the dark

pH	Incubation time (hours)						
	0	**2**	**4**	**6**	**8**	**24**	**48**
1.2	106	82	65	50	38.5	<2	<2
13	103.5	93.5	79.5	73	63	19.5	<2

Values given as percentage of nominal initial concentration of 200 mg/L

Table 7.2.1.1- 2: Recovery of fosetyl-Al after incubation at 70 °C in aqueous buffer solutions at pH 3, 5, 6, 8 and 9 in the dark

pH	Incubation time (days)				
	0	**5**	**8**	**20**	**33**
3	91.5	59	38.5	5.5	<2
5	98	96	91	95.5	81.5
6	100.5	101	94	106	101.5
8	108	106	102	116	107
9	108	103.5	100.5	111.5	102

Values given as percentage of nominal initial concentration of 200 mg/L

Table 7.2.1.1- 3: Recovery of fosetyl-Al after incubation at 22 °C in aqueous test solutions at pH 1.2 and 13 in the dark

pH	Incubation time (days)						
	0	1	2	7	14	21	30
1.2	106	97.5	100.5	85	69.5	55	43.5
13	103.5	101.5	93.5	72	49.5	33	23

All values given as percentage of nominal initial concentration of 200 mg/L

Table 7.2.1.1- 4: Recovery of fosetyl-Al after incubation at 22 °C in aqueous buffer solutions at pH 3, 5, 6, 8 and 9 in the dark

pH	Incubation time (days)			
	0	**8**	**20**	**33**
3	103.5	97.5	104	101
5	96.5	87.5	89	84.5
6	98.5	93	99.5	94
8	103.5	99	108	106
9	105	98.5	106.5	104.5

Values given as percentage of nominal initial concentration of 200 mg/L

Table 7.2.1.1- 5: Recovery of fosetyl-Al after incubation at 70 °C in aqueous buffer solutions at pH 3, 6 and 9 in the dark

pH	Incubation time (days)					
	0	**2**	**4**	**8**	**16**	**32**
3	100	59	46	12.5	<2	<2
	Incubation time (days)					
6	0	7	14	28		
	113	104	103	100		
	Incubation time (days)					
9	0	8	16	32		
	100	94.5	107	103		

Values given as percentage of nominal initial concentration of 10 mg/L

Table 7.2.1.1- 6: Recovery of fosetyl-Al after incubation at 22 °C in aqueous buffer solutions at pH 3, 6 and 9 in the dark

pH	Incubation time (days)			
	0	**8**	**16**	**32**
3	100	42.5	12	<2
	Incubation time (days)			
6	0	7	14	28
	113	112	101	92
	Incubation time (days)			
9	0	8	16	32
	100	85	110	125

Values given as percentage of nominal initial concentration of 10 mg/L

B. MATERIAL BALANCE

Total material balances of fosetyl-Al including recoveries of phosphonic acid at 70 °C and 200 mg/L:
Values for material balances for a pH of 1.2 ranged from 71 to 106%.
Material balances for a pH of 3 ranged from 102 to 110%.
Material balances for a pH of 5 ranged from 88.5 to 98%.
Material balances for a pH of 6 ranged from 94 to 106%.
Material balances for a pH of 8 ranged from 106 to 116%.
Material balances for a pH of 9 ranged from 102 to 111.5%.
Material balances for a pH of 13 ranged from 92.5 to 103.5%.

Total material balances of fosetyl-Al including recoveries of phosphonic acid at 22 °C and 200 mg/L:
Values for material balances for a pH of 1.2 ranged from 92 to 107.5%.
Material balances for a pH of 3 ranged from 97.5 to 108%.
Material balances for a pH of 5 ranged from 87.5 to 96.5%.
Material balances for a pH of 6 ranged from 93 to 101%.
Material balances for a pH of 8 ranged from 99 to 108%.
Material balances for a pH of 9 ranged from 98.5 to 106.5%.
Material balances for a pH of 13 ranged from 86.5 to 105%.

Total material balances of fosetyl-Al including recoveries of phosphonic acid at 70 °C and 10 mg/L:
Material balances for a pH of 3 ranged from 78.5 to 112%.
Material balances for a pH of 6 ranged from 100 to 113%.
Material balances for a pH of 9 ranged from 98.5 to 126%.

Total material balances of fosetyl-Al including recoveries of phosphonic acid at 22 °C and 10 mg/L:
Material balances for a pH of 3 ranged from 95.5 to 112%.
Material balances for a pH of 6 ranged from 92 to 113%.
Material balances for a pH of 9 ranged from 85 to 125%.

Apart from few exceptions at 70 °C and at a pH of 1.2 and 3, material balances were thus mostly in an acceptable range.

C. TRANSFORMATION OF TEST SUBSTANCE

Fosetyl-Al was found to be stable under conditions of aqueous buffer hydrolysis of pH 5, 6, 8 and 9 following 33 days of incubation in maximum at 70 or 22 °C.

Fosetyl-Al was found to be hydrolysed in aqueous test solutions of pH 1.2 and 13 following 24 hours (pH 1.2) or 48 hours (pH 13) of incubation in maximum at 70 °C.
Fosetyl-Al was also found to be hydrolysed in aqueous test solutions of pH 1.2 and 13 following 30 days of incubation in maximum at 22 °C.

Gas chromatography after derivatization showed the presence of phosphonic acid as major transformation product besides recovered fosetyl.

III. CONCLUSIONS

Fosetyl-Al was found to be stable under conditions of aqueous buffer hydrolysis of pH 5, 6, 8 and 9 following 33 days of incubation in maximum at 70 or 22 °C.
Fosetyl-Al was degraded hydrolytically under conditions not representative for the environment in terms of pH and temperature.

The study results were consistent with other data available on the behaviour under conditions of abiotic hydrolysis testing in sterile aqueous buffer.

Being overall scientifically valid, the study was replaced by additional data in line with actual requirements in testing of hydrolysis in sterile aqueous buffer according to OECD 111.
The study was therefore regarded as supplemental information.

Report:	KCA 7.2.1.1/02 [redacted].; 2001; M-203000-01-1
Title:	Fosetyl-aluminium Hydrolysis under laboratory conditions at pH 4, 7 and 9
Report No.:	C010596
Document No.:	M-203000-01-1
Guideline(s):	European Union Directive 91/414/EEC as amended by European Commission Directive 95/36/EC and OECD Guideline for Testing of Chemicals 111, Hydrolysis as a function of pH; Equivalent to US EPA OPPTS Guideline No. 835.2110
Guideline deviation(s):	none
GLP/GEP:	yes

Executive Summary

The rate of hydrolysis of fosetyl-Al was investigated in sterile aqueous buffer at pH 4, 7 and 9 in the dark at 50 °C for 5 days in maximum. The nominal test concentration of fosetyl-Al was 100 mg/L.

Fosetyl-Al was found to be stable under conditions of sterile aqueous buffer hydrolysis at pH 4, 7 and 9 following 5 days of incubation at 50 °C.

The design of the study was in line with actual requirements in testing of hydrolysis in sterile aqueous buffer according to OECD 111.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Fosetyl-Al
Sample ID: 12/1080
Chemical Purity: 97.6%

2. Test Buffer

Sterile aqueous buffer solutions (0.05 M) were prepared by adjusting aqueous solutions of potassium biphthalate to pH 4 and of boric acid to a pH of 7 and 9, respectively.

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in borosilicate glass vials each filled with approx. 30 mL of the corresponding solution of fosetyl-Al in sterile aqueous buffer. The nominal test concentration of fosetyl-Al was 100 mg/L. The test vials were incubated in the dark at 50 ± 1 °C for 5 days.

2. Sampling

Single replicates were removed for analysis after 0, 2, and 5 days of incubation.

3. Analytical Procedures

Following removal, the pH was determined from a sub-sample.

Analysis for fosetyl-Al was by direct injection into an ion chromatographic system and conductimetric detection. The limit of quantification (LOQ) was 3 mg/L each for fosetyl-Al and phosphonic acid. The LOQ for phosphoric acid was 8 mg/L.

II. RESULTS AND DISCUSSION

Results of pH determinations in aqueous buffers indicated constant values during incubation.
Recoveries of phosphonate following incubation in sterile aqueous buffer of pH 4, 7 and 9 at 50 °C for five days in maximum were summarized in Table 7.2.1.1- 7.

A. DATA

Table 7.2.1.1- 7: Recovery of fosetyl-Al after incubation in sterile aqueous buffer solutions at pH 4, 7 and 9 at 50 °C in the dark

pH	Incubation time (days)					
	0		2		5	
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
4	82.4	100	83.7	101.6	83.7	101.6
7	100.3	100	102.1	101.8	102.0	101.7
9	88.5	100	90.0	101.7	90.9	102.7

B. MATERIAL BALANCE

Values in terms of applied fosetyl-Al recovered were from 100 to 102.7% for the range of pH tested and the total incubation period.

C. TRANSFORMATION OF TEST SUBSTANCE

Fosetyl-Al was found to be stable under conditions of sterile aqueous buffer hydrolysis of pH 4, 7 and 9 following 5 days of incubation at 50 °C.

Ion chromatography of control samples showed the absence of fosetyl-Al or its potential transformation products.

III. CONCLUSIONS

Fosetyl-Al was found to be hydrolytically stable under the conditions of the test.

The design of the study was in line with actual requirements in testing of hydrolysis in sterile aqueous buffer according to OECD 111.

Report:	KCA 7.2.1.1/03 [redacted], 1997, M-179049-01-1
Title:	Hydrolysis of phosphorous acid at pH 4, 5, 7 and 9
Report No.:	R009302
Document No.:	M-179049-01-1
Guideline(s):	EU (=EEC); US-EPA (=FIFRA): 161-1
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The rate of hydrolysis of phosphonic acid was investigated in sterile aqueous buffer at pH 4, 5, 7 and 9 in the dark at 25 °C for 31 days in maximum. The nominal test concentration of phosphonic acid was 250 mg/L.

Phosphonic acid was found to be stable under conditions of sterile aqueous buffer hydrolysis at pH 4, 5, 7 and 9 following 31 days of incubation at 25 °C.

The design of the study was in line with actual requirements in testing of hydrolysis in sterile aqueous buffer according to OECD 111.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Phosphonic acid (non-labelled)
Sample ID: Lot No. 490361
Chemical Purity: 99.2 %

2. Test Buffer

Sterile aqueous buffer solutions (0.1 M) were prepared by adjusting aqueous solutions of citrate to pH 4, acetate to pH 5, TRIS to pH 7 and of borate to pH 9, respectively.

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in sterilised 7 mL amber glass vials each filled with approx. 5 mL of the corresponding solution of phosphonic acid in sterile aqueous buffer. The nominal test concentration was 200 mg/L. The test vials were incubated at 25 ± 1 °C in the dark for 31 days in maximum.
The actual application rate was determined by averaging the results of the Day zero analyses.

2. Sampling

Duplicate samples were removed for analysis after 0, 3, 7, 12, 20 and 31 days of incubation. Sterility was checked for all samples of day zero and for samples after 31 days of incubation.

3. Analytical Procedures

Following removal, the pH was determined. Sterility was checked by culturing aliquots of the test solutions on agar plates in an incubator at 35 °C for 48 hours. The cultures were evaluated for microbial growth.

Analysis for phosphonic acid and its potential transformation product phosphoric acid was by anion exchange HPLC and by comparison with authentic reference material.

The identity of phosphonic acid was confirmed by nuclear magnetic resonance (NMR) using a ^{31}Phosphorus probe each for a replicate of each pH after 31 days of incubation.

II. RESULT AND DISCUSSION

Results of pH determinations in aqueous buffers indicated constant values during incubation.
Recoveries of phosphonate following incubation in sterile aqueous buffer of pH 4, 5, 7 and 9 at 25°C for 31 days in maximum were summarized in Table 7.2.1.1- 8.

A. DATA

Table 7.2.1.1- 8: Recovery of phosphonic acid after incubation in sterile aqueous buffer solutions at pH 4, 5, 7 and 9 at 25 °C in the dark

pH	Compound		Incubation time (days)					
			0	3	7	12	20	31
4	Phosphonic acid	Mean	94.9	92.4	94.2	91.8	98.6	99.2
		SD	±0.2	±0.0	±3.2	±2.1	±0.3	±0.9
	Phosphoric acid	Mean	2.1	2.9	3.8	5.5	4.4	3.1
		SD	±0.2	±0.2	±0.4	±0.2	±0.6	±0.4
	Total	Mean	97.0	95.3	98.0	97.3	103.0	102.3
		SD	±0.0	±0.1	±2.8	±2.3	±0.4	±1.3
5	Phosphonic acid	Mean	94.7	94.5	99.9	93.2	98.3	98.3
		SD	±0.0	±0.2	±2.9	±1.2	±0.5	±1.3
	Phosphoric acid	Mean	0.0	2.6	0.0	0.0	0.0	1.1
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±1.1
	Total	Mean	94.7	97.1	99.9	93.2	98.3	99.4
		SD	±0.0	±0.2	±2.9	±1.2	±0.5	±0.2
7	Phosphonic acid	Mean	99.9	95.0	99.2	99.4	100.6	102.2
		SD	±1.0	±0.7	±0.7	±0.9	±1.2	±0.5
	Phosphoric acid	Mean	2.3	1.4	1.4	2.8	3.5	3.1
		SD	±0.0	±1.4	±1.4	±2.8	±0.0	±0.4
	Total	Mean	102.2	96.4	100.6	102.2	104.1	105.3
		SD	±1.0	±2.1	±0.6	±3.7	±1.2	±0.1
9	Phosphonic acid	Mean	95.7	92.0	94.8	93.4	98.5	97.1
		SD	±0.9	±0.5	±3.7	±1.4	±0.5	±0.0
	Phosphoric acid	Mean	1.7	0.0	0.0	0.0	1.4	1.2
		SD	±0.2	±0.0	±0.0	±0.0	±1.4	±1.2
	Total	Mean	97.4	92.0	94.8	93.4	99.8	98.3
		SD	±0.7	±0.5	±3.7	±1.4	±1.8	±1.2

All values given as percentage of dose applied
SD: standard deviation

B. MATERIAL BALANCE

Total material balances were 95.3 to 103.0% for pH 4, 93.2 to 99.9% for pH 5, 96.4 to 105.3% for pH 7 and 92.0 to 99.8% for pH 9.

C. TRANSFORMATION OF TEST SUBSTANCE

The recovery of phosphonic acid was from 94.9% by day zero to 99.2% after 31 days of incubation at pH 4, from 94.7% by day zero to 98.3% after 31 days of incubation at pH 5, from 99.9% by day zero to 102.2% after 31 days of incubation at pH 7 and from 95.7% by day zero to 97.1% after 31 days of incubation at pH 9.

Phosphoric acid was found at 2.1% by day zero to 3.1% after 31 days of incubation at pH 4, from 0.0% by day zero to 1.1% after 31 days of incubation at pH 5, from 2.3% by day zero to 3.1% after 31 days of incubation at pH 7 and from 1.7% by day zero to 1.2% after 31 days of incubation at pH 9. The maximum occurrence was at 5.5% after 12 days of incubation in samples of pH 4.

At all pH tested the values determined for phosphonic acid or phosphoric acid thus followed no clear trend with time indicating stability of the two compounds towards abiotic hydrolysis under the conditions of the test.

III. CONCLUSIONS

Phosphonic acid was found to be hydrolytically stable under the conditions of the test.

The design of the study was in line with actual requirements in testing of hydrolysis in sterile aqueous buffer according to OECD 111.

Report:	KCA 7.2.1.1/04 [redacted]; [redacted]; [redacted]; 2000; M-189210-01-1
Title:	Phosphorus acid: Oxidation at pH 4, 7 and 9
Report No.:	R014225
Document No.:	M-189210-01-1
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary

The potential of phosphonic acid to undergo oxidation in sterile aqueous buffer solutions at pH 4, 7 and 9 was studied under laboratory conditions at 22 °C for 30 days in maximum. The tests were performed at a test concentration of 1 g/L.

Phosphonic acid was not oxidized in sterile, aerated aqueous buffer solution of pH 4, 7 and 9 under the conditions of the test.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Analytical grade phosphonic acid was used.

2. Test Solutions

Sterile aqueous buffer solutions (0.02 M) were prepared by adjusting aqueous solutions of citric acid to pH 4, of imidazole to pH 7 and of boric acid to pH 9, respectively.

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed under flow-through conditions allowing sterilised air to pass through 125 mL glass flasks filled with 50 mL sterilised aqueous buffer solution containing phosphonic acid at a test concentration of approx. 1 g/L. The test vessels were incubated at approx. 22 °C for 30 days in maximum. Another series of samples was kept under a stream of nitrogen to serve as control.

2. Sampling

Duplicates of aerated samples were removed for analysis after 16 and 30 days of incubation. The control samples under nitrogen were removed after 30 days of incubation.

3. Analytical Procedures

After 16 days, the aerated samples were disconnected and aliquots of 2.7 mL were transferred to NMR tubes. Afterwards, the samples were re-connected and the incubation continued until 30 days.

At each sampling interval samples were analysed by ^{31}Phosphorus-NMR.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Material balances were not established.

B. FINDINGS

Values for phosphate were low to very low for all samples, i.e. phosphate was detected in a pH 4 sample after 16 days, but the value did not increase after 30 days of incubation as summarized in Table 7.2.1.1- 9. No transformation was observed for samples of pH 7 and 9.

Table 7.2.1.1- 9: Relation of phosphate versus phosphonate after incubation at 22 °C

pH	Sample		Day 16	Day 30
4	Aerated	Mean	0.7	0.6
		SD	± 0.7	± 0.6
	Nitrogen (control) [1]		0	0
7	Aerated	Mean	0	0
		SD	± 0	± 0
	Nitrogen (control) [1]		0	0
9	Aerated	Mean	0	0
		SD	± 0	± 0
	Nitrogen (control) [1]		0	0

Values expressed as percentage phosphate area per percentage phosphonate area observed in ^{31}P-NMR
SD: standard deviation
[1] Single replicate

III. CONCLUSIONS

Phosphonic acid was not oxidized in sterile, aerated aqueous buffer solution of pH 4, 7 and 9 under the conditions of the test.

CA 7.2.1.2 Direct photochemical degradation

Report:	KCA 7.2.1.2/01 [redacted],; 1981; M-227366-01-2
Title:	Fosetyl-Al: UV absorption characteristics
Report No.:	R000762
Document No.:	M-227366-01-2
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Report:	KCA 7.2.1.2/02 [redacted],; 2001; M-203005-01-1
Title:	Phosphorous acid: Aqueous photolysis
Report No.:	C012598
Document No.:	M-203005-01-1
Guideline(s):	EU (=EEC): 94/37/EC, SECT 2.9.2; SETAC: PART 1, SECT 10
Guideline deviation(s):	none
GLP/GEP:	**yes**

The potential for direct photolysis of fosetyl-aluminium (fosetyl-Al) was investigated in:

- aqueous solutions of non-labeled fosetyl-Al and the recording of the UV absorption spectra for various test concentrations (KCA 7.2.1.2/01).

The direct photolysis of metabolite phosphonic acid was investigated in:

- sterile aqueous buffer at pH 7 following application of non-labeled test substance and irradiation at 20 °C (KCA 7.2.1.2/02). Direct photolysis of phosphonic acid was also investigated under the same conditions, but the presence of iron oxide or titanium oxide as catalysts.

This data requirement was addressed under Point 2.9.2 as well as under Point 7.2.1.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The test designs of studies KCA 7.2.1.2/01 and KCA 7.2.1.2/02 are in line with actual designs in testing of direct photolysis in sterile aqueous buffer solution.
In summary this allows for the conclusion that the studies are consistent with no major deviation from designs or requirements according to OECD 316.

For the active substance fosetyl-Al the evaluation revealed that there was no potential for photolytic degradation in water due to the low extinction coefficient (Ɛ) of 1.03 mole/L to be significantly below the value of 10 mole/L at wave lengths of 290 nm and higher.

For phosphonic acid the evaluation revealed that the compound showed stability towards direct aqueous photolysis under the conditions of the test.
Photolytical degradation of phosphonic acid in water was induced in the presence of catalytic amounts of titanium oxide while iron oxide had no effect.

No photolytic half-life was therefore determined for the active substance fosetyl-Al and phosphonic acid in sterile aqueous buffer solution.

Photolytic processes are therefore rather unlikely to contribute to the elimination of fosetyl-Al or phosphonic acid from the aquatic environment.

Study summaries of existing studies and publications on photochemical degradation of the active substance and metabolites, i.e. phosphonic acid:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.2.1.2/01 [redacted]; 1981; M-227366-01-2
Title:	Fosetyl-Al: UV absorption characteristics
Report No.:	R000762
Document No.:	M-227366-01-2
Guideline(s):	none
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Executive Summary
The UV absorption characteristics of fosetyl-Al were determined between 200 and 360 nm.

The change of absorbance as a function of the concentration (5, 10, 25 and 50 g/L) of the solutions was determined at 290 nm. The molar extinction coefficient was graphically determined.

Additionally, comparative experiments were carried out in parallel on fosetyl-Na (5, 10, 25 and 50 g/L) and various inorganic aluminium salts. To investigate the contribution of impurities of fosetyl-Al, photometric examination of a solution of $FeCl_3$ was performed.

For fosetyl-Al a molar extinction coefficient of 1.03 L mol^{-1} cm^{-1} was calculated at 290 nm.
For fosetyl-sodium the value for the molar extinction coefficient at 290 nm was calculated to 0.053 L mol^{-1} cm^{-1}. The value was significantly lower than the one for fosetyl-Al. It was concluded that the higher absorption observed for fosetyl-Al was not essentially due to the phosphonate moiety.
For Al^{3+} cations the molar extinction coefficient was found to vary between 0.05 L mol^{-1} cm^{-1} and 0.30 L mol^{-1} cm^{-1}. Adsorption of Al^{3+} thus corresponded only to a small proportion of the overall value of absorption determined for fosetyl-Al.

Consequently, the light absorption of fosetyl-Al observed at 290 nm was attributed mainly to the absorption of the aluminium cation and the presence of other metal ions such as iron at trace level.
The light adsorption observed for fosetyl-sodium was assigned to a photometric reaction of the fosetyl anion itself. The value determined was significantly below the limit of 0.1 L mol^{-1} cm^{-1} adopted by the US EPA for the conduct of photo-transformation tests.
Any effect of photo-transformation on the overall elimination of fosetyl residues from the aquatic environment can thus be considered to be negligible.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

Experiments were performed with non-labelled fosetyl-Al (batch EA. 1167-1) and fosetyl-sodium (batch EA – 1124-2) dissolved in distilled water.

B. STUDY DESIGN

Aqueous solutions of fosetyl-Al were prepared at concentrations of 5, 10, 25 and 50 g/L each followed by filtration through cellulose acetate membranes to minimize micro-particles causing scattering phenomena.

Absorption spectra were continuously recorded for the range between 200 and 360 nm by a UV-spectrophotometer with reference to distilled water.

The change of absorbance as a function of the concentration of the solutions was determined at 290 nm, the latter serving as reference wavelength in EPA instructions for performance of photo-transformation studies.
The influence of counter-ions on UV absorption was investigated by comparison of solutions containing fosetyl-Al and fosetyl-sodium (5, 10, 25 and 50 g/L), respectively.

The resulting molar extinction coefficients were determined graphically.

II. RESULTS AND DISCUSSION

The results in terms of absorbance of fosetyl-Al at 290 nm were summarized in Table 7.2.1.2- 1.
Values of absorption increased towards lower wavelengths reaching a relative maximum at about 225 nm. For fosetyl-Al a molar extinction coefficient of 1.03 L mol^{-1} cm^{-1} was calculated at 290 nm.

Table 7.2.1.2- 1: Absorbance of fosetyl-Al at 290 nm for various concentrations

Concentration of fosetyl-Al (g/L)	Absorbance at 290 nm
5	0.014
10	0.028
25	0.076
50	0.146

Results of the comparative experiments with fosetyl-sodium were summarized in Table 7.2.1.2- 2.

Table 7.2.1.2- 2: Absorbance of fosetyl-sodium at 290 nm for various concentrations

Concentration of fosetyl-Na (g/L)	Absorbance at 290 nm
5	< 0.005
10	< 0.005
25	0.009
50	0.020

For fosetyl-sodium the value for the molar extinction coefficient at 290 nm was calculated to 0.053 L mol^{-1} cm^{-1}. The value was significantly lower than the one for fosetyl-Al. It was concluded that the higher absorption observed for fosetyl-Al was not essentially due to the phosphonate moiety.

For Al^{3+} cations the molar extinction coefficient was found to vary between 0.05 L mol^{-1} cm^{-1} and 0.30 L mol^{-1} cm^{-1}. Adsorption of Al^{3+} thus corresponded only to a small proportion of the overall value of absorption determined for fosetyl-Al.
The UV absorption of fosetyl-Al and that of the other aluminium salts may therefore not be associated with intrinsic characteristics of the compound but should be attributed to other secondary phenomena such as the content of heavy metals like iron. Impurities by iron were very likely the cause of UV absorption observed for fosetyl-Al.

III. CONCLUSIONS

The light absorption of fosetyl-Al observed at 290 nm was attributed mainly to the absorption of the aluminium cation and the presence of other metal ions such as iron at trace level.
The light adsorption observed for fosetyl-sodium was assigned to a photometric reaction of the fosetyl anion itself. The value determined was significantly below the limit of 0.1 L mol^{-1} cm^{-1} adopted by the US EPA for the conduct of photo-transformation tests. Consequently, an effect of photo-transformation on the overall elimination of fosetyl residues from the aquatic environment can be considered as negligible.

Report:	KCA 7.2.1.2/02 [redacted], 2001; M-203005-01-1
Title:	Phosphorous acid: Aqueous photolysis
Report No.:	C012598
Document No.:	M-203005-01-1
Guideline(s):	EU (=EEC): 94/37/EC, SECT. 2.9.2; SETAC, PART I, SECT. 10
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary
The direct photo-transformation of phosphonic acid was studied in sterile aqueous borate buffer solution of pH 7 at 20 °C for 7 days in maximum. The test was performed at a nominal test concentration of 100 mg/L.

In addition, the indirect photo-transformation of phosphonic acid was studied in the presence of photolytic catalysts, i.e. iron (III) oxide and titanium dioxide.

No direct photo-transformation was observed for phosphonic acid following irradiation in sterile aqueous buffer solution of pH 7 at 20 °C for 7 days.

No clear contribution of iron (III) oxide to the indirect photo-transformation of phosphonic acid was observed under the conditions of the test.

There was observed a clear contribution of the photo-sensitizer titanium dioxide to the indirect photo-transformation of phosphonate/phosphonic acid to phosphate/phosphoric acid under the conditions of the test.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Phosphonic acid
Sample ID: 04911DN
Chemical Purity: 96.2%

2. Test Solutions

The test was performed in sterile 0.05 M borate buffer solution of pH 7.
In order to investigate the potential influence photolytic sensitizers, portions of iron (III) oxide (2.5 mM) or titanium dioxide (2.5 mM) were added for separate irradiation series.

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in 50 mL borosilicate glass flasks filled with 50 mL of sterile aqueous buffer solution containing phosphonic acid at a nominal test solution concentration of 100 mg/L. The flasks had outer glass jackets for cooling and screw caps fitted with a quartz top window. For dark controls 30 mL borosilicate glass flasks were filled with 30 mL of the treated sterile aqueous buffer.

Samples were irradiated with a xenon light source simulating natural sunlight (Heraeus Suntest CPS) at a light intensity of 425 W/m². Light below 290 nm wave length was cut-off.
The test was performed at 20 ± 3 °C for 7 days at maximum. Dark controls were incubated at the same temperature in the dark for the same time.

2. Sampling

Duplicate samples were removed for analysis after 0, 0.25, 1, 2, 4 and 7 days of irradiation.
Samples containing iron (III) oxide in addition were removed for analysis at the same time points of incubation.
Samples containing titanium dioxide were removed for analysis after 0, 1, 2, 4, 6, 8 and 16 (irradiated) or 25 (dark) hours after treatment (HAT).
Sterility tests were performed at the first and the last sampling interval.

3. Analytical Procedures

Following removal of undissolved catalyst by centrifugation, where applicable, sub-samples were subject to analysis by ion-chromatography followed by conductometric detection. The limit of quantification (LOQ) for phosphonic acid was 3 mg/L. The limit of quantification for phosphoric acid was 8 mg/L.

II. RESULTS AND DISCUSSION

A. DATA

The results of photo-transformation tests of phosphoric acid in sterile aqueous borate buffer solution of pH 7 were summarized in Table 7.2.1.2- 3 for tests in the absence of photo-sensitizing agents. The data demonstrating the potential for influence on photo-transformation by photosensitizers was summarized in Table 7.2.1.2- 4 for iron (III) oxide and in Table 7.2.1.2- 5 for titanium dioxide.

Table 7.2.1.2- 3: Photo-transformation of phosphonic acid at 20 °C in sterile aqueous buffer of pH 7

			Incubation time (days)					
		Replicate	0 [1]	0.25	1	2	4	7
Irradiated	Phosphonic acid	Mean	100.0	101.7	102.8	103.7	104.3	92.2
		SD	±0.5	±0.5	±0.6	±1.1	±0.4	±1.4
Dark	Phosphonic acid	Mean	100.0	100.5	100.8	102.7	103.5	86.7
		SD	±0.5	±0.1	±1.1	±1.3	±1.1	±9.9

[1] Day zero samples were taken as applied dose (100%) for both irradiated and dark samples;
All values given as percentages of applied test concentration by day zero

Table 7.2.1.2- 4: Photo-transformation of phosphonic acid at 20 °C in sterile aqueous buffer of pH 7 in the presence of iron (III) oxide

			Incubation time (days)					
		Replicate	0 [1]	0.25	1	2	4	7
Irradiated	Phosphonic acid	Mean	100.0	86.9	67.0	85.9	86.0	92.1
		SD	±1.8	±10.1	±5.1	±0.4	±1.1	±7.5
Dark	Phosphonic acid	Mean	100.0	85.3	76.9	86.8	88.0	78.5
		SD	±1.8	±8.4	±2.7	±1.5	±1.4	±2.0

[1] Day zero samples were taken as applied dose (100%) for both irradiated and dark samples;
All values given as percentages of applied test concentration by day zero

Table 7.2.1.2- 5: Photo-transformation of phosphonic acid at 20 °C in sterile aqueous buffer of pH 7 in the presence of titanium dioxide

			Incubation time (hours)						
		Replicate	0 [1]	1	2	4	6	8	16 / 25 [2]
Irradiated	Phosphonic acid	Mean	100.0	100.8	96.8	89.7	78.5	72.1	39.3
		SD	±2.8	±3.0	±3.9	±2.7	±2.5	±2.2	±2.2
Dark	Phosphonic acid	Mean	100.0	104.5	109.6	104.0	94.7	100.0	96.6
		SD	±2.8	±1.5	±1.4	±0.1	±2.0	±1.7	±2.9
Irradiated	Phosphoric acid	Mean	n.d.	8.3	11.3	20.4	26.0	35.1	66.7
		SD	n.d.	±0.0	±0.1	±0.4	±1.7	±2.2	±4.3
Dark	Phosphoric acid	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected
[1] Day zero samples were taken as applied dose (100%) for both irradiated and dark samples; All values given as percentages of applied test concentration by day zero
[2] Incubation was 16 hours for irradiated and 25 days for dark controls

B. TRANSFORMATION OF TEST SUBSTANCE

For samples irradiated in the absence of photo-sensitizers, recoveries of phosphonic acid were 92.2 to 104.3% in the course of the study. Recoveries for dark controls ranged from 86.7 to 103.5% during the same time of incubation. The potential photo-transformation product phosphoric acid was not detected in irradiated samples or in dark controls.
No photo-transformation was therefore observed for phosphonic acid under the conditions of the test.

For samples irradiated in the presence of iron (III) oxide as potential photo-sensitizer, recoveries of phosphonic acid were 67.0 to 100.0% in the course of the study. Recoveries for dark controls ranged from 76.9 to 100.0% during the same time of incubation. Overall, recoveries were more scattering with no clear trend for a decrease of values of phosphonic acid in the course of the test. The potential photo-transformation product phosphoric acid was not detected in irradiated samples or in dark controls.
No clear contribution of iron (III) oxide to the photo-transformation of phosphonic acid was therefore observed under the conditions of the test.

For samples irradiated in the presence of titanium dioxide as potential photo-sensitizer, recoveries of phosphonic acid decreased from 100.0% by day zero to 39.3% after 0.67 days (16 hours). Recoveries for dark controls ranged from 94.7 to 109.6% after 1.04 days (25 hours) of incubation. Recoveries for irradiated samples in the presence of titanium dioxide thus showed a clear trend for decrease of values of phosphonic acid in the course of the test. In parallel, the potential photo-transformation product phosphoric acid was detected at 66.7% in irradiated samples after 0.67 days (16 hours) of irradiation.
There was observed a clear contribution of the photo-sensitizer titanium dioxide to the photo-transformation of phosphonate/phosphonic acid to phosphate/phosphoric acid under the conditions of the test.

The DT_{50}- and DT_{90}-values for photolytic transformation of phosphonic acid in the presence of titanium dioxide were estimated to 11.6 and 38.5 hours, respectively.

III. CONCLUSIONS

No direct photo-transformation was observed for phosphonic acid following irradiation in sterile aqueous buffer solution of pH 7 at 20 °C for 7 days.

No clear contribution of iron (III) oxide to the indirect photo-transformation of phosphonic acid was observed under the conditions of the test.

There was observed a clear contribution of the photo-sensitizer titanium dioxide to the indirect photo-transformation of phosphonate/phosphonic acid to phosphate/phosphoric acid under the conditions of the test.

CA 7.2.1.3 Indirect photochemical degradation

Being a new potential data requirement no data were submitted in the existing Dossier and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

In the following data are submitted from a test that had been performed in order to fulfil data requirements outside the EU, i.e. Japan. The new information is more detailed below.

Report:	KCA 7.2.1.3/01 [redacted],; 2005; M-255973-01-1
Title:	[2-14C]Fosetyl-aluminium (AE F053616): Phototransformation in natural water and destilled water
Report No.:	MEF-05/178
Document No.:	M-255973-01-1
Guideline(s):	Japanese MAFF, 12 Nousan 8147, Annex 2-6-2
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The photolysis of 2-^{14}C-labeled fosetyl-aluminium (fosetyl-Al) was investigated in sterile natural water (pH 8.1) and pure water at a test concentration of 5 mg a.s./L. Samples were continuously irradiated at 25 ± 2 °C with artificial sunlight (<290 nm cut-off filter) for 7 experimental days (168 experimental hours) equivalent to 74 environmental days when considering the light intensity at Tokio, Japan, at sea level in June.
The recovered radioactivity was above 94.0% AR for irradiated samples. Values of ^{14}C-fosetyl-Al decreased from 100.8% of AR (101.3%) at time zero to 50.3% (30.2%) at the end of irradiation in natural and pure water, respectively. Three photo-transformation products ethyl phosphate, ethanol and acetic acid were observed while no degradation occurred in dark controls.

The photolytic transformation of fosetyl-Al in sterile natural and in pure water was found to be negligible to result in mean photolytic half-lives of 77 and 35 environmental days, respectively, when being referenced to natural light conditions of Tokio at sea level in June.

Direct (pure water) or indirect photolysis (natural water) therefore does not contribute significantly to the overall elimination of fosetyl-Al from the aquatic environment.

I. Material and Methods

A. Materials

1. Test Material: [2-^{14}C]fosetyl-aluminium

Specific radioactivity:	0.83 MBq/mg (22.43 µCi/mg)
Radiochemical purity:	98.8%/99.4% (radio-TLC, two methods)
Chemical purity:	not reported
Sample ID:	SEL/1588

2. Test water

The natural water used for the test was collected from river [redacted] Germany. Water samples were characterized as summarized in Table 7.2.1.3- 1.
The natural water used for the test was prepared from a Milli-Q biocel A10 water purification unit equipped with a Quantum EX ultrapure filter cartridge. The water had a resistivity of 18.2 MΩ*cm at 25°C (equivalent to 0.055 µSiemens/cm) and a total organic carbon content of 8 µg/L (8 ppb).

Sterilised water and natural water were used in the test.

Table 7.2.1.3- 1: Physico-chemical characteristics of natural water

Water	[redacted]
pH	8.1
Oxygen saturation (%)	85.6
Redox potential (mV)	209
Conductivity (µS/cm)	527
Suspended solids (mg/L)	14
Evaporation residue (mg/L)	390
Water hardness (° dH)	11.7
Total organic carbon (TOC, mg/L)	4
Dissolved organic carbon (DOC, mg/L)	3
Nitrate (mg/L)	13
Ortho-Phosphate (mg/L)	0.18

B. Study design

1. Experimental conditions:
The test was performed with 2-^{14}C-fosetyl-Al at an initial concentration of 5 mg/L. The 'static' test systems consisted of quartz glass vessels attached to traps for volatile components. The samples were continuously irradiated in a "Suntest system" at 25 ± 2 °C with simulated sunlight (xenon burner, range of wave length spectrum 290 to 3000 nm, i.e. spectral distribution similar to that of natural sunlight) with cut-off of UV radiation < 290 nm by the use of filters. In parallel, samples were incubated under flow-through conditions at the same temperature in the dark thus serving as dark controls. Based on intensity measurements a continuous light exposure of 7 days in maximum (168 experimental hours) was equivalent to about 74 environmental days under light conditions at sea level at Tokio or, to about 36 environmental days under light conditions at sea level at Phoenix, Arizona, US, each at summer solstice, i.e. in June.
Duplicate or triplicate samples were removed each for analysis after 0, 1, 2, 3, 4, and 7 experimental days of irradiation. Duplicate samples of dark controls were removed for analysis at 4, and 7 days of incubation. Sterile water and natural water was used for incubation.

2. Analytical procedures:
Following determination of oxygen saturation and pH samples were analysed directly with no additional steps for extraction, clean-up, or sample concentration using LSC for determination of total radioactivity and HPLC with ^{14}C-flow-through detection as the chromatographic method. Representative samples were analysed by TLC as confirmative analytical method.

3. Kinetic evaluation:
The kinetic evaluation of fosetyl-aluminium transformation data was performed by use of the software Model Manager, version 1.1. Values for half-lives and DT_{90} were calculated for irradiated samples and dark controls. The quality of fit was expressed in terms of the correlation co-efficient r^2.

II. Results and Discussion

The total irradiation time of 7 days (168 experimental hours) in maximum corresponded to about 74 environmental days under light conditions at sea level at Tokio or, to about 36 environmental days under light conditions at sea level at Phoenix, Arizona, US, each at summer solstice, i.e. in June to reflect a worst-case approach.
Tests were performed with sterile samples throughout the whole testing period. The temperature was maintained at 25 ± 2 °C for irradiated samples and dark controls during the test.

For natural water and pure sterile water the material balances and distribution of radioactivity are summarized for irradiated samples and dark controls in Table 7.2.1.3- 2 and in Table 7.2.1.3- 3, respectively. For natural water material balances ranged from 99.7 to 101.4% AR for irradiated samples and from 100.9 to 101.9% for dark controls. For pure water material balances ranged from 96.9 to 101.3% AR for irradiated samples and from 100.7 to 101.4% for dark controls. Formation of ^{14}C-carbon dioxide was therefore insignificant for both types of water tested.

In irradiated samples of natural water, fosetyl-Al decreased from 100.8% AR at time zero to 50.3% (mean value of two irradiation series) after 7 experimental days. Degradation was negligible in dark controls as it is demonstrated by a value of 100.9% AR after the same time of incubation in the dark. In irradiated samples, three components were formed to occur at 24.3% (ethyl phosphate), 14.3% (ethanol) and 6.9% (acetic acid) in maximum each after 7 experimental days (see Table 7.2.1.3- 2). In dark controls, the test substance remained stable with no detection of transformation products.

In irradiated samples of pure water, fosetyl-Al decreased from 101.3% AR at time zero to 30.2% (mean value of two irradiation series) after 7 experimental days. Degradation was negligible in dark controls as it is demonstrated by a value of 100.7% AR after the same time of incubation in the dark. In irradiated samples, three components were formed to occur at 12.9% (ethyl phosphate), 9.6% (ethanol) and 44.6% (acetic acid) in maximum each after 7 experimental days (see Table 7.2.1.3- 3). In dark controls, the test substance remained stable with no detection of transformation products.

The transformation products formed were all considered to be readily biodegradable thus with no further assessment in environmental exposure assessments required.

The findings should be considered also against the fact that 7 experimental days for irradiated samples were equivalent to 73.5 days under natural light conditions of Tokio (i.e. comparable to light conditions of Athens, EU). In view of the total irradiation time and intensity during the test indirect photolytic processes were found to contribute to a negligible extent to the overall elimination of fosetyl-aluminium from the aquatic environment.
It should be noted in addition, that fosetyl-Al was stabilized under the rather artificial conditions of the test due to sterilization of samples. This should be compared to the non-sterile situation under outdoor conditions to result in fast biotical induced hydrolysis of fosetyl-Al (see, for example, also Section CA 7.2.2.3). As a result of ready degradation of fosetyl-Al no material would be available for photolytic transformation processes in a natural aquatic environment for a prolonged time.

The DT_{50} values for fosetyl-Al in irradiated and dark samples were calculated by applying the simple first order kinetic model.

For natural water, the half-life was determined to 77 days under outdoor light conditions of Tokio being also equivalent to those at Athens in the EU. No value for the DT_{50} could be estimated for dark controls due to insignificant degradation.
For pure water, the half-life was determined to 35 days under outdoor light conditions of Tokio being equivalent to those at Athens in the EU. No value for the DT_{50} could be estimated for dark controls due to insignificant degradation.

Table 7.2.1.3- 2: Phototransformation of [2-^{14}C]fosetyl-Al in sterile natural water

Component		Sampling interval (experimental days)					
	Irradiated	**0**	**1**	**2**	**3**	**4**	**7**
	Dark control	**-**	**-**	**-**	**-**	**4**	**7**
Fosetyl-aluminium	Irradiated*	100.8	94.2	83.7	78.4	72.9	50.3
	SD	±0.1	±0.7	±8.1	±0.2	±0.1	±0.5
	Dark control*	-	-	-	-	101.9	100.9
	SD	-	-	-	-	±0.1	±0.5
Ethyl phosphate	Irradiated*	n.d.	4.3	9.5	13.0	13.4	24.3
	SD	-	±0.2	±1.4	±1.5	±2.5	±1.2
	Dark control*	-	-	-	-	n.d.	n.d.
	SD	-	-	-		-	-
Ethanol	Irradiated*	n.d.	2.8	5.8	6.0	9.1	14.3
	SD		±0.1	±0.4	±2.0	±0.9	±0.9
	Dark control*	-	-	-	-	n.d.	n.d.
	SD	-	-	-	-	-	-
Acetic acid	Irradiated*	n.d.	n.d.	2.4	3.5	5.9	6.9
	SD	-	-	±0.6	±1.0	±1.8	±2.8
	Dark control*	-	-	-	-	n.d.	n.d.
	SD	-	-	-	-	-	-
Unidentified	Irradiated*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-
	Dark control*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-
Total volatiles							
Total% recovery	Irradiated*	100.8	101.3	101.4	100.9	101.3	99.7
	SD	±0.1	±0.3	±0.1	±0.2	±0.1	±0.2
	Dark control*	-	-	-	-	101.9	100.9
	SD	-	-	-	-	±0.1	±0.1

* mean values of two replicates; SD = standard deviation; n.d. = not determined
All values expressed as percentage of total applied radioactivity

Table 7.2.1.3- 3: Phototransformation of [2-^{14}C]fosetyl-Al in pure sterile water

Component		Sampling interval (experimental days)					
	Irradiated	**0**	**1**	**2**	**3**	**4**	**7**
	Dark control	**-**	**-**	**-**	**-**	**4**	**7**
Fosetyl-aluminium	Irradiated*	101.3	90.6	66.4	63.3	33.2	30.2
	SD	±0.1	±1.3	±2.3	±8.1	±12.0	±6.7
	Dark control*	-	-	-	-	101.4	100.7
	SD	-	-	-	-	±0.1	±0.2
Ethyl phosphate	Irradiated*	n.d.	2.6	4.8	6.9	11.0	12.9
	SD	-	±0.2	±0.6	±2.1	±3.6	±3.7
	Dark control*	-	-	-	-	n.d.	n.d.
	SD	-	-	-	-	-	-
Ethanol	Irradiated*	n.d.	2.1	5.2	7.3	8.5	9.6
	SD	-	±0.1	±0.7	±0.2	±1.6	±1.3
	Dark control*	-	-	-	-	n.d.	n.d.
	SD	-	-	-	-	-	-
Acetic acid	Irradiated*	n.d.	5.8	23.5	22.4	44.2	44.6
	SD	-	±1.2	±2.4	±6.4	±9.0	±4.1
	Dark control*	-	-	-	-	n.d.	n.d.
	SD	-	-	-	-	-	-
Unidentified	Irradiated*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-
	Dark control*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	SD	-	-	-	-	-	-
Total volatiles							
Total% recovery	Irradiated*	101.3	101.1	99.8	100.1	96.9	97.3
	SD	±0.1	±0.1	±0.1	±0.7	±0.9	±1.0
	Dark control*	-	-	-	-	101.4	100.7
	SD	-	-	-	-	±0.1	±0.2

* mean values of two replicates; SD = standard deviation; n.d. = not determined
All values expressed as percentage of total applied radioactivity

III. Conclusion

The indirect photolytic transformation of fosetyl-Al in sterile natural water and direct photolytic transformation in pure water was found to be negligible to result in mean photolytic half-lives of 77 and 35 environmental days, respectively, when being referenced to natural light conditions of Tokio at sea level in June.

Irradiation of ^{14}C-fosetyl-Al in sterile natural and pure sterile water resulted in the formation of the three photo-transformation products ethyl phosphate (24.3%), ethanol (14.3%) and acetic acid (44.6%) in maximum.

Overall direct (pure water) and indirect photolysis (natural water) is therefore unlikely to contribute significantly to the overall elimination of fosetyl-Al from the aquatic environment.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

Report:	KCA 7.2.2.1/01 [redacted]; [redacted]; [redacted]; 1985; M-159568-01-1
Title:	BOD of the product fosetyl-Al
Report No.:	R000927
Document No.:	M-159568-01-1
Guideline(s):	Dutch NEN 3235-5.4, 1972
Guideline deviation(s):	none
GLP/GEP:	**no**

Report:	KCA 7.2.2.1/02 [redacted]; 1996; M-184475-01-1
Title:	Fosetyl-Al: Assessment of ready biodegradability; CO2 evolution test.
Report No.:	R011742
Document No.:	M-184475-01-1
Guideline(s):	EU (=EEC): 92/69/EEC, Method C.4-C; OECD: 301B, (1992)
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.2.2.1/03 [redacted]; 2001; M-204283-01-1
Title:	Phosphorous acid: Assessment of the biodegradability of phosphorous acid in an aqueous medium
Report No.:	C013264
Document No.:	M-204283-01-1
Guideline(s):	EU C.4A, 1992
Guideline deviation(s):	none
GLP/GEP:	**yes**

The ready biodegradability of fosetyl-aluminium (fosetyl-Al) was investigated experimentally in:

- activated sludge following application of non-labelled fosetyl-Al at four test concentrations of up to 8 mg/L in maximum and incubation at 20 °C under the conditions of a biochemical oxygen demand (BOD) test for a maximum of 21 days (KCA 7.2.2.1/01);
- aqueous buffer of pH 7.4 inoculated with activated sludge following application of non-labelled fosetyl-Al at a test concentration of 98.3 mg/L[15] and incubation at 21 °C under the conditions of a carbon dioxide evolution test for a maximum of 29 days (KCA 7.2.2.1/02).

The ready biodegradability of phosphonic acid was investigated experimentally in:

- aqueous buffer inoculated with activated sludge following application of non-labelled phosphonic acid at a test concentration of 20 mg/L and incubation at 22 °C under the conditions of an ultimate biodegradability test for a maximum of 28 days (KCA 7.2.2.1/03).

The data requirement was addressed under Point 7.2.1.3.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

[15] equivalent to 19.5 mg carbon/L

Requirements in design and testing of chemicals according to OECD 301 did not change since adoption of the guideline in 1992 including no major changes at times before. In summary this allows for the conclusion that the studies KCA 7.2.2.1/01 to KCA 7.2.2.1/03 are consistent with no major deviation from designs or requirements according to OECD 301.

The evaluation revealed that fosetyl-Al was significantly degraded (i.e. 75% after 28 days, study KCA 7.2.2.1/02) thus fulfilling the classification criteria to be readily biodegradable.
No transformation was found for phosphonic acid under the conditions of the test (KCA 7.2.2.1/03). Phosphonic acid therefore did not fulfill the criteria to be classified as readily biodegradable following the strict criteria set for evaluation of this type of test.

Study summaries of existing studies and publications on ready biodegradability of the active substance and metabolites, i.e. phosphonic acid:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.2.2.1/01 [redacted],; [redacted]; [redacted]; 1985; M-159568-01-1
Title:	BOD of the product fosetyl-Al
Report No.:	R000927
Document No.:	M-159568-01-1
Guideline(s):	Dutch NEN 3235-5.4, 1972
Guideline deviation(s):	none
GLP/GEP:	no

Executive Summary
The biological oxygen demand (BOD) of fosetyl-Al in active sludge was determined at 20 °C for 21 days in maximum. The test was performed at fosetyl-Al concentrations of 0, 2, 4, and 8 mg/L.

The value for the biological oxygen demand after five days (BOD_5) found for fosetyl-Al was insignificant. However, there were indications for some oxygen consumption after 21 days to result in a BOD_{21} of 0.16 ± 0.04 mg O_2/mg fosetyl-Al. This corresponded to about 18% of the theoretical oxygen demand.

In view of results from tests on ready biodegradability available following OECD 301, the study was regarded as supplemental information.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fosetyl-Al	
Sample ID:	Batch DA318
Chemical Purity:	technical

2. Active Sludge

A sample of active sludge was taken from an oxidation ditch for treatment of domestic sewage. The original sludge (2 g of solid substance/L) was allowed to settle and 1 mL of the decanted supernatant was used to inoculate 1 L of BOD dilution water. The inoculated dilution was aerated vigorously before use.

B. STUDY DESIGN

The BOD of fosetyl-Al was determined in test BOD-bottles in quadruplicate samples of following concentrations: 0, 2, 4, and 8 mg/L. A stock solution of the substance was made by dissolving 0.032 g of fosetyl-Al in 100 mL of BOD dilution water.

The activity of the inoculum was checked using glucose and glutamic acid. The toxicity of the test substance to the inoculum was tested in dilution water containing glucose and glutamic acid using a concentration of fosetyl-Al of 8 mg/L. A nitrification control was included by addition of allylthiourea using a concentration of fosetyl-Al of 2 mg/L.

The oxygen concentration was measured after 0, 5 and 21 days by means of an oxygen electrode.

The test was performed at 20 °C for 21 days in maximum.

II. RESULTS AND DISCUSSION

No significant value (BOD_5) was found for the test substance after five days of incubation (see Table 7.2.2.1- 1). The incubation time was thus prolonged to 21 days. After 21 days of incubation, the controls containing inoculum had a BOD_{21} value of only 4.5 mg O_2/L. A check on the activity of the inoculum to glucose/glutamic acid led to BOD_{21} values of 9.0 mg O_2/L and even higher in the presence of test substance.

The BOD_{21} values found for fosetyl-Al appear to be significant with 0.16 ± 0.04 mg O_2/mg fosetyl-Al possibly independent of concentration. This amounts to about 18% of the theoretical oxygen demand of fosetyl-Al (0.9 mg O_2/mg).

The controls containing only inoculum were found to have a very high BOD value of 2.9 mg O_2/L after 5 days of incubation. However, since the inoculum activity control (addition of glucose and glutamic acid) was normal, the background was regarded as acceptable. Testing the activity of the inoculum towards the glucose/glutamic acid mixture in the absence and presence (8 mg/L) of fosetyl-Al, BOD_5 values of 3.8 and 4.8 mg O_2/L were found, respectively, showing that the test substance did not significantly inhibit the activity of the inoculum. The result in the presence of 8 mg/L test substance indicates that it stimulates the oxygen consumption on glucose/glutamic acid.

Table 7.2.2.1- 1: Results of the determination of the BOD of Fosetyl-Al

Incubation time	BOD	Additive	Applied fosetyl-Al [mg/L]			
			0	2	4	8
5 days	BOD_5 [mg O_2/L]	-	2.88	3.00	2.8 [1]	3.13
		glucose and glutamic acid	6.70			7.65
		allylthiorea		2.63		-
	BOD [2] [mg O_2/mg]	-	-	~ 0.04	0	~ 0
21 days	BOD_{21} [mg O_2/L]	-	4.70	5.15	5.4 [1]	5.68
		glucose and glutamic acid	8.98			> 9
		allylthiorea		5.00		
	BOD [2] [mg O_2/mg]	-	-	0.20	0.17	0.12

[1] One of the 4 replicates was deviating; mean of three measurements.
[2] The BOD of the control has been subtracted.

III. CONCLUSIONS

The BOD_5 value found for fosetyl-Al was insignificant. However, there were indications for some oxygen consumption after 21 days to result in a BOD_{21} of 0.16 ± 0.04 mg O_2/mg fosetyl-Al. This corresponded to about 18% of the theoretical oxygen demand.

In view of results from tests on ready biodegradability available following OECD 301, the study was regarded as supplemental information.

Report:	KCA 7.2.2.1/02 [redacted]; 1996; M-184475-01-1
Title:	Fosetyl-Al: Assessment of ready biodegradability; CO2 evolution test.
Report No.:	R011742
Document No.:	M-184475-01-1
Guideline(s):	EU (EEC): 92/69/EEC, Method C.4-C; OECD: 301B, (1992)
Guideline deviation(s):	none
GLP/GEP:	yes

Executive Summary
The potential of fosetyl-Al to undergo ready biodegradation was investigated in an aqueous medium inoculated with micro-organisms from activated sewage sludge at 21 °C under aerobic conditions in the dark for 28 days in maximum. Fosetyl-Al was applied at a test concentration equivalent to 19.52 mg carbon/L.

The evaluation revealed that fosetyl-Al was significantly degraded (i.e. 75% after 28 days) thus fulfilling the classification criteria to be readily biodegradable.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Fosetyl-Al (non-labelled)
Sample ID: 960203
Chemical Purity: 97.6%

2. Test Solution

A mixed population of activated micro-organisms originating from sewage sludge was used to inoculate the test medium.

B. STUDY DESIGN

1. Experimental Conditions

The test was performed under flow-through conditions by flushing 5 L sealed culture vessel containing 3 L of test solution with CO_2-free air and the collection of CO_2 formed by traps.

The test was performed at a test concentration of fosetyl-Al equivalent to 19.52 mg carbon/L in the test solution (i.e. inoculated culture medium). Reference samples with sodium benzoate were prepared at a concentration of 10 mg C/L in inoculated culture medium. A toxicity control (one vessel only) was prepared with the test material plus the standard material in inoculated culture medium at a final concentration of 29.52 mg C/L to assess any toxic effect of the test material on the sewage sludge micro-organisms used in the study. In addition, a control vessel was prepared consisting of inoculated culture medium only.

The incubation was performed under continuous stirring in the dark at 21 °C for 28 days in maximum. By day 28, inorganic carbonates formed were driven off by the addition of 1 mL concentrated hydrochloric acid to each vessel. The vessels were resealed, aerated overnight and the final samples taken from both absorber vessels on day 29.

2. Sampling

Duplicate samples were removed for analysis after 0, 1, 2, 3, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 27 and 28 days of incubation. By day 29 samples were processed and analysed after addition of hydrochloric acid to the test vessels the previous day.

3. Analytical Procedures

At each sampling interval (except DAT-12 and DAT-18) the first absorber vessel was analysed for CO_2 immediately. The second absorber vessel was sampled on DAT-0 and DAT-29. On DAT-0 and DAT-28 samples were removed from the test vessels and centrifuged prior to analysis for dissolved organic carbon (DOC).

The samples from the absorber vessels were analysed for CO_2 using a total organic carbon (TOC) analyser. Aliquots of the samples were injected into the inorganic carbon channel of the total carbon Analyser. The samples from the test vessels were analysed for DOC using a TOC analyser. Samples were injected into the total carbon and inorganic carbon channels of the TOC analyser. Each analysis was carried out in triplicate.

II. RESULTS AND DISCUSSION

The results of biodegradation tests of fosetyl-Al, sodium benzoate (reference) and the toxicity control were summarized in Table 7.2.2.1- 2.

Table 7.2.2.1- 2: Biodegradation of fosetyl-Al, sodium benzoate (reference), and toxicity control at 21 °C

Component	Incubation time (days)													
	1	2	3	6	8	10	14	16	20	22	24	27	28	29 [1]
Fosetyl-Al	7	8	13	16	17	28	57	58	64	67	71	73	75	77
Sodium benzoate	7	25	42	47	61	61	75	75	92	89	91	86	86	94
Toxicity control (fosetyl-Al + sodium benzoate)	6	12	19	23	36	39	52	53	57	53	56	58	58	58

All values given as percentages of applied
[1] DAT-29 values corrected to include any carry-over of CO_2 detected in trap 2

The biodegradation of fosetyl-Al increased from 7% at day 0 (study start) to 75% at day 28. Fosetyl-Al attained ≥ 60% degradation after 28 days but more than 10 days were between this result and 10% of biodegradation. Thus, the 10-day window validation criterion was not met and therefore fosetyl-AI cannot be considered to be readily biodegradable under the strict terms and conditions of OECD Guideline No. 301 B.

Sodium benzoate attained 86% degradation after 28 days thereby confirming the suitability of the inoculum and test conditions.

The toxicity control (fosetyl-Al plus sodium benzoate) attained 58% degradation after 28 days thereby confirming that the test material was not toxic to the sewage treatment microorganisms used in the study. The relatively low degradation rate observed in the toxicity control vessel was considered to be due to the sewage treatment microorganisms being unable to degrade both the sodium benzoate and test material present simultaneously and hence the degradation rate obtained was lower than that for either sodium benzoate or the test material vessel.

Inorganic carbon analysis of the second absorber vessels after 29 days of incubation confirmed that no significant carry-over of CO_2 into the second absorber vessels occurred.

Analysis of the test media from the test material culture vessels by Day zero and after 28 days of incubation for dissolved organic carbon (DOC) gave a mean percentage degradation value of 85%.

III. CONCLUSIONS

The evaluation revealed that fosetyl-Al was significantly degraded (i.e. 75% after 28 days) thus fulfilling the classification criteria to be readily biodegradable.

The study followed in its design actual requirements of the corresponding OECD Guideline 301.

Report:	KCA 7.2.2.1/03 [redacted]+; 2001; M-204283-01-1
Title:	Phosphorous acid: Assessment of the biodegradability of phosphorous acid in an aqueous medium
Report No.:	C013264
Document No.:	M-204283-01-1
Guideline(s):	EU C-4A, 1992
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The possible biological degradation of phosphonic acid by microorganisms was studied in an aqueous test system under aerobic conditions in the dark at 22 °C for 28 days in maximum. The test was performed at a phosphonic acid concentration of 20 mg/kg. Sodium acetate was serving as reference item.

No degradation of phosphonic acid was observed. Phosphonic acid had no influence on the microbial degradation of sodium acetate in aqueous medium under the conditions of the test.

The study followed in its design actual requirements of the corresponding OECD Guideline 301.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Phosphonic acid (non-labelled)	
Sample ID:	04911DN
Chemical Purity:	98.3%

2. Biological Reagents

Microorganisms used in this study were obtained from the influent of the [redacted] (Rhone, France) waste water treatment plant dealing with domestic sewage. Gross particulate matter was removed from the sample by coarse filtration. The inoculum was then concentrated by centrifugation, washed and placed in a Ringer solution 1/4. It was kept under aerobic conditions and used within 24 hours after the preparation. Microorganism concentration was evaluated using a spectrophotometer and was comprised between 10^6 and 10^7 cells/mL. The inoculum was used at a dilution of 1% in the test.

B. STUDY DESIGN

1. Experimental Conditions

The test was performed in 1 L Erlenmeyer flasks containing 500 g of test medium and 2 mL of the inoculum. An initial concentration of phosphonic acid of 20 mg/kg was applied.

Samples were incubated in the dark at 22 ± 1 °C for 28 days in maximum.

In addition, samples containing only the inoculum (blanks), reference item and inoculum (controls) and test item, reference item plus NaN_3 but without inoculum (test for possible abiotic transformation) were incubated under the same conditions and removed for analysis at selected time points.

2. Sampling

Triplicate samples for tests with the test item and duplicate samples for blanks and controls were analysed 0, 7, 14, 21 and 28 days after treatment (DAT).

3. Analytical Procedures

At each sampling interval the amount of phosphonic acid was determined by ion chromatography. The amount of dissolved organic carbon (DOC) was analysed at each sampling interval with a carbon analyser.

The degree of biodegradation of the reference item was calculated by expressing the concentration of DOC removed (corrected for that in the blank inoculum control) as a percentage of the concentration initially present.

II. RESULT AND DISCUSSION

Recovered residues of phosphonic acid ranged from 99.2 to 102.7% of applied at all sampling intervals as summarized in Table 7.2.2.1- 3. Thus, no trend for degradation of phosphonic acid was observed under the test conditions.

The reference item sodium acetate was completely biodegraded after 7 days of incubation in the presence or absence of phosphonic acid. Phosphonic acid had therefore no effect on microbial degradation of sodium acetate in the aqueous medium.

Table 7.2.2.1- 3: Residues of phosphonic acid as a function of time

Component		Incubation time (days)				
		0	7	14	21	28
Phosphonic acid	Mean	102.7	102.0	99.2	99.7	101.2
	SD	± 1.3	± 2.0	± 1.2	± 1.4	± 1.5

SD: standard deviation

Expressed as mean percentage of applied of three replicates

III. CONCLUSIONS

No degradation of phosphonic acid was observed. Phosphonic acid had no influence on the microbial degradation of sodium acetate in aqueous medium under the conditions of the test.

The study followed in its design actual requirements of the corresponding OECD Guideline 301.

CA 7.2.2.2 Aerobic mineralisation in surface water

Being a new data requirement this point had not been addressed in the existing Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

Report:	KCA 7.2.2.2/01 [redacted],; [redacted]; 2015; M-529940-01-1
Title:	[2-14C]Fosetyl-aluminium: Aerobic mineralization in surface water
Report No.:	M-529940-01-1
Document No.:	M-529940-01-1
Guideline(s):	OECD Test Guideline No. 309 Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The mineralisation of ethyl-2-^{14}C-labeled active substance fosetyl-aluminium (fosetyl-Al) was investigated in non-sterile natural water at pH 8.0 at test concentrations of 10.2 µg/L (low dose) and 101.3 µg/L (high dose). Samples were incubated at 20 ± 2 °C in the dark for 63 days in maximum. Microbial activity of the test water was demonstrated by incubation of phenyl-UL-^{14}C-labeled benzoic acid serving as reference.

The mean material balances were 99.4 ± 3.0% AR for low dosed and 97.5 ± 4.2% for the high dosed samples.

Values of the test substance in the test water decreased from 100.9% of AR for the low dose (100.5% for high dose) at time zero to 4.2% (2.1% for high dose) after 63 days of incubation.

Fosetyl-Al was transformed predominantly to carbon dioxide amounting to 44.2% AR for the low dose and 58.1% for the high dose each after 63 days of incubation. Formation of other volatile components was negligible amounting to less than 3.6% AR (LOQ of low dose) and 0.4% (LOQ of high dose) in maximum for both concentrations tested.

Formation of other transformation products was observed to occur at 4.0% in total for all components in the course of the study.

Values of the DT_{50} of fosetyl-Al under conditions of mineralization testing were calculated to be 6.9 days (low dose) and 7.6 days (high dose) following simple first order (SFO) kinetic evaluation as the best fits to measured data.

I. Material and Methods

A. Materials

1. Test Material: [ethyl-2-^{14}C]fosetyl-aluminium
Specific radioactivity: 2.11 MBq/mg (56.91 µCi/mg)
Radiochemical purity: >99% (TLC)
Sample ID: 8316AKV001-8

2. Test water

The natural water used for the test was fresh collected (0 to 10 cm depth) from lake [redacted] Germany. Water samples were characterized as summarized in Table 7.2.2.2- 1.

Table 7.2.2.2- 1: Physico-chemical characteristics of test water

Water	[redacted]
pH	8.0
Colour	not reported
Water temperature	9.7
Redox potential (mV)	200
Oxygen saturation (%)	84
Biological oxygen demand (mg/L)	n.a.
Total organic carbon (TOC, mg/kg)	< 2
Dissolved Organic Carbon (DOC, mg/L)	< 2
Total phosphorus (mg/L)	< 0.03
Total nitrogen (mg/L)	2.8

n.a.: not applicable due to low value for DOC

Before start of incubation the test water was passed through a 0.063 mm filter.

B. Study design

1. Experimental conditions:
Samples of 100 mL test water each were filled into Erlenmeyer flasks and pre-equilibrated prior to treatment at approximate study conditions (darkness, 20 °C) for five days. The test was performed with [ethyl-2-^{14}C]fosetyl-Al at initial concentrations of 10.2 µg/L (low dose) and 101.3 µg/L (high dose). Following application traps containing soda lime and a polyurethane foam allowing for the determination of ^{14}C-carbon dioxide and other volatile organic compounds were attached to each sample.

Samples were incubated at 20 ± 2 °C in the dark for 63 days in maximum.

In addition, samples containing untreated water, solvent controls and biological controls were incubated under the same conditions and removed for analysis at selected time points. Solvent controls and biological controls contained the reference substance phenyl-UL-^{14}C-benzoic acid.

2. Sampling:
Duplicate samples each of both test concentrations were removed for analysis after 0, 3, 7, 15, 21, 30, 39, 46 and 63 days of incubation.

Samples for determination of microbial activity (biological controls) and solvent controls were investigated after 0 and 3 days of incubation. Finally, sterile controls were removed for analysis after 65 days of incubation.

The complete samples were immediately processed and TLC analysis was usually performed the same day. Therefore no additional investigations of storage stability were necessary.
The pH, oxygen concentration and the redox potential was determined at each sampling interval.

3. Analytical procedures:
The water of samples was analysed directly without a concentration step prior to analysis. The ^{14}C-material balance was established for each sample following analysis of the water and determination of volatile radioactivity in the traps. Following quantitation of radioactivity in water by LSC, analysis was performed by reversed phase TLC followed by ^{14}C-detection (phosphor imaging). Representative samples were analysed by HPLC and ^{14}C-flow-through detection.
The LOQ was estimated to be about 3.3% of AR for low dosed and about 1.7% AR for high dosed samples.

4. Kinetic evaluation:
The kinetic evaluation was performed for the active substance fosetyl-Al with the software KinGUI II following FOCUS kinetic guidance (2006) to obtain best fits to the measured data.

II. Results and Discussion

The temperature was maintained at 20 ± 2 °C during the test. Biological activity of the test water was confirmed by the degradation of reference substance phenyl-UL-^{14}C-benzoic acid within 3 days of incubation. The pH, oxygen concentration and redox potential of the test water was shown to be within the same range for treated samples and for untreated controls.

The material balances and distribution of radioactivity are summarized in Table 7.2.2.2- 2 (low dose) and Table 7.2.2.2- 3 (high dose). The mean material balances were 99.4 ± 3.0% AR (range: 94.7 to 105.5%) for low dose samples and 97.5 ± 4.2% (range: 92.4 to 105.9%) for the high dose demonstrating no significant losses of radioactivity from samples in the course of the test including processing till analysis.

Formation of ^{14}C-carbon dioxide was observed as the predominant transformation product to account for 44.2% of AR (low dose) and 58.1% (high dose) at the end of the study, day 63. For low dosed samples, maximum formation of ^{14}C-carbon dioxide was observed at 46.7% AR after 39 days of incubation. Formation of other volatile components was negligible amounting to less than 3.6% AR (LOQ of low dose) and 0.4% (LOQ of high dose) in maximum for both concentrations tested.

Biotransformation of ^{14}C-labeled fosetyl-Al resulted in a decline from 100.9% AR at time zero to 4.2% for the low dose and from 100.5% AR at time zero to 2.1% for the high dose each after 63 days of incubation. Degradation of active substance was negligible in sterile controls as documented by values of 101.9% (low dose) and 105.6% of AR (high dose) for fosetyl-Al after 65 days of incubation. The total radioactivity representing minor components was 4.0% (low dose, day 46) or 3.0% (high dose, day 21) each in the course of the study.

Chromatographic analysis included the detection of immobile radioactivity at the start of the TLC lane. Its detection is a common observation in TLC analysis in particular in case of chemicals undergoing significant degradation till full mineralization (see also TLC results of ^{14}C-benzoic acid as reference substance at day 3) and, as proposed by the structure of fosetyl-Al and its route of degradation. Formation of ^{14}C-carbon dioxide was confirmed in addition thus supporting the fact that significant mineralization had occurred. This included the potential for (re-) incorporation of already mineralised material into the matrix, i.e. biological material and cells. The immobile radioactivity observed at the start of the TLC lane (maximum 55.7% AR by day 21 for the low dose and 59.6% by day 15 for the high dose therefore consisted of such radioactivity undergoing (re-)incorporation.

The kinetic evaluation of the data resulted in DT_{50}-values of 6.9 days for the low dose and 7.6 days for the high dose. The values were derived from the SFO kinetic model as the best fits to measured data. The results of kinetic evaluations are summarized in Table 7.2.2.2- 4.

Table 7.2.2.2- 2: Low dose: Degradation of [ethyl-2-^{14}C]fosetyl-Al in aerobic natural water, expressed as percentage of total applied radioactivity

Component		Sampling interval (days)						
		0	3	7	15	21	30	39
Fosetyl-aluminium	Mean*	100.9	96.4	73.5	4.6	6.7	4.3	6.0
	SD	±0.1	±0.7	±8.1	±0.2	±0.1	±0.5	±0.3
TLC origin	Mean*	n.d.	2.5	14.6	55.2	55.7	52.9	40.7
	SD		±0.6	±3.0	±10.5	±7.4	±11.9	±3.7
Sum of unidentified/diffuse components	Mean*	<LOD	<LOD	3.9	1.8	3.0	3.7	1.2
	SD			±1.5	±0.2	±0.2	±1.3	±0.0
Total radioactivity in water	Mean*	100.9	98.9	92.0	61.6	65.3	60.9	47.9
	SD	±0.1	±0.1	±3.6	±11.0	±7.8	±11.1	±2.7
$^{14}CO_2$	Mean*	n.a.	1.4	7.6	34.2	23.5	33.4	46.7
	SD		±0.1	±1.9	±10.9	±3.1	±8.7	±3.4
Other volatiles	Mean*	n.a.	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	SD							
Biofilm	Mean*	n.a.	n.a.	n.a.	2.9	5.7	3.0	0.7
	SD				±1.0	±1.7	±0.4	±0.1
Total radioactivity (%)	Mean*	100.9	100.4	99.6	98.7	94.5	97.3	97.8
	SD	±0.1	±0.2	±1.7	±1.2	±3.0	±2.8	±1.9

Values given as percentages of initially applied radioactivity
SD = standard deviation; * Mean values of two replicates
n.a. = not analysed or not applicable, n.d. = not detected
LOD for TLC: 1.0% AR; LOD for other volatiles: 3.6% AR

Table 7.2.2.2- 2 (continued): Low dose: Degradation of [ethyl-2-^{14}C]fosetyl-Al in aerobic natural water, expressed as percentage of total applied radioactivity

Component		Sampling interval (days) 46	63
Fosetyl-aluminium	Mean*	3.6	4.2
	SD	±0.2	±1.3
TLC origin	Mean*	51.7	42.8
	SD	±1.7	±0.2
Sum of unidentified/diffuse components	Mean*	4.0	2.7
	SD	±1.6	±0.9
Total radioactivity in water	Mean*	59.3	49.6
	SD	±0.2	±0.6
$^{14}CO_2$	Mean*	39.2	44.2
	SD	±1.2	±2.2
Other volatiles	Mean*	<LOD	<LOD
	SD		
Biofilm	Mean*	n.a.	n.a.
	SD		
Total radioactivity (%)	Mean*	100.4	93.8
	SD	±0.3	±1.6

Values given as percentages of initially applied radioactivity
SD = standard deviation; * Mean values of two replicates
n.a. = not analysed or not applicable;
LOD for TLC: 1.1% AR, LOD for other volatiles: 3.6% AR

Table 7.2.2.2- 3: High dose: Degradation of [ethyl-2-^{14}C]fosetyl-Al in aerobic natural water, expressed as percentage of total applied radioactivity

Component		Sampling interval (days)						
		0	3	7	15	21	30	39
Fosetyl-aluminium	Mean*	100.5	97.3	90.9	7.6	4.4	2.0	3.0
	SD	±0.0	±0.1	±3.1	±0.8	±0.2	±0.5	±0.2
TLC origin	Mean*	n.d.	0.8	6.1	59.6	53.5	39.4	41.6
	SD		±0.1	±2.0	±0.4	±3.7	±4.8	±4.7
Sum of unidentified/diffuse components	Mean*	n.d.	<LOD	<LOD	2.6	3.0	1.9	2.1
	SD				±1.1	±0.3	±0.0	±0.5
Total radioactivity in water	Mean*	100.5	98.1	97.1	69.8	60.9	44.1	46.7
	SD	±0.0	±0.3	±1.1	±0.1	±3.8	±5.2	±4.0
$^{14}CO_2$	Mean*	n.a.	0.6	2.8	19.2	28.7	45.4	52.7
	SD		±0.1	±0.1	±1.9	-**	±3.7	±0.1
Other volatiles	Mean*	n.a.	0.4	<LOD	<LOD	<LOD	0.4	0.4
	SD		±0.4			-**	±0.4	±0.3
Biofilm	Mean*	n.a.	n.a.	n.a.	4.3	4.2	2.4	0.6
	SD				±0.3	±1.1	±0.7	±0.1
Total radioactivity (%)	Mean*	100.5	99.2	99.9	93.3	93.8	92.4	100.4
	SD	±0.0	±0.8	±1.2	±1.8	-**	±1.9	±4.2

Values given as percentages of initially applied radioactivity
SD = standard deviation; * Mean values of two replicates; ** Values for volatiles of replicate B excluded
n.a. = not analysed or not applicable; LOD = 0.4% AR

Table 7.2.2.2- 3 (continued): High dose: Degradation of [ethyl-2-^{14}C]fosetyl-Al in aerobic natural water, expressed as percentage of total applied radioactivity

Component		Sampling interval (days) 46	63
Fosetyl-aluminium	Mean*	2.2	2.1
	SD	±0.1	±0.2
TLC origin	Mean*	36.9	32.3
	SD	±2.1	±1.8
Sum of unidentified/diffuse components	Mean*	2.6	2.1
	SD	±0.3	±0.0
Total radioactivity in water	Mean*	41.6	36.5
	SD	±2.5	±2.0
$^{14}CO_2$	Mean*	52.2	58.1
	SD	-**	±1.7
Other volatiles	Mean*	<LOD	<LOD
	SD	-**	
Biofilm	Mean*	n.a.	n.a.
	SD	-**	
Total radioactivity (%)	Mean*	94.2	94.6
	SD	-**	±0.3

Values given as percentages of initially applied radioactivity
SD = standard deviation; * Mean values of two replicates; ** Values for volatiles of replicate B excluded
n.a. = not analysed or not applicable; LOD = 0.4% AR

Table 7.2.2.2- 4: Kinetic evaluation of the degradation of [ethyl-2-^{14}C]fosetyl-Al in aerobic natural water under conditions of OECD 309 testing

Compound / Dose	Kinetic Model	DT_{50} (days)	DT_{90} (days)	Error for Chi^2 (%)	Visual Assessment
Fosetyl-aluminium / Low dose	**SFO**	**6.9**	**23.0**	**26.4**	**O**
	FOMC	6.9	23.0	27.9	O
	DFOP	6.9	23.0	29.7	O
Fosetyl-aluminium / High dose	**SFO**	**7.6**	**25.3**	**33.4**	**O**
	FOMC	7.6	25.3	35.3	O
	DFOP	7.6	25.3	37.6	O

Best fits marked bold

III. Conclusion

The overall biotransformation including mineralization of fosetyl-Al and its residues was significant under the ‘pelagic’ conditions of the test in non-sterile natural water.

Its simple structure combined with the known route of degradation in non-sterile aqueous media allowed for the degradation to ^{14}C-carbon dioxide as the predominant transformation product under the conditions of the test.

Under conditions of aerobic mineralisation testing the DT_{50} of fosetyl-Al in water was calculated to be 6.9 days for low dosed and 7.6 days for the high dosed samples thus indicating no significant dependency of transformation rate on the test concentration.

Overall the results confirmed the behavior and observations made in existing water/sediment tests.

CA 7.2.2.3 Water/sediment study

Report:	KCA 7.2.2.3/01 [redacted]; [redacted]; [redacted]; 1986; M-159703-01-1
Title:	Determination of the biodegradabilty - Fosetyl-Al in water / sediment systems
Report No.:	R000991
Document No.:	M-159703-01-1
Guideline(s):	Dutch CtB, Section G.2.1
Guideline deviation(s):	none
GLP/GEP:	**no**

Report:	KCA 7.2.2.3/02 [redacted]; [redacted]; [redacted]; [redacted]; 1998; M-226781-02-1
Title:	14c Fosetyl aluminium Degradation in Two water/Sediment Systems
Report No.:	C012742
Document No.:	M-226781-02-1
Guideline(s):	BBA: part IV section 5-1 december 1990; EU (=EEC): Directive 95/36/EC annex 1 section 7.2,1
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.2.2.3/03 [redacted]; [redacted]; 2015; M-528987-01-1
Title:	Fosetyl-Al.- Kinetic evaluation of aerobic aquatic metabolism in water / sediment systems according to FOCUS Kinetics using KinGUI 2
Report No.:	EnSa-15-0530
Document No.:	M-528987-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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**

Report:	KCA 7.2.2.3/04 [redacted],; [redacted]; 2005; M-251520-01-1
Title:	Phosphorous acid: Aerobic aquatic metabolism
Report No.:	C048583
Document No.:	M-251520-01-1
Guideline(s):	OECD: 308, (2002); SETAC: March 1995
Guideline deviation(s):	none
GLP/GEP:	**yes**

Report:	KCA 7.2.2.3/05 [redacted],; 2010; M-369224-01-1
Title:	Kinetic evaluation of an aerobic aquatic metabolism study of phosphorous acid according to FOCUS using KinGUI - Following a request by French AFSSA
Report No.:	MEF-10/303
Document No.:	M-369224-01-1
Guideline(s):	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**

The degradation of fosetyl-aluminium (fosetyl-Al) under conditions of water/sediment testing was investigated in:

- two sediments and their associated water following application of ethyl-1-^{14}C-labeled fosetyl-Al at two test concentrations and incubation at 20 °C for 96 days in maximum (KCA 7.2.2.3/01);
- two contrasting EU sediments and their associated water following application of ethyl-1-^{14}C-labeled fosetyl-Al and incubation at 20 °C for 100 days in maximum (KCA 7.2.2.3/02).

The data requirement was addressed under Point 7.2.1.3.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005). Consequently there is no detailed description of this existing data in this Supplementary Dossier.

The study design and conduct of study KCA 7.2.2.3/02 followed important predecessor guidelines, namely BBA Part IV, Section 5-1, serving as the basis for OECD 308 design. In summary this allows for the conclusion that the study KCA 7.2.2.3/02 is consistent with no major deviation from designs or requirements according to OECD 308.

The results of study KCA 7.2.2.3/01 were regarded as supplemental information and thus excluded from use in aquatic risk assessment due to the lack of detail in reporting and major deviations in design from established guidelines, in particular originating from high water-to-sediment ratios.

For study KCA 7.2.2.3/02 the evaluation revealed that fosetyl-Al was degraded *via* formation of ethanol as a major metabolite while formation and decline of estimated transformation products phosphonic acid and the fate of aluminium ions could not be followed up due to the position of radiolabel. The degradation was accompanied by significant formation of ^{14}C-carbon dioxide as the predominant terminal product of transformation. The route of degradation in aquatic systems was thus found to occur, in principle, via the same pathways as observed in aerobic soil.

When following simple first order kinetics half-lives of degradation of fosetyl-Al ranged from 3.9 to 4.5 days in total systems and from 3.75 to 4.3 days in water while no values were derived for sediment.

Due to its occurrence at more than 10% AR in water/sediment testing, ethanol fulfilled formally the criteria for definition as residue to be considered within the existing environmental risk assessments for surface water. However, the compound had been excluded due to its clearly transient character. The results of degradation tests in water/sediment systems under conditions of the laboratory resulted in the metabolic pathway summarized in Figure 7.2.2.3- 1.

The data from the existing water/sediment test (KCA 7.2.2.3/02) were kinetically re-evaluated according to actual FOCUS guidance (2006, 2011) as detailed in document KCA 7.2.2.3/03.

For ethanol and considering complete/spontaneous hydrolysis of fosetyl-Al to ethanol as a worst case, the maximum PEC of ethanol in surface water can be estimated to 55.8 µg/L (basis: FOCUS Step3 for surface water, late application on pome fruit, please refer to Document MCP, Section CP 9.2.5, of the representative formulation Fosetyl-Al WG 80). In comparison, tests in water/sediment were performed at a test concentration of about 7 000 µg fosetyl-Al/L translating into about 21 000 µg ethanol/L in theory. Despite this significantly higher concentration, ethanol was degraded rapidly under the conditions of the test. This is also supported by findings of a test on ready biodegradability resulting in the fact that fosetyl-Al and its residues are readily degradable (see Section CA 7.2.2).
The corresponding actual EFSA Conclusion (2013) for fosetyl-Al confirmed this view by stating that "fosetyl-Al degrades rapidly in surface water systems to form ethanol (which also degrades rapidly, so is only transient)" and that "ethanol is further dissipated by volatilisation or degraded and incorporated in natural constituents of plant and animal tissues".
In conclusion, ethanol is not expected to pose a risk in water.

The contribution of fosetyl-Al to the existing portion of Al in soil is minimal (see Section CA 7.1.1.1). Furthermore, for soils at pH > 5 (representative for most of soils in agricultural use in the EU), aluminium (Al) ions released from use of fosetyl-Al are immediately adsorbed (ion exchange, formation of minerals as indicated above for soil) and thus transformed into water-insoluble fractions of soil, thus being not available for transfer via leaching, run-off or drainage to surface water. This view is supported by the actual EFSA Conclusion for fosetyl-Al.
Entry of Al ions into surface water may also occur via spray drift. As for soils, Al never occurs as the free metal ion in aquatic environments[16]; 'Al^{3+} ions' are linked to other ubiquitous occurring elements. The process is influenced by a wide range of environmental parameters including pH, temperature, dissolved organic carbon and the nature of the available ligands ('counter ions') actually available. Above a pH of 5, Al-hydroxides (i.e. 'AlO^{+}' species plus counter-ion) are the most common, but short-lived species of Al components in water. It should be noted that 95% of European surface waters (n = 3075) with a documented history of exposure to plant protection products fall into the pH range 7.0 to 8.5[17]. Therefore, Al-hydroxides are the dominant species of Al potentially occurring in water surrounded by arable land, but as they are labile, exposure is expected to be negligible. This meets the EFSA conclusion for fosetyl (2013).

16 [redacted]. 2006. Aluminium speciation in environmental samples: a review. *Anal. Bioanal. Chem.* 386, 999–1012.

17 [redacted]. 2016. Narrow pH range of surface water bodies receiving pesticide input in Europe. *Bull Environ Contam Toxicol.* 96, 3-8.

The degradation of phosphonic acid under conditions of water/sediment testing was investigated in:

- two contrasting EU sediments and their associated water following application of non-labeled phosphonic acid as test substance and incubation at 20 °C for 76 days in maximum (KCA 7.2.2.3/04).

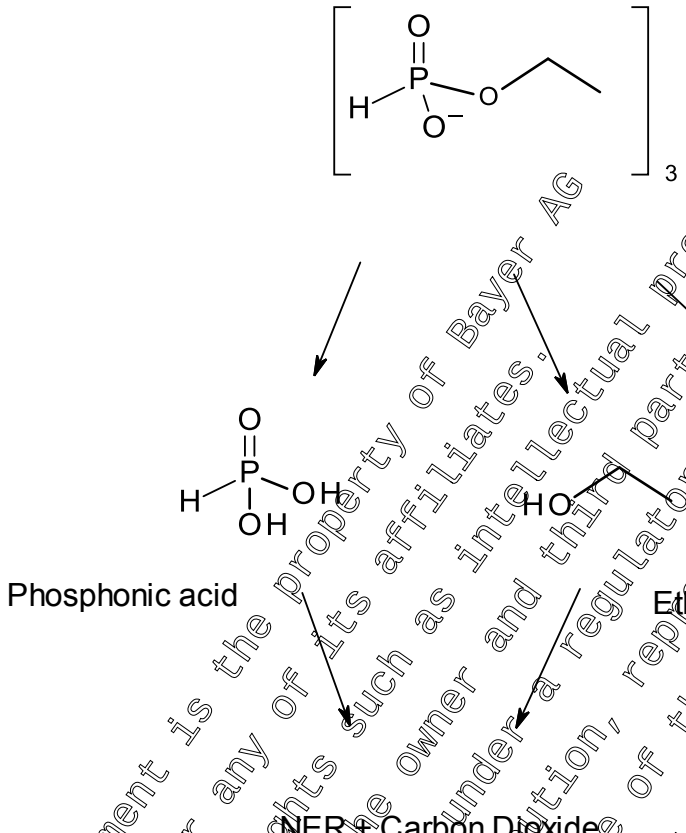
The study had not been submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC. The data are summarized in the following.

Finally, the data of study KCA 7.2.2.3/04 were kinetically evaluated according to FOCUS guidance (2006) as detailed in document KCA 7.2.2.3/05.

Owing to the fact of binding of phosphate via ageing to soil, a contribution via leaching of phosphate to groundwater or entries via drainage or runoff into surface water can be considered negligible. For the intended uses the maximum concentration of phosphonate in surface water of 14.35 µg/L (FOCUS Step3, application in apples, 3 x 3.6 kg as/ha, please refer to Document MCP, Section CP 9.2.5, of the representative formulation Fosetyl-Al WG 80) would translate into a theoretical concentration of 16.63 µg/L for phosphate ions (i.e. instantaneous and complete transformation of phosphonate) or 5.4 µg P/L in equivalents of elemental phosphorus. This maximum peak is well below annual average concentrations of 35 to 100 µg P/L for eutrophic and >100 µg P/L for hypereutrophic water bodies[18].
In contrast to phosphate, phosphonates are not readily available to aquatic organisms as a macro-nutrient and, as such, do not contribute to e.g. algal blooms. Following rapid adsorption of phosphonates to sediment ($DT_{50,sw}$ = 9.2 days) these are slowly converted ($DT_{50,sediment}$ = 105 days) via oxidation to phosphate ([redacted] s, [redacted]; 2005; M-251520-01-1, KCA 7.2.2.3/04).
The contribution of phosphate from fosetyl-Al use to surface water is low when considering additionally Council Directive 91/271/EEC concerning urban waste-water treatment. In order to protect the environment from adverse effects coming from high urban wastewater discharges, a threshold value has been set for phosphate to 1 000 to 2 000 µg/L (see Annex III of the Directive). These levels of continuous emission are around 100 times higher than the maximum phosphate concentration resulting from fosetyl-Al application (see above).
It can therefore be concluded that residues from use of fosetyl-Al in arable landscapes do not contribute significantly to eutrophication of aquatic ecosystems.

[18] Vollenweider, R.A. and Kerekes, J. (1982), Eutrophication of Waters. Monitoring Assessment and Control. Organization for Economic Co-Operation and Development (OECD), Paris. 156 pp.

Figure 7.2.2.3- 1: Proposed pathway of metabolism of fosetyl-aluminium in water/sediment systems



Study summary on aerobic aquatic degradation taken from the DAR

In addition and at the special request of the RMS France, summaries of existing studies on aerobic degradation in water/sediment already evaluated for the the Annex I inclusion of fosetyl under Directive 91/414/EEC were taken from the DAR of the RMS France (February 2005) and its Final Addendum (September 2005). A summary of the study is provided, from which data were used for the new kinetic evaluations and the actual risk assessment. This study summary is written in grey typeface in the following to distinguish from new studies.

Report:	KCA 7.2.2.3/02 [redacted]>; [redacted]; [redacted]; [redacted]; 1998; M-226781-02-1
Title:	14c Fosetyl aluminium Degradation in Two water/Sediment systems
Report No.:	C012742
Document No.:	M-226781-02-1
Guideline(s):	BBA: part IV section 5-3 december 1990; EU=EEC: Directive 95/36/EC annex 1 section 7,2,1
Guideline deviation(s):	none
GLP/GEP:	**yes**

Comment RMS: GLP, BBA guideline. Acceptable.

- **Methods**

Aluminium 1-^{14}C-ethylphosphonate (purity > 99 %) was applied at a rate equivalent to 20 kg/ha (1.77 mg/flask) to 2 water sediment systems (11 g sediment + 260 - 266 ml water; see characteristics in Table 8.4.3.2-2). Incubation was at 20 °C for 100 d. CO_2 was trapped. Water phase was analysed by LSC and HPLC. Sediment was extracted with 0.1 M sulfuric acid and extract was analysed by TLC and HPLC. Unextractable RA was determined by combustion. First aqueous samples were also analysed by HPLC-MS and GC-MS.

- **Results**

Recoveries (88.9 to 104.5%) were acceptable (Tables 8.4.3.2-3 and -4). Fosetyl was no longer detected in water after 30 d and negligible amounts were in sediment. The ethyl moiety was highly mineralized (70.3 to 72.9% after 100 d). The corresponding bound residue peaked at 24.0 to 28.8% after 14 - 30 d and was about 20% after 100 d. Ethanol was the main metabolite (max. 16% in water and 4.2% in sediment) and an unknown metabolite A was 4.1% in sediment. Both metabolites were transient. DT50 and DT90 for fosetyl were calculated to be 3.75 to 4.5 d and 12.5 to 14.2 d for water phase, and 3.9 to 4.5 d and 12.9 to 14.8 d for whole systems, respectively (Table 8.4.3.2-5). Phosphonic acid and Al ions are expected to be released from degradation of fosetyl.

Table 8.4.3.2-2: Characteristics of water sediment systems

	[redacted], UK	[redacted], UK
Sand (> 50 µm) %	53.4	43.6
Silt (2-50 µm) %	33.0	27.3
Clay	13.6	29.1
Textural class	sandy loam	clay loam
OC %	5.8	2.7
CEC (meq/100 g)	55.5	15.3
pH water/KCl/$CaCl_2$	6.7/6.1/6.1	8.1/7.7/7.7
Total N mg/kg	2044	2324
Total P mg/kg	1485	1392
Biomass start/end µg C/g	131/295	7/128
Water OC content mg/L	2.2	5.5
Water pH	6.9	7.9
Water Redox potent. mV	386	215

Table 8.4.3.2-3: Degradation of ^{14}C-fosetyl in the [redacted] system (mean of 2 replicates, % AR)

DAT	CO_2	Water phase				Sediment extract				Bound	Recov
		Total	Fosetyl	Ethanol	Met A	Total	Fosetyl	Ethanol	Met A		
0		102.8	102.8	-	-	-	-	-	-	0	102.8
0.25	0.2	92.6	92.0	0.6	-	6.6	0.5	2.0	4.1	2.4	101.8
1	2.3	82.3	78.5	3.8	-	6.7	0.6	2.5	3.7	6.9	98.2
2	6.4	71.2	65.2	6.0	-	5.7	0.6	1.9	3.3	14.6	97.9
7	30.6	31.8	27.6	4.2	-	3.6	0.3	0.8	2.5	22.9	88.9
14	53.5	10.3	9.0	1.3	-	2.2		0.1	2.1	28.8	94.9
30	68.4	1.4	0.9	0.5	0.1	1.0	0.2	0.4	0.5	27.3	98.1
61	71.4	0.5	-	-	-	0.9	-	-	-	23.6	96.4
100	76.9	0.3	-	-	-	0.7	-	-	-	19.4	96.3

Table 8.4.3.2-4: Degradation of ^{14}C-fosetyl in the [redacted] system (mean of 2 replicates, % AR)

DAT	CO_2	Water phase				Sediment extract				Bound	Recovery
		Total	Fosetyl	Ethanol	Met A	Total	Fosetyl	Ethanol	Met A		
0		104.4	104.4	-	-	-	-	-	-	0	104.5
0.25	0.1	93.1	91.8	1.3	-	4.2	-	4.2	-	2.0	99.4
1	1.3	81.2	70.5	10.7	-	3.4	-	-	-	5.4	91.3
2	4.6	70.8	54.8	16.0	-	3.2	-	3.2	-	10.6	89.2
7	36.3	34.4	18.9	15.4	-	2.5	-	2.5	-	18.9	92.0
14	57.4	7.7	4.5	3.2	-	2.5	-	-	-	22.7	90.3
30	69.4	0.9	0.4	0.5	0.02	1.2	0.1	0.9	0.3	24.0	95.5
61	71.9	0.5	-	-	-	1.3	-	-	-	22.5	96.2
100	70.3	0.3	-	-	-	1.0	-	-	-	20.8	92.4

Table 8.4.3.2-5: Rate of degradation of fosetyl in water sediment systems (days)

		First order			KIM model		
		DT50	DT90	R^2	DT50	DT90	Fit
[redacted]	Water	3.75	12.5	0.94	2.1	10.3	0.99
	Whole system	3.9	12.9	0.93	2.1	10.3	0.99
[redacted]	Water	4.3	14.2	0.98	3.3	13.8	0.99
	Whole system	4.5	14.8	0.98	3.4	13.9	0.99

- **Conclusion**

Following application to water sediment systems, fosetyl is no longer detected in water after 30 d and negligible amounts are in sediment. The ethyl moiety is highly mineralized (70.3 to 75.9% after 100 d). The corresponding bound residue peaks at 24.0 to 28.8% after 14 to 30 d and is about 20% after 100 d. Ethanol is the main metabolite (max. 16% in water and 4.2% in sediment) and an unknown metabolite A can reach 4.1% in sediment. Both metabolites are transient. DT50 and DT90 for fosetyl are calculated to be 3.75 to 4.3 d and 12.5 to 14.2 d for water phase, and 3.9 to 4.5 d and 12.9 to 14.8 d for whole system, respectively. Phosphonic acid and Al ions are expected to be released from degradation of fosetyl (100% assumed in water). Due to adsorption, phosphorous acid is expected to be rapidly adsorbed on sediment (100% assumed) where it could be slowly oxidized to phosphate.

<u>Overall conclusion on study on water/sediment degradation of fosetyl-aluminium:</u>

The study was performed prior to the availability of OECD 308. However, BBA Guideline Part IV, 1990, was followed. The design following BBA was very near to the actual OECD 308 when considering the number of water/sediment systems, their origin and characterisation, handling till application of test substance, incubation and work-up including analysis.
In view of no major deviations observed or reported the study is still able to adequately describe the behavior of fosetyl-aluminium under conditions of water/sediment testing. In view of the rapid degradation observed being also a consequence of the simple structure the conduct of a new study to actual guidelines would not contribute to a better understanding of the active substance in the aquatic emvironment.

Report:	KCA 7.2.2.3/03 [redacted],; [redacted]; 2015; M-528987-01-1
Title:	Fosetyl-Al - Kinetic evaluation of aerobic aquatic metabolism in water / sediment systems according to FOCUS Kinetics using KinGUI 2
Report No.:	EnSa-15-0530
Document No.:	M-528987-01-1
Guideline(s):	Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Document Reference: None, version 1.1, 2015 amending 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

Degradation in total systems:

The kinetics of degradation in total systems was evaluated for fosetyl-aluminium (fosetyl-Al) and its metabolite ethanol from two datasets resulting from a two differing water/sediment systems with 1-^{14}C-labeled active substance at 20 °C (KCA 7.2.2.3/02).

For metabolite ethanol results of a combined modelling approach with active substance data were additionally considered.

The kinetic evaluation followed FOCUS guidance to derive values for the degradation in total sediment/water systems from best fits to measured data for use as modelling endpoints in aquatic exposure assessments. Analysis was performed for fosetyl-Al at Level I for total systems with results summarised in Table 7.2.2.3- 1.

For the active substance fosetyl-Al the kinetic evaluation resulted in a geometric mean value for the $DegT_{50}$ of 3.00 days in total systems for use as modelling endpoint (see Table 7.2.2.3- 1).

Table 7.2.2.3- 1: Total system $DegT_{50}$ values for fosetyl-Al according to FOCUS Level I

Water/Sediment system	Total system $DegT_{50}$ (days)	Kinetic model
[redacted]	3.68	SFO
[redacted]	2.44	SFO
Geometric mean a)	**3.00**	

* Study KCA 7.2.2.3 /02
a) Evaluation on the basis of SFO kinetic model

For metabolite ethanol the kinetic evaluation resulted in a geometric mean values for the $DegT_{50}$ in total systems of 1.98 days (see Table 7.2.2.3- 2).

Table 7.2.2.3- 2: Metabolite ethanol: Total system $DegT_{50}$ values for according to FOCUS Level I

Water/Sediment system	Total system DT_{50} (days)		Kinetic model
[redacted]	1.50 a)	6.02 b)	SFO
[redacted]	2.62 a)	n.a. b)	SFO
Geometric mean c)	**1.98**	**6.02**	

* Study KCA 7.2.2.3 /02
a) $DegT_{50}$ from fit with active substance data
b) $DisT_{50}$ from fit of decline from maximum data
c) Geometric mean in case of more than one value

Dissipation from water phase:
Considering the same set of data, the kinetic evaluation again followed FOCUS guidance to derive values for the dissipation from the water phase from best fits to measured data. Analysis was performed for fosetyl-Al at Level I for total systems with results summarised in Table 7.2.2.3- 3.

For the active substance fosetyl-Al the kinetic evaluation resulted in a geometric mean value for the $DisT_{50}$ of 9.4 days for the dissipation from the water phase (see Table 7.2.2.3- 3).

Table 7.2.2.3- 3: Values of the $DisT_{50}$ from water for fosetyl-Al according to FOCUS Level I

Water/Sediment system	Total system $DegT_{50}$ (days)	Kinetic model
[redacted]	3.64	SFO
[redacted]	2.44	SFO
Geometric mean [a)]	**2.98**	

* Study KCA 7.2.2.3 /02
a) Evaluation on the basis of SFO kinetic model

For metabolite ethanol the kinetic evaluation resulted in a geometric mean values for the $DisT_{50}$ from water of 6.77 days (see Table 7.2.2.3- 4).

Table 7.2.2.3- 4: Metabolite ethanol: Values of the $DisT_{50}$ from water for according to FOCUS Level I

Water/Sediment system	Total system $DegT_{50}$ (days)	Kinetic model
[redacted]	6.77	SFO
[redacted]	-	
Geometric mean [a)]	**6.77**	

* Study KCA 7.2.2.3 /02
a) Geometric mean in case of more than one value

Dissipation from sediment phase:
No values of the $DisT_{50}$ from sediment were calculated for fosetyl-Al or its metabolite ethanol since radioactive residues were below 5% AR in the test systems at all sampling intervals.

I. Material and Methods

For fosetyl-Al the kinetic evaluation was based on water/sediment data (KCA 7.2.2.3/02) conducted with 1-^{14}C-labeled fosetyl-aluminium in two different water/sediment systems (sandy loam [redacted]) and a clay loam sediment ([redacted]) and their associated water at 20 °C in the dark for a maximum of 100 days.
For the metabolite phosphonic acid a separate water/sediment study was performed (KCA 7.2.2.3/04) by applying non-labeled test substance to the test systems and the data kinetically evaluated in KCA 7.2.2.3/05.

Data pre-processing
Generally, replicates were taken into account separately. The data were checked for consistency and clear outliers. Data for non-extractable residues (NER) and CO_2 were not fitted within the evaluation (open system).

For the residues in the water the following procedure was applied:

- For data processing of day zero samples, radioactivity assigned to metabolites, non-extractable residues (NER) and CO_2 was added to the parent compound and thus metabolite concentrations were set to 0 %. Parent compound was attributed to the water phase only thus resulting in a value of zero for the sediment phase, since the test substance was applied to the water phase.
- Residues values below the limit of detection (LOD = 0.005% of AR) were set to 0.5 times the LOD for the first non-detect at the end of the curve. The curve could be cut at this time point in case of no later detects. For metabolites, the last non-detect at the beginning of a curve was set to 0.5 times the LOD for occurrences later than day 0.

<u>Kinetic models</u>

The inferring of kinetic degradation parameters followed the proposed metabolic pathway for 'carbon containing compounds' as given in Figure 7.2.2.3- 1.

Following the recommended procedure for determining modelling endpoints [FOCUS, 2006, 2011], all datasets were evaluated using SFO kinetics with free optimisation of parameters, along with FOMC, DFOP and HS kinetics where appropriate.

Each compound was represented by one compartment as the total of measured occurrences in water and sediment with no values associated with a sink compartment. Between compartments transformation reactions were assumed to proceed only one-way. The initial amount of the parent compound was free fitted and the initial amount for metabolites was fixed to a value of zero. All data were weighted equally thus corresponding to an absolute error model.

At least four kinetic models consisting of single first-order (SFO), first-order multiple-compartment (FOMC, Gustafson-Holden), double first-order in parallel (DFOP), and the hockey-stick (HS) model were available, in principle, according to the set of models proposed by FOCUS.

While best-fits should be taken to derive trigger or persistence endpoints SFO should be used to derive modeling input parameters if an acceptable fit can be obtained.

Before a use of bi-phasic kinetic models FOMC, DFOP and HS the following major cases were taken into account:

1. A check whether a degradation or dissipation to 10% of the initial amount M_0 was reached within experimental period, then the estimation of the DT_{50} could be simplified according to the relation $DT_{50} = DT_{90}/(\ln(10)/\ln(2))$. By this method the equivalent SFO-curve meets the bi-phasic curve at the time $DT_{90\text{ bi-phasic}}$ and consequently the residue values at earlier times are over-predicted.
2. In case a value of 10% for M_0 was not reached within the runtime of the study, however, FOMC should not be used to derive modelling endpoints.
3. In case a value of 10% for M_0 was not reached within the runtime of the study, the DT_{50} could be derived for DFOP and HS models from the slower part of the bi-phasic curve using the relation $DT_{50} = \ln(2)/k_2$.

The kinetic evaluations were performed according to the respective decision flowcharts for the determination modelling endpoints for parent (Level P-1) and metabolites and to result in dissipation kinetics in water and sediment. No evaluations according to Level II were performed since not regarded as mandatory. For lower-tier calculations or the comparison with persistence triggers a Level I evaluation of the dissipation may be often appropriate.

Contrary to the parent, for metabolites it may be often neither feasible nor meaningful to differentiate between SFO and the bi-phasic models, using Level I and a simultaneous fit of the complete metabolic pathway (i.e. considering formation and decline of metabolites). A bi-phasic approach would result in too many free parameters needed to describe such systems. Even for SFO the number of free parameters is often at the limit and the use of bi-phasic kinetics could easily multiply the number of free parameters.

Statistical evaluation

The identification of the most appropriate kinetic model for the description of experimental data according to FOCUS is mainly based on the three criteria of visual assessment of fits of calculated transformation curves to experimental data, the value of error of Chi-square (χ^2) test and a single-sided significance t-test.
The choice of the appropriate kinetic model was primarily based on visual assessment of the fit and the Chi^2- (χ^2-) error.
Within the current evaluation, single first-order (SFO) kinetics had been tested first, since SFO is being used as the simplest kinetic model almost exclusively in environmental exposure models. In case the SFO fit should not be visually acceptable or in case of a significant exceedance of value for χ^2-error of 15%, bi-phasic models were tested. Finally the model was chosen which was visually acceptable and provided a significantly better fit in terms of the χ^2-error.
The approach avoided the use of over-parameterised models simply and only being chosen on the basis of a marginally better fit. Finally it should be noted that a value of χ^2-error below 15% should only be considered as guidance and not as an absolute cut-off criterion. This is true, in particular, for the modelling of metabolite data with errors for χ^2 being higher, but with fits still representing a reasonable description of their formation and degradation behaviour.

The kinetic evaluations and the statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-squares (IRLS) optimisation.

II. Results and Discussion

The kinetic evaluation of water-sediment data was performed according to FOCUS Level I to result in degradation kinetics in total systems and in dissipation kinetics in water and sediment. No evaluations according to Level II were performed.
SFO and FOMC kinetics were initially applied to all datasets. FOMC showed some improvement over SFO kinetics for all datasets, but DFOP proved to be most adequate for some datasets of the active substance. For metabolite ethanol, SFO kinetics was derived as best-fit in a first approach, with no improvement when following FOMC according to the acceptance criteria set.

Degradation in total systems:
For the active substance fosetyl-Al, values of the DegT$_{50}$ from total systems were detailed in Table 7.2.2.3- 5 for system [redacted] and Table 7.2.2.3- 6 for system [redacted]. Following FOCUS Guidance the various approaches and the corresponding evaluations were summarized for metabolite ethanol in Table 7.2.2.3- 7 to Table 7.2.2.3- 12.

Table 7.2.2.3- 5: Values of the DegT$_{50}$ in total system [redacted] for fosetyl-Al according to FOCUS Level I

Kinetic model	DT$_{50}$ (days)	DT$_{90}$ (days)	M$_0$ (%)	k$_1$ / α	k$_2$ / β	tb / g	P k$_1$ / α	P k$_1$ /β	VA$^{a)}$	Chi² (%)
SFO	3.68	12.22	98.5	0.188	-	-	<0.01	-	+	3.38
FOMC	3.35	13.87	100.2	3.899	17.235	-	<0.01	0.02	++	2.49
DFOP	3.48	12.89	102.8	4.271	0.171	0.094	0.03	<0.01	++	0.63
HS	3.32	13.41	100.3	0.221	0.160	2.671	<0.01	<0.01	++	2.62

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually acceptable accompanied by low error for Chi^2. Fit appropriate as modelling endpoint.
Slightly better fit from FOMC model thus DFOP and HS tested in addition. DFOP as best fit and chosen for trigger endpoint evaluation.
Conclusion DegT$_{50}$ in total system: Trigger endpoint: 3.48 days (DFOP)
Modelling endpoint: 3.68 days (SFO)

Table 7.2.2.3- 6: Values of the $DegT_{50}$ in total system [redacted] for fosetyl-Al according to FOCUS Level I

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	2.44	8.12	99.7	0.284	-	-	<0.01	-	+	5.52
FOMC	2.14	10.29	102.5	2.391	6.354	-	<0.01	0.01	++	2.87
DFOP	2.23	9.84	104.4	1.918	0.211	0.206	0.04	<0.01	++	0.32
HS	2.28	9.89	103.2	0.390	0.211	1.180	<0.01	<0.01	++	1.66

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually acceptable accompanied by low error for Chi². Fit appropriate as modelling endpoint.
Slightly better fit from FOMC model thus DFOP and HS tested in addition. DFOP as best fit and chosen for trigger endpoint evaluation.
Conclusion $DegT_{50}$ in total system: Trigger endpoint: 2.23 days (DFOP)
Modelling endpoint: 2.44 days (SFO)

Table 7.2.2.3- 7: Metabolite ethanol: Values of the $DisT_{50}$ in total system [redacted] according to FOCUS Level I (SFO); decline from maximum in total system

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	6.0	20.0	8.0	0.1152	-	-	<0.01	-	o	10.5
FOMC	6.0	20.0	8.0	73.320	632.00	-	0.49	0.01	o	13.1

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually acceptable accompanied by low error for Chi². Fit appropriate as modelling endpoint.
No better fit from FOMC model.
Conclusion $DisT_{50}$ in total system: Trigger endpoint: 6.02 days (SFO)
Modelling endpoint: 6.02 days (SFO)

Table 7.2.2.3- 8: Metabolite ethanol: Values of the $DisT_{50}$ in total system [redacted] according to FOCUS Level I (SFO); decline from maximum in total system

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	7.5	24.8	20.9	0.0927	-	-	0.09	-	o	24.6
FOMC	7.5	24.8	20.9	12744	137485	-	0.19	<0.01	o	30.7

a) VA: Visual assessment: + = good, o = moderate, - = poor
No visually and statistically acceptable fit could be derived from use of SFO or FOMC kinetic model. DFOP or HS could not be used due to four sampling intervals only.
Conclusion: Not used for trigger or modelling endpoint calculation

Table 7.2.2.3- 9: Metabolite ethanol: Values of the $DegT_{50}$ in total system [redacted] according to FOCUS Level I (SFO); combined fit with active substance (DFOP); all parameters free

Kinetic model	DT_{50} (days)	DT_{90} (days)	k_1	ff	t-test (k)	Std error ff			VA[a)]	Chi² (%)
SFO	1.5	5.0	0.4635	0.3466	<0.01	0.0328			+	9.3

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually acceptable accompanied by low error for Chi². Fit appropriate as modelling endpoint.
Conclusion $DegT_{50}$ in total system: Trigger endpoint: 1.50 days (FFO)
Modelling endpoint: 1.50 days (SFO); ff = 0.347

Table 7.2.2.3- 10: Metabolite ethanol: Values of the $DegT_{50}$ in total system [redacted] according to FOCUS Level I (SFO); combined fit with active substance (DFOP); all parameters free

Kinetic model	DT_{50} (days)	DT_{90} (days)	k_1	ff	t-test (k1)	Std error ff			VA[a)]	Chi² (%)
SFO	3.31	11.0	0.2093	0.4595	<0.01-	0.069			o	18.46

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit for metabolite statistically not acceptable.
Conclusion: Not used for trigger or modelling endpoint calculation

Table 7.2.2.3- 11: Metabolite ethanol: Values of the $DegT_{50}$ in total system [redacted] according to FOCUS Level I (DFOP); combined fit with active substance (DFOP); only metabolite parameters fitted

Kinetic model	DT_{50} (days)	DT_{90} (days)	k_1	K_2	g	ff	t-test (k1)	t-test (k2)	Std error ff	VA[a)]	Chi² (%)
DFOP	0.06	7.7	224600	0.2094	0.4933	0.9075	<0.01	<0.01	0.0371	o	23.23

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit for metabolite statistically not acceptable.
Conclusion: Not used for trigger or modelling endpoint calculation

Table 7.2.2.3- 12: Metabolite ethanol: Values of the $DegT_{50}$ in total system [redacted] according to FOCUS Level I (SFO); combined fit with active substance (SFO); all parameters free

Kinetic model	DT_{50} (days)	DT_{90} (days)	k_1	ff	t-test (k)	Std error ff			VA[a)]	Chi² (%)
SFO	2.62	8.7	0.26482	0.5795	<0.01	0.084			+	11.33

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit acceptable accompanied by low error for Chi². Fit appropriate as trigger and modelling endpoint.
Conclusion $DegT_{50}$ in total system: Trigger endpoint: 2.62 days (FFO)
Modelling endpoint: 2.62 days (SFO), ff = 0.580

Dissipation from water phase:

For the active substance fosetyl-Al, values of the $DisT_{50}$ from water were summarized more detailed in Table 7.2.2.3- 13 (system [redacted]) and Table 7.2.2.3- 14 (system [redacted]). Following FOCUS Guidance the various approaches and the corresponding evaluations were summarized for metabolite ethanol in Table 7.2.2.3- 15 and Table 7.2.2.3- 16.

Table 7.2.2.3- 13: Values of the DisT50 from water system [redacted] for fosetyl-Al according to FOCUS Level I

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	3.64	12.10	98.2	0.190	-	-	<0.01	-	+	3.64
FOMC	3.30	13.84	100.0	3.679	15.913	-	<0.01	0.02	+	2.70
DFOP	3.43	12.82	102.8	4.3954	0.171	0.100	0.02	<0.01	++	0.67
HS	3.24	13.39	100.1	0.225	0.159	2.711	<0.01	<0.01	++	2.84

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually acceptable accompanied by low error for Chi². Fit appropriate as modelling endpoint.
Slightly better fit from FOMC model thus DFOP and HS tested in addition. DFOP as best fit and chosen for trigger endpoint evaluation.
Conclusion $DegT_{50}$ in total system: Trigger endpoint: 3.43 days (DFOP)
Modelling endpoint: 3.64 days (SFO)

Table 7.2.2.3- 14: Values of the $DisT_{50}$ from water system [redacted] for fosetyl-Al according to FOCUS Level I

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	2.44	8.12	99.7	0.284	-	-	<0.01	-	+	5.52
FOMC	2.14	10.28	102.5	2.401	6.386	-	<0.01	0.02	++	2.89
DFOP	2.23	9.84	104.4	1.919	0.211	0.205	0.03	<0.01	++	0.26
HS	2.28	9.89	103.2	0.390	0.212	1.180	<0.01	<0.01	++	1.65

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually acceptable accompanied by low error for Chi². Fit appropriate as modelling endpoint.
Slightly better fit from FOMC model thus DFOP and HS tested in addition. DFOP as best fit and chosen for trigger endpoint evaluation.
Conclusion $DegT_{50}$ in total system: Trigger endpoint: 2.23 days (DFOP)
Modelling endpoint: 3.68 days (SFO)

Table 7.2.2.3- 15: Metabolite ethanol: Values of the $DisT_{50}$ from water system [redacted] according to FOCUS Level I (SFO)

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	6.8	22.5	6.2	0.1024	-	-	0.02	-	+	10.2
FOMC	6.8	22.5	6.2	13940	136200	-	0.09	<0.01	+	12.8

a) VA: Visual assessment: + = good, o = moderate, - = poor
SFO fit visually and statistically better fit than FOMC model. Fit appropriate as trigger and modelling endpoint
Conclusion $DegT_{50}$ in total system: Trigger endpoint: 6.77 days (SFO)
Modelling endpoint: 6.77 days (SFO)

Table 7.2.2.3- 16: Metabolite ethanol: Values of the $DisT_{50}$ from water system [redacted] according to FOCUS Level I (SFO)

Kinetic model	DT_{50} (days)	DT_{90} (days)	M_0 (%)	k_1 / α	k_2 / β	tb / g	P k_1 / α	P k_1 /β	VA[a)]	Chi² (%)
SFO	7.7	25.5	17.7	0.0903	-	-	0.09	-	o	24.9
FOMC	7.7	25.5	17.7	8243.9	9243	-	0.19	<0.01	o	31.1

a) VA: Visual assessment: + = good, o = moderate, - = poor
No visually or statistically acceptable fits from use of SFO or FOMC kinetic model.
Conclusion: Not used for trigger or modelling endpoint calculation

Dissipation from sediment:
No values of the $DisT_{50}$ from sediment were calculated for fosetyl-Al or its metabolite ethanol since radioactive residues were below 5% AR in the test systems at all sampling intervals.

III. Conclusion

Kinetic evaluation for total systems:
For the active substance fosetyl-Al good model fits were derived by an SFO approach for each of the two systems to result in a geometric mean value for the $DegT_{50}$ of 3.0 days.
For metabolite ethanol a good model fit was derived by an SFO approach for each of the two systems to result in a geometric mean value for the $DegT_{50}$ of 1.98 days. For system [redacted], a $DegT_{50}$ of 6.02 days was derived by use of the SFO model and a decline from maximum approach.

Kinetic evaluation for dissipation from water phase:
For the active substance fosetyl-Al good model fits were derived by an SFO approach for each of the two systems to result in a geometric mean value for the $DisT_{50}$ of 2.98 days.

For metabolite ethanol a good model fit was derived by an SFO approach for one system to result in $DisT_{50}$ of 6.77 days for system [redacted] while no $DisT_{50}$ could be derived for system [redacted] via this approach.

Kinetic evaluation for dissipation from the sediment:
No values of the $DisT_{50}$ from sediment were calculated for the active substance fosetyl-Al or its metabolite ethanol since radioactive residues were below 5% AR in the test systems at all sampling intervals.

The results can therefore be used as input parameters for modelling in environmental risk assessments.

Report:	KCA 7.2.2.3/04 [redacted],; [redacted]; 2005; M-251520-01-1
Title:	Phosphorous acid: Aerobic aquatic metabolism
Report No.:	C048583
Document No.:	M-251520-01-1
Guideline(s):	OECD: 308, (2002); SETAC: March 1995
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The biotransformation of non-labelled phosphonic acid was studied in two differing water-sediment systems [redacted] and [redacted] at 20 ± 2 °C in the dark for 76 days in maximum.

For system [redacted], dissipation from water was documented by a decline from 100% by day zero to 0.7% of the initial concentration after 76 days of incubation. Dissipation from sediment was indicated by a decline from 100% by day zero to 34.5% of the initial concentration after 150 days of incubation.
For system [redacted], dissipation from water was observed by a decline from 100% by day zero to 0.9% of the initial concentration after 29 days of incubation. Dissipation from sediment was from 100% by day zero to 37.5% of the initial concentration after 150 days of incubation.

Half-lives for the dissipation from the water were calculated to 9.2 days for system [redacted] and 3.3 days for [redacted], both determined from best fits to measured data following application of the SFO kinetic model.
Half-lives for the dissipation from sediment were calculated to 105 days for system [redacted] and 98 days for [redacted], both resulting from best fits following application of the SFO kinetic model.

I. Material and Methods

A. Materials

1. Test Material: Phosphonic acid, phosphorous acid
Purity: 98% / 99.8%
Lot/Batches No. A015546301 / A017963001 (Acros Organics)
Sample ID: none

2. Test System:

The study was carried out with two contrasting water/sediment systems collected at two locations in Germany. Sediment and its associated water were each collected from the same area. While system "[redacted]" originated from the standing water of a pond, system "[redacted]" was from an artificially dammed creek and thus originating from flowing water. No pesticide was applied to or around either area prior to collection. Sediments and water were collected from the top 0 to 20 cm and

stored at ambient temperature overnight prior to further processing. Before set-up of samples, the wet sediment was passed through a 2 mm sieve by use of the associated water. The characteristics of the sediments and their associated water are summarised in Table 7.2.2.3- 17 and Table 7.2.2.3- 18.

Table 7.2.2.3- 17: Physico-chemical characteristics of water

Water	[redacted]	[redacted]
Temperature at collection (°C)	4.3	1.8
pH at sampling	7.6	7.1
Hardness (degrees German hardness)	10.1	3.2
Oxygen concentration at collection (% saturation)	101.3	95.5
Total Organic Carbon (TOC, mg/L) Initial, day zero Final, day 76	 <2 6	 18 8
Dissolved Organic Carbon (DOC, mg/L)	<2	<2
Total phosphorous (mg/L)	<0.03	0.23
Total nitrogen (mg/L)	5.0	5.4
Redox potential at collection (mV)	120	130

Table 7.2.2.3- 18: Physico-chemical characteristics of associated sediments

Sediment	[redacted]	[redacted]
Geographic location	[redacted] Germany	[redacted], Germany
Latitude and longitude	not reported	not reported
Texture class [USDA]	sand	silt loam
Sand (2000-50 µm); (%) Silt (50-2 µm); (%) Clay (< 2 µm); (%)	95.1 4.2 0.7	24.6 59.4 16.0
pH (0.01 M $CaCl_2$) pH (water)	6.6 7.1	5.2 5.5
Organic matter (%) - Before filling into vessels - Initial, i.e. day zero samples - At termination, day 76	 1.5 1.4 1.1	 9.6 8.6 9.6
Organic carbon (%) - Before filling into vessels - Initial, i.e. day zero samples - At termination, day 76	 0.85 0.81 0.62	 5.57 4.97 5.59
Microbial biomass (mg/kg dry weight) Post collection Initial, day zero Final, day 76, without test substance Final, day 76, including test substance	 16 14 7 6	 43 42 25 27
Cation exchange capacity (meq/100 g sediment)	3.7	17.7
Total nitrogen (%)	0.08	0.39
Total phosphorus (mg P/kg dry weight)	148	653
Dry matter content (%)	78	33

B. Study design

1. Experimental conditions:

The tests were performed in individual glass cylinders as test vessels filled with sieved sediment to a depth of 2 cm. Associated water was added to each test vessel up to a depth of 6 cm above the

sediment to result in a sediment-to-water ratio of 1:3 (v/v). The test vessels were pre-incubated at 20 ± 2 °C in the dark for 6 days in order to equilibrate the systems with regard to oxygen content, pH, redox potential and phase separation. During periods of acclimation and incubation the water phase was aerated by gentle agitation of the water phase by an orbital shaker.
The nominal initial test concentration of 4.87 mg test substance/L was derived by assuming a ten-fold factor for analytical reasons for the originally calculated dose. This resulted when assuming full overspray at the maximum single application rate of 7 kg/ha for the active substance fosetyl-aluminium being equivalent to 4.87 kg phosphonic acid/ha. Assuming full overspray this translated into a test concentration of 487 µg phosphonic acid/L for a water depth of 100 cm. The actual test concentrations was about 5 mg test substance/L to result in a dose of 2 mg applied per test vessel.
Following decantation, the water phase was analysed at each sampling interval.

Background levels of phosphate were determined to 250 to 600 mg/kg for the two sediments. This level was too high for the analytical method applied to differentiate between the background level and the phosphate formed from application of phosphonic acid. The study design was therefore amended: Following decantation of the water phase from test vessels the remaining sediment was treated by a second application with 2 g phosphorous acid per test vessel corresponding to test concentrations of about 10 g/kg sediment for [redacted] and 35 g/kg sediment for [redacted].
Each sample was dosed by applying an aqueous solution of phosphonic acid dropwise onto the water surface or sediment surface, respectively.
Two replicates were prepared for each sampling interval. The water/sediment samples were incubated under static conditions (gentle shaking of test vessels, test flasks permeable to air) at 20 ± 2 °C for a maximum period of 76 days. The sediment was incubated at 20 ± 2 °C in the dark for 150 days in maximum after a second application at the higher dose.
Non-sterile, untreated samples were prepared in parallel for each water/sediment system for monitoring of total organic carbon (TOC) in the water and the microbial biomass in the sediment phase, respectively. One sample per water/sediment system was analyzed at time zero and after 76 days of incubation.

2. Sampling:
Duplicate samples of both systems were removed for analysis of water after 0, 1, 3, 7, 14, 29 and 76 days of incubation. Duplicate samples of both systems were removed for analysis of sediment after 28/30, 70/73, 120 and 150 days of incubation.

3. Analytical procedures:
At each sampling interval for water analysis, the dissolved oxygen content was measured in the water. In addition, the pH and redox potential was determined in the water phase and the sediment.
Water and sediment were separated by decantation. Following the second application of sediment and incubation an aliquot was extracted with 2N aqueous sulfuric acid by gentle boiling the suspension for 30 min.
Water samples and sediment extracts were analysed for phosphate and for phosphonic acid ('total oxidizable portion of phosphorous') by oxidation (sulfuric acid/peroxodisulfate) to phosphate. Analysis for both compounds was by colorimetric determination at a wave length of 880 nm in the form of molybdate blue. The LOQ of the colorimetric analytical method was estimated to 0.1% in water and to 1 g/kg in sediment. For phosphate the LOQ in sediment was estimated to 1 g/kg.

C. Determination of degradation kinetics:

Dissipation rates from the water phase after the first application and, from sediment after the second application were calculated by use of the software ModelManager, version 1.1. A separate kinetic analysis of the water phase and the sediment degradation data was performed according to FOCUS kinetics in another report in order to derive input data for modelling within aquatic environmental risk

assessments (KCA 7.2.2.3/05).

II. Results and Discussion

A. Findings

The anticipated test conditions were maintained throughout the incubation period each after application of the test substance.
The pH in the water of system [redacted] remained constant at 7.3 at start (day zero) and at the last sampling interval, day 76. The pH in the water of system [redacted] showed a negligible decrease from 6.4 by day zero to 6.2 at the last sampling interval.
Measurements of the redox potential in water and sediment and the oxygen content in the water indicated aerobic conditions for both water/sediment systems during incubation (see Table 7.2.2.3- 19 and Table 7.2.2.3- 20).
The results of microbial biomass determinations in sediments showed that biological activity of the test systems was given during the entire incubation period. From lower values of biomass after 76 days of incubation some trend for a reduction could be derived for both systems. The decrease may be regarded as a typical situation within laboratory tests on soils and sediments with microbial activity suffering from a lack of nutrients under the 'closed' conditions in test flasks and separated from the outdoor environment.

Table 7.2.2.3- 19: Measurements of dissolved oxygen, pH and redox potential in system [redacted]

Sampling interval * (day)	Water			Sediment	
	O_2-Sat. (%)	pH	E_{obs} (mV)	pH	E_{obs} (mV)
-6	95.8 / 98.4	7.9 / 8.0	197 / 196	7.2 / 7.2	174 / 197
-5	94.4 / 93.8	7.9 / 8.0	172 / 170	7.2 / 7.3	170 / 76
-4	91.3 / 92.4	8.1 / 8.1	204 / 197	7.5 / 7.6	63 / 167
-1	86.1 / 89.2	8.0 / 8.0	207 / 253	7.2 / 7.3	290 / 183
0	75.7 / 76.0	7.7 / 7.7	202 / 180	7.3 / 7.2	45 / 131
1	78.9 / 77.8	7.9 / 8.0	188 / 163	7.3 / 7.2	172 / 160
3	78.7 / 78.1	8.0 / 8.1	170 / 204	7.4 / 7.4	168 / 177
7	80.7 / 78.5	8.2 / 8.2	195 / 199	7.4 / 7.1	194 / 202
14	81.5 / 81.2	8.2 / 8.2	197 / 192	6.9 / 6.7	165 / 92
29	91.6 / 91.2	8.3 / 8.3	185 / 209	7.0 / 7.3	287 / 200
76	81.0 / 80.4	8.0 / 8.0	203 / 265	7.6 / 7.0	226 / 236

E_{obs} = Redox potential as measured with reference electrode (Ag/AgCl). The redox potential referring to the hydrogen standard electrode (E_h) results from the sum of the measured value (Eobs) and a fixed value of +197 mV for the potential of the reference electrode used (E_{ref}), i.e. $E_h = E_{obs} + E_{ref}$.

Table 7.2.2.3- 20: Measurements of dissolved oxygen, pH and redox potential in system [redacted]

Sampling interval * (day)	Water			Sediment	
	O_2-Sat. (%)	pH	E_{obs} (mV)	pH	E_{obs} (mV)
-6	98.6 / 99.4	7.0 / 6.5	203 / 190	6.4 / 6.2	55 / 55
-5	96.8 / 96.0	6.6 / 6.4	208 / 175	6.2 / 6.2	24 / 39
-4	95.0 / 95.5	6.7 / 6.6	180 / 207	6.2 / 6.2	60 / 165
-1	85.6 / 87.0	6.5 / 6.4	192 / 199	6.4 / 6.3	151 / 144
0	75.9 / 77.0	5.8 / 5.7	208 / 198	6.3 / 6.5	83 / 162
1	79.5 / 79.6	6.3 / 6.3	206 / 146	6.2 / 6.2	154 / 95
3	80.2 / 82.0	6.5 / 6.6	197 / 197	6.1 / 6.2	122 / 80
7	79.9 / 81.4	7.2 / 6.9	198 / 202	6.5 / 6.4	141 / 115
14	79.6 / 77.2	7.7 / 8.3	196 / 188	6.3 / 6.3	148 / 27
29	91.0 / 88.6	7.8 / 7.3	175 / 193	6.3 / 6.0	62 / 40
76	76.8 / 73.8	7.6 / 7.3	212 / 204	6.0 / 6.4	81 / 59

E_{obs} = Redox potential as measured with reference electrode (Ag/AgCl). The redox potential referring to the hydrogen standard electrode (E_h) results from the sum of the measured value (Eobs) and a fixed value of +197 mV for the potential of the reference electrode used (E_{ref}), i.e. $E_h = E_{obs} + E_{ref}$.

B. Data

For system [redacted] the results of determination of total recovered test substance was summarized in Table 7.2.2.3- 21 for the dissipation from water and in Table 7.2.2.3- 22 for the sediment. The corresponding data was summarized for system [redacted] in Table 7.2.2.3- 23 and Table 7.2.2.3- 24.

Table 7.2.2.3- 21: Biotransformation of phosphonic acid in water of system [redacted] at 20 °C

Compound	Sampling interval (day)						
Phosphorous acid	0	1	3	7	14	29	76
Replicate A (mg/L)	6.76	6.49	4.64	4.48	2.55	0.30	<LOQ*
Replicate B (mg/L)	7.55	5.90	5.46	4.45	2.83	0.17	<LOQ*
Mean concentration (mg/L)	7.16	6.20	5.05	4.47	2.69	0.24	0.05**
% of initial concentration	100	86.6	70.5	62.4	37.6	3.3	0.7

* LOQ = 0.1 mg/L
** Value of half of LOQ

Table 7.2.2.3- 22: Biotransformation of phosphonic acid in sediment of system [redacted] at 20 °C

Compound	Sampling interval (day)				
Phosphorous acid	0	28	73	120	150
Replicate A (mg/L)	-	1.70	1.66	0.82	0.77
Replicate B (mg/L)	-	1.70	1.51	0.72	0.61
Mean concentration (mg/L)	2.0	1.70	1.59	0.77	0.69
% of initial concentration	100	85.0	79.3	38.5	34.5

Table 7.2.2.3- 23: Biotransformation of phosphonic acid in water of system [redacted] at 20 °C

Compound	**Sampling interval (day)**						
Phosphorous acid	**0**	**1**	**3**	**7**	**14**	**29**	**76**
Replicate A (mg/L)	5.72	3.77	2.40	1.04	1.43	<LOQ*	<LOQ*
Replicate B (mg/L)	5.67	3.85	2.43	1.32	1.65	<LOQ*	<LOQ*
Mean concentration (mg/L)	5.70	3.81	2.42	1.18	1.54	0.05**	0.05**
% of initial concentration	100	66.9	42.4	20.7	27.0	0.9	0.9

* LOQ = 0.1 mg/L
** Value of half of LOQ

Table 7.2.2.3- 24: Biotransformation of phosphonic acid in sediment of system [redacted] at 20 °C

Compound	**Sampling interval (day)**				
Phosphorous acid	**0**	**28**	**73**	**120**	**150**
Replicate A (mg/L)	-	1.49	1.36	0.73	0.77
Replicate B (mg/L)	-	1.52	1.15	0.74	0.73
Mean concentration (mg/L)	2.0	1.51	1.26	0.74	0.75
% of initial concentration	100	75.3	62.8	36.8	37.5

C. Mass balance

No full mass balances were determined due to the use of non-labelled test substance.

D. Residues in water and extractable residues in sediment:

In [redacted] water/sediment systems, total recovered phosphonic acid in the water phase decreased from 100% at day zero to 0.7% at the last sampling interval (day 76). The total recovered residues in the sediment decreased from 100% by day zero to 34.5% after 150 days of incubation.
In [redacted] systems, total recovered phosphonic acid in the water phase decreased from 100% at day zero to 0.9% after 29 days of incubation. Total recovered residues in the sediment decreased from 100% by day zero to 37.5% after 150 days of incubation.

E. Volatilisation

No volatile products were determined due to the use of non-labelled test substance.

F. Transformation of test substance:

Phosphonic acid undergoes bacteria-mediated oxidation to phosphate as demonstrated in various publications. Although the study design was altered by application of exaggerated levels of phosphonic acid, this was not documented by correspondingly higher phosphate levels determined in sediment samples. This result can be explained by the fact that the phosphonic acid transformed can be taken up directly as a nutrient by microbes thus being not detectable in the free form as phosphate in the samples.

G. Degradation kinetics:

The evaluation of degradation kinetics from the water and the sediment was performed by use of the software ModelManager (Environmental Kinetics, Version 1.1). The data were kinetically evaluated by use of the simple first order (SFO) model. The results of the kinetic evaluation are provided in Table 7.2.2.3- 25.

The dissipation half-life of phosphonic acid from water was estimated to 9.2 days for system [redacted] and 3.3 days for system [redacted]. The corresponding values of the DT_{90} were 31 days for system [redacted] and 11 days for system [redacted].

The dissipation half-life of phosphonic acid from sediment was estimated to 105 days for system [redacted] and 98 days for system [redacted]. The corresponding values of the DT_{90} were 349 days for system [redacted] and 327 days for system [redacted].

Degradation kinetics was also evaluated in a separate report to derive input parameters for modeling purposes in environmental exposure assessments. These results are presented under KCA 7.2.2.3/05. .

Table 7.2.2.3- 25: Kinetic evaluation of the dissipation of phosphonic acid from water and sediment after incubation at 20 °C

System	Matrix	Label position	Kinetic model	DT_{50} (days)	DT_{90} (days)	r^2
[redacted]	Water phase	-	SFO	9.2	31	0.982
	Sediment	-	SFO	105	349	0.902
[redacted]	Water phase	-	SFO	3.3	11	0.916
	Sediment	-	SFO	98	327	0.969

Best fits according to the criteria set are marked bold.

III. Conclusion

Once applied to water surfaces phosphonic acid is rapidly eliminated from the water phase presumably *via* sorption processes to the sediment. The processes are paralleled by a microbial oxidation to result in formation of phosphate taken up as nutrient. Following sorption to sediment the transformation to phosphate proceeded more slowly.

The data were evaluated by use of the simple first order (SFO) kinetic model to result in half-lives for the dissipation from water of 9.2 days ([redacted]) and 3.3 days ([redacted]).

For the dissipation from sediment, the corresponding half-lives were 105 days for the sandy system [redacted] and 98 days for the silt loam system [redacted].

Data for the dissipation of phosphonic acid from sediment should be regarded as worst case since samples had to be clearly overdosed for analytical reasons. The conversion of phosphonates to form phosphate as nutrient is expected to be significantly faster at the lower concentrations in aquatic systems of the environment.

Request from the RMS:
Please note that the design of the study by [redacted] and [redacted] (2005) is not suitable for the derivation of degradation data in the whole water/sediment system. No reliable degradation data usable in FOCUS modelling can be derived from this study.

Response from BCS:

The study by [redacted].; [redacted]; 2005; M-251520-01-1 (KCA 7.2.2.3/04) deviated from standards in water/sediment testing regarding two aspects:

(a) Concentrations of phosphonic acid in the sediment have not been determined following incubation in the initial phase of the study, while

(b) Degradation tests performed for phosphonic acid separately in isolated sediments after initial incubation are not a standard procedure in water/sediment testing.

Nevertheless, the study is able to clearly show that phosphonic acid dissipated fast (DT_{50} = 3.3 and 9.2 days) from the water to the sediment. For degradation in sediment incubated separately, a DT_{50} of ~100 days was determined. As a conservative interpretation, the sediment phase was demonstrated to be the main compartment for degradation of phosphonic acid in the water/sediment system and the corresponding DT_{50} value can be used for surface water risk assessment.

Dissipation from water in terms of the DT_{50} was shown to be significantly faster than DT_{50} for degradation in the sediment. The degradation in sediment thus allows also for a good estimate for the degradation in total systems. The degradation rate for the water phase is uncertain, however, it does not play a significant role due to fast transport to sediment. Overall, the study results can be summarised as follows: Phosphonic acid is transported from the water phase to the sediment where it declines with a DT_{50} of ~100 days. The transport from water to sediment can be described by TOXSWA without the necessity of special input parameters.

Report:	KCA 7.2.2.3/05 [redacted].; 2010; M-369224-01-1
Title:	Kinetic evaluation of an aerobic aquatic metabolism study of phosphorous acid according to FOCUS using KinGUI - Following a request by French AFSSA
Report No.:	MEF-10/303
Document No.:	M-369224-01-1
Guideline(s):	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 kinetics of dissipation of phosphonic acid from water and sediment was evaluated from data of tests performed in two water/sediment systems with non-labelled test substance (KCA 7.2.2.3/04).

The kinetic evaluation followed FOCUS guidance to derive values for the dissipation each in water and sediment from best fits to measured data for use as modelling endpoints in aquatic exposure assessments. Analysis was performed for fosetyl-aluminium at Level I with results summarised in Table 7.2.2.3- 26 and Table 7.2.2.3- 27.

SFO kinetics was applied to all datasets as the best-fit.

The kinetic evaluation for the dissipation of phosphonic acid from water resulted in a geometric mean value for the $DisT_{50}$ of 5.5 days (see Table 7.2.2.3- 26). For the dissipation from sediment a geometric mean value for the $DisT_{50}$ of 101.6 days was derived (see Table 7.2.2.3- 27).

Table 7.2.2.3- 26: Modelling endpoint: Values of the $DisT_{50}$ from water for phosphonic acid according to FOCUS Level I

System	DT_{50} (days)	DT_{90} (days)
[redacted]	9.2	30.6
[redacted]	3.3	10.9
Geometric mean	**5.5**	

Table 7.2.2.3- 27: Modelling endpoint: Values of the DisT$_{50}$ from sediment for phosphonic acid according to FOCUS Level I

System	DT$_{50}$ (days)	DT$_{90}$ (days)
[redacted]	105.0	349
[redacted]	98.4	327
Geometric mean	**101.6**	

I. Material and Methods

The kinetic evaluation was based on data of water/sediment study KCA 7.2.2.3/04 conducted with non-labelled phosphonic acid in two contrasting water/sediment systems (sandy loam [redacted] and silt loam [redacted] and their associated water at 20 °C in the dark for a maximum of 76 days for the dissipation from water and 150 days for the dissipation from sediment. Time zero residues for phosphonic acid had been reported and were set to 100%. Following the recommended procedure for determining modelling and persistence endpoints, [FOCUS, 2006], all datasets were evaluated using SFO kinetics with free optimisation of parameters.

The determinations of the kinetic values followed the recommendations of FOCUS guidance [FOCUS, 2006] to derive DT$_{50}$ values for use as model input. The kinetic evaluations were performed according to the respective decision flowcharts for the determination of trigger and modelling endpoints for parent (Level P-1) [FOCUS, 2006].
The identification of the most appropriate kinetic model for the description of experimental data according to FOCUS was mainly based on the three criteria of visual assessment of fits of calculated transformation curves to experimental data, the value of error of Chi-square (χ^2) test and a single-sided significance t-test.
Within the current evaluation, the single first-order (SFO) kinetic model was applied to all data sets.
The kinetic evaluations and the statistical calculations were performed with the software KinGUI (version 1.1).

II. Results and Discussion

The kinetic evaluation of the data was performed according to FOCUS Level I to result in dissipation kinetics from the water phase and the sediment for phosphonic acid. No evaluations according to Level II were performed. SFO kinetics was applied to all datasets thus to serve as best-fit to derive modelling inputs.

For phosphonic acid, values of the DT$_{50}$ in water according to SFO kinetics were summarized in Table 7.2.2.3- 28. The corresponding values of the DT$_{50}$ in sediment were summarized in Table 7.2.2.3- 29.

Table 7.2.2.3- 28: DT$_{50}$-values for phosphonic acid in water as modelling input according to FOCUS Level I (SFO)

Sediment system	Label position	DT$_{50}$ (days)	DT$_{90}$ (days)	Chi² (%)	t-test	VA[a)]
[redacted]	-	9.2	30.6	7.49	0.00024	n. r.
[redacted]	-	3.3	10.9	20.85	0.008	n. r.
Geometric mean		**5.5**				

Study KCA 7.2.2.3/04
a) VA: Visual assessment: + = good, o = moderate, - = poor
n.r. = not reported

Table 7.2.2.3- 29: DT_{50}-values for phosphonic acid in sediment as modelling input according to FOCUS Level I (SFO)

Sediment system	Label position	DT_{50} (days)	DT_{90} (days)	Chi² (%)	t-test	VA[a)]
[redacted]	-	105	349	9.71	0.0096	n. r.
[redacted]	-	98.4	327	5.36	0.0016	n. r.
Geometric mean		**101.6**				

Study KCA 7.2.2.3/04
a) VA: Visual assessment: + = good, o = moderate, - = poor
n.r. = not reported

III. Conclusion

The kinetic modelling evaluations for phosphonic acid following the SFO model resulted in acceptable fits.
The kinetic evaluation resulted in geometric mean DT_{50}-values of 5.5 days for the dissipation from water and of 101.6 days for the dissipation from sediment.

The results can therefore be used as input parameters in environmental risk assessments.

Study summaries of existing studies and publications on water/sediment studies of the active substance:

Following another request by the RMS, this document was updated by inclusion of summaries for the existing data, i.e. studies and publications submitted and evaluated during the process of Annex I inclusion of fosetyl under Directive 91/414/EEC and being still of relevance for the EU approval renewal process.

Report:	KCA 7.2.2.3/01 [redacted]; [redacted]; [redacted]; 1986; M-159703-01-1
Title:	Determination of the biodegradabilty of Fosetyl-Al in water / sediment systems
Report No.:	R000991
Document No.:	M-159703-01-1
Guideline(s):	Dutch CTB, Section G.2.0
Guideline deviation(s):	none
GLP/GEP:	**no**

Executive Summary

The bio-transformation of [^{14}C]-fosetyl-Al was studied in 'non-polluted' water/sediment systems 'ditch' and the 'polluted' systems "Kromme Rijn". The test was performed in the dark at 20 °C for 96 days in maximum and at a test concentration of 1.0 mg a.s./L. For assessment of carbon dioxide evolution additional test systems were investigated at 0.3 mg a.s./L.

Material balances for the ditch systems ranged from of 95 to 102% AR with an exception for samples incubated for 28 days (86% AR) and 42 days (79% AR). For the Kromme Rijn systems material balances were from 94 to 106% AR.

The formation of carbon dioxide was 38% AR (ditch systems) and 17% AR (Kromme Rijn systems) each after 42 days of incubation.

Residues in water decreased from 97% AR by day zero to 41% AR after 42 days of incubation (ditch systems) and from 93% AR (day zero) to 80% AR after 42 days for Kromme Rijn test systems.

Residues extractable from sediments were very low to amount to 3% AR in maximum at any sampling interval for both test systems. Non-extractable residues were 18% AR (ditch) and 7% AR (Kromme Rijn) each after 35 days of incubation.

The amounts of fosetyl-Al and its degradation products were not determined.

Fosetyl-Al was bio-degraded in the two water/sediment systems 'ditch' and Kromme Rijn under the conditions of the test.

Owing to a number of gaps in design, conduct and reporting the study was regarded as supplemental information.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material

Fosetyl-Al	
Sample ID:	not reported
Chemical Purity:	≥ 95%
[14C]-fosetyl-ammonium	
Sample ID:	not reported
Specific Activity:	1295 kBq/mg
Radiochemical Purity:	100%

2. Water/Sediment Systems

Samples of water were taken from a ditch surrounding the premises of TNO at Schoemakerstraat 97, Delft. A sediment sample from the top 5 cm of the bottom of the same ditch was also taken. A second sediment sample was taken from the river "Kromme Rijn" near Odijk. The TNO ditch is not polluted with biocides and other organic compounds, whereas the "Kromme Rijn" must be considered to be polluted. The sediment samples were allowed to settle in vessels at the laboratory. The supernatant was drawn off and the content of dry solids of the sediment was determined. The pH of the water was 7.5.

The inhibition of microbial respiration by fosetyl-Al was tested in a BOD-test. Neither the value of BOD_5 nor that of BOD_{21} was affected by a concentration of 2 mg fosetyl-Al/L. It was therefore concluded that concentrations of 0.3 and 1.0 mg/L of fosetyl-Al could be used in the biodegradability test without risk of biodegradation being inhibited by the test compound.

B. STUDY DESIGN

1. Experimental Conditions

The test system for degradation in water/sediment under aerobic conditions consisted of 500 mL cylindrical flasks closed with screw caps containing a carbon dioxide trap. One system contained both water and sediment from a ditch which for many years has not been contaminated with biocides (non-polluted system) and one system contained non-contaminated water plus sediment from "Kromme Rijn" which has for many years been in contact with biocides (polluted system).

For preparation of the test systems, 100 mL of ditch water was placed in each flask, together with a sufficient amount of wet sediment to give a 1% content of dry solids.

The test concentration was 1.0 mg of labelled and unlabelled fosetyl-Al per litre. For assessment of carbon dioxide evolution test systems were additionally applied with 0.3 mg fosetyl-Al per litre. The amount of radiolabelled compound was 195 Bq per flask. The test item (labelled and non-labelled) was added to the flasks from an aqueous solution (100 µL). The pH of the water was checked in a parallel experiment was run without radioactive label. To prevent lack of oxygen, the air in the reaction vessels was regularly refreshed.

The test was performed under aerobic conditions in the laboratory in the dark at 20 °C for 96 days at maximum.

2. Sampling

Duplicate samples were processed and analysed 0, 7, 14, 21, 28, 35 and 42 days after treatment (DAT).

In addition, carbon dioxide evolution was monitored by replacing the scintillation vials from the carbon dioxide traps of eight flasks with fresh ones after 7, 14, 21, 28, 35, 42, 65, 82 and 96 days, and by determining the trapped radioactivity.

The pH measurements were carried out on DAT-0, 21, 28 and 62.

3. Analytical Procedures

The amount of $^{14}CO_2$ formed by biodegradation was determined by liquid scintillation counting (LSC) after addition of methanol and scintillation liquid.

Water and sediment were separated by centrifugation and the radioactivity in the water was determined by LSC.

The solids were extracted with 15 mL portions of acetonitrile, methanol and water and the radioactivity of the three extracts was determined.

Non-extractable residues (NER) in the extracted solid samples were determined after 0, 14 and 35 days by combustion/LSC.

II. RESULTS AND DISCUSSION

In the polluted and non-polluted systems, the pH remained constant up to day 62 of the test.at7.6 and 7.3, respectively,

A. DATA

Table 7.2.2.3- 30: Formation of ^{14}C-carbon dioxide following application of [^{14}C]-fosetyl-Al to two water/sediment systems at 20 °C and at two test concentrations

System	Test Concentration (mg/L)	Incubation time (days)										
		0	7	14	21	28	35	42	49	68	82	96
[redacted]	0.3	0	6	12	17	22	27	31	34	41	48	53
	1	0	8	15	22	29	35	40	44	53	62	67
[redacted]	0.3	0	4	7	9	11	13	14	16	19	23	26
	1	0	4	8	11	15	17	20	21	25	28	31

All values expressed as percentage of total applied radiolabel

Table 7.2.2.3- 31: Transformation of [^{14}C]-fosetyl-Al in a ditch water/sediment systems at 20 °C at a test concentration of 1 mg/L

Component	**Incubation time (days)**						
	0	**7**	**14**	**21**	**28**	**35**	**42**
Carbon Dioxide	-	7	13	25	29	32	38
Water phase	97	87	76	70	55	50	41
Sediment extract	1	1	2	3	2	2	-
NER	1	-	11	-	-	18	-
Total Recovery	99	95	102	98	86	102	79

All values expressed as percentage of total applied radiolabel

Table 7.2.2.3- 32: Transformation of [^{14}C]-fosetyl-Al in [redacted] water/sediment systems at 20 °C at a test concentration of 1 mg/L

Component	**Incubation time (days)**						
	0	**7**	**14**	**21**	**28**	**35**	**42**
Carbon Dioxide	-	5	7	9	14	15	17
Water phase	93	91	87	86	84	83	80
Sediment extract	0	1	1	1	2	1	-
NER	1	-	6	-	-	7	-
Total Recovery	94	97	101	96	100	106	97

All values expressed as percentage of total applied radiolabel

B. MATERIAL BALANCE

Material balances for ditch test systems were from 95 to 102% AR with an exception to be made for samples incubated for 28 days (86% AR) and 42 days (79% AR), respectively. For the Kromme Rijn systems material balances were from 94 to 106% AR.

C. RESIDUES IN WATER

Residues in water decreased from 97% AR at day zero to 41% AR after 42 days for the ditch systems and from 93% AR by day zero to 80% AR after 42 days in Kromme Rijn systems.

D. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Residues extractable from sediments were very low to amount to 3% AR in maximum at any sampling interval for both test systems. Non-extractable residues increased from1% AR by day zero to 18% AR (ditch) and 7% AR (Kromme Rijn) after 35 days of incubation.

E. VOLATILES

Formation of carbon dioxide was 7% AR (ditch) and 5% AR ([redacted]) after 7 days to 38% AR (ditch) and 17% AR ([redacted]) after 42 days.

CO_2 evolution test:

The formation of carbon dioxide in ditch test systems was 53% AR by day 96 at a test concentration of 0.3 mg a.s/L. Formation of carbon dioxide was 67% AR after 96 days at a test concentration of 1 mg a.s./L.

For the [redacted] test systems formation of carbon dioxide was 26% AR after 96 days at 0.3 mg a.s./L and 31% AR at 1 mg/L at the same time.

F. TRANSFORMATION OF TEST SUBSTANCE

The distribution of radioactivity in the water phase and sediment extracts into transformation products was not investigated.

III. CONCLUSIONS

Fosetyl-Al was bio-degraded in the two water/sediment systems 'ditch' and [redacted] under the conditions of the test.

Owing to a number of gaps in design and reporting the study was regarded as supplemental information.

Report:	KCA 7.2.2.3/02 [redacted],; [redacted]; [redacted]; [redacted]; 1998; M-226781-02-1
Title:	14c Fosetyl aluminium Degradation in Two water/Sediment Systems
Report No.:	C012742
Document No.:	M-226781-02-1
Guideline(s):	BBA: part IV section 5-1 december 1990; EU (=EEC): Directive 95/36/EC annex 1 section 7,2,1
Guideline deviation(s):	none
GLP/GEP:	**yes**

Executive Summary

The bio-transformation of [1-ethyl-^{14}C]-fosetyl-Al was studied in two differing UK water-sediment systems [redacted] and [redacted] at 20 °C in the dark for 100 days in maximum.
Based on a single maximum treatment rate of 20 kg a.s./ha in the field the tests were performed at an actual initial test concentration of about 7 mg/L in the water phase.

For the sandy loam system ([redacted]) the mean material balances of two replicates ranged from 94.9 to 102.8% AR with the exception for one sampling interval (88.9% AR, day 7).
For the clay loam system ([redacted]) the mean material balances of two replicates ranged from 90.3 to 104.5% AR again with the exception for one sampling interval (89.2% AR, day 2).
A full material balance was therefore established for the predominant number of samples.

For [redacted] systems, total radioactivity in water decreased from 102.8% AR by day zero to 0.3% AR after 100 days of incubation. For [redacted] systems, the corresponding values were 104.4% AR by day zero and 0.3% AR after 100 days.
Total radioactivity extractable from sediment decreased from 6.6% AR after 0.25 days to 0.7% AR ([redacted]) and from 4.2% AR (day 0.25) to 1.0% AR ([redacted]) each by the end of the study after 100 days.

Non-extractable radioactivity in sediment was 0.0% AR by day zero, to peak at 28.8% AR after 14 days and to decrease to 19.4% AR after 100 days for [redacted] systems. In [redacted] systems, NER were 0.0% AR (day zero), peaked at 24.0% AR after 30 days to decrease to 20.8% AR after 100 days.
Maximum formation of ^{14}C-carbon dioxide was 75.9% AR for [redacted] systems after 100 days and 71.9% AR for [redacted] systems after 61 days of incubation. Formation of other organic volatile components was negligible (< 0.1% AR).

Ethanol was found as a transformation product amounting to 6.0% AR in maximum by day 2 in water of [redacted] systems and to 2.5% AR in the sediment by day 1. The same metabolite was found in [redacted] systems to amount to 16.0% AR in maximum in the water (day 2) and to 4.2% AR in the sediment (day 0.25). Degradation was paralleled by the observation of a minor transformation product not exceeding 4.1% AR ([redacted]) and 0.3% AR ([redacted]) at any sampling interval.

The half-life for the dissipation of fosetyl-Al from the water was reported to 4.3 and 3.3 days (Timme/Frehse and KIM approach, [redacted] systems) and to 4.5 and 3.4 days (Timme/Frehse and

KIM, [redacted] systems) each after application of SFO as kinetic model.
For the degradation in total systems half-lives were calculated to 3.8 and 2.1 days (Timme/Frehse and KIM, [redacted] systems) and 3.9 and 2.1 days (Timme/Frehse and KIM, [redacted] systems), again each after application of the SFO model.

Conclusively, fosetyl-Al was rapidly bio-transformed under conditions of water/sediment testing to predominantly form carbon dioxide as the terminal product.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[1-ethyl-^{14}C]-fosetyl-Al	
Sample ID:	LBE0088
Specific Activity:	770 MBq/mmol
Radiochemical Purity:	> 99%
fosetyl-Al	
Sample ID:	12/1080
Chemical Purity:	97.4%

2. Water/Sediment Test Systems

The study was carried out in two contrasting water/sediment systems collected at two locations in the UK. Water and associated sediment were collected for each system from the same area. Prior to collection of samples the temperature and oxygen saturation of water and the pH and redox potential of water and sediment were determined. Water and associated sediment was sieved to ≤ 0.2 mm and ≤ 2 mm, respectively. The characteristics of sediment and water were summarized in Table 7.2.2.3-33.

Table 7.2.2.3- 33: Physico-chemical properties of test water/sediment systems

Parameter		System	
Water/Sediment System Designation		[redacted]	[redacted]
Geographic Location City Country		[redacted] UK	[redacted] UK
Properties of Water			
Temperature (°C) [1]		19.2	15.9
pH [1]		6.94	7.90
Redox Potential (mV) [1]		386	215
Oxygen Saturation (%) [1]		42	57
Total Organic Carbon (TOC) [mg/L]		2.2	5.5
Total Phosphorous (TOC) [mg/L]		0.7	1.1
Properties of Sediment			
Textural Class (USDA)		Sandy loam	Clay loam
Sand [%]	[50 µm – 2 mm] (%)	53.38	43.62
Silt [%]	[2 µm – 50 µm] (%)	33.04	27.32
Clay [%]	[< 2 µm] (%)	13.58	29.06
pH (0.01 M $CaCl_2$)		6.1	7.7
Organic Carbon (%)		5.8	2.7
Cation Exchange Capacity (meq/100 g)		55.5	15.3
Microbial biomass (µg microbial C/g)	initial	131	7
	final	295	128

[1] determined at sampling site immediately prior to sample collection

B. STUDY DESIGN

1. Experimental Conditions

The tests were performed in individual cylindrical flasks per sample each filled with sediment to a depth of two to 2.5 cm. Associated waters were added to each test vessel to result in a depth of 6 cm above the sediment zone. Each of the flow-through test vessels was attached to traps for volatile components formed, i.e. 2 M aqueous potassium hydroxide for ^{14}C-carbon dioxide and a trap with Tenax ® polymer plus molecular sieve for other volatiles.

Based on a single maximum treatment rate of 20 kg a.s./ha in the field this resulted in an actual initial test concentration of about 7 mg/L in the water phase of samples. Each sample was dosed by applying an aqueous solution of [^{14}C]-fosetyl-Al drop wise onto the water surface of each test vessel.
Non-sterile, untreated samples were prepared in parallel for each water/sediment system for monitoring of microbial biomass in the sediment phase by day zero and at the end of the incubation period.
The water/sediment samples were incubated under flow-through conditions in the dark at 20 ± 2 °C for 100 days in maximum.

2. Sampling

Duplicate samples of each water/sediment system were removed for analysis after zero, 0.25, 1, 2, 7, 14, 30, 61 and 100 days of incubation.

3. Analytical Procedures

At each sampling interval the pH, redox potential and oxygen saturation was determined for the water phase and the sediment.

Water and sediment were separated by decantation. The sediment was extracted three times successively with 0.1 M aqueous sulphuric acid at ambient temperature for 30 minutes, with each extraction step followed by centrifugation. For later time-point samples an additional sonication step of 15 minutes was added after the third extraction.

Radioactivity in water and sediment extracts was determined by liquid scintillation counting (LSC).

Water and sediment extracts were analysed by HPLC/^{14}C-radio-detection. Sediment extracts were concentrated prior to analysis. Owing to the low total radioactivity water and sediment extracts of day 30 were profiled by fraction collection followed by HPLC.

Selected samples of water (0, 2 and 14 days, both systems) and of sediment extract (day one, [redacted] system) were analysed by negative ion electrospray mass spectrometry/mass spectrometry (LC-MS/MS), positive ion electron impact mass spectrometry (GC-MS) and the use of authentic reference substances including ^{14}C-ethanol.

Extracted sediment was air-dried prior to quantification of non-extractable radioactivity (NER) *via* combustion/LSC. NER were further characterised by organic matter fractionation of samples of day 61 of each of the two water/sediment systems.

Radioactivity in traps was determined by LSC. Identity of ^{14}C-carbon dioxide was confirmed by co-precipitation as barium carbonate.

4. Determination of degradation kinetics

Dissipation rates from the water phase and degradation rates for the total systems of fosetyl-Al were calculated by use of the approaches of Timme and Frehse (software not specified) and the program KIM, version 1.0 (Thomae).

II. RESULT AND DISCUSSION

A. DATA

Measurements of the redox potential in water and sediment and the oxygen content in the water indicated aerobic conditions for both water/sediment systems during incubation (see Table 7.2.2.3-34 and Table 7.2.2.3-35).

The pH in water of [redacted] systems ranged from approx. 7.7 to 8.3 in the course of the incubation. The corresponding range was approx. 8.2 to 8.5 for system [redacted].

The results of microbial biomass determination indicated that biological activity of the test systems was given.

Following incubation the results of aerobic biotransformation of [1-^{14}C]fosetyl-Al in water/sediment systems [redacted] and [redacted] were summarised in Table 7.2.2.3- 36 to Table 7.2.2.3- 37.

Table 7.2.2.3- 34: Measurements of oxygen saturation, pH and redox potential in the [redacted] system

Sampling interval (day)	Water			Sediment
	Oxygen saturation (%)	pH	Redox E_h (mV)	Redox E_h (mV)
0.25*	72	7.69	327	-295
1*	78	7.90	173	-292
2*	75	7.83	161	-250
7*	78	7.84	263	-230
14*	70	7.91	240	-151
30*	76	8.47	146	-187
61*	53	7.99	164	-223
100*	68	8.31	223	-233
Maximum**	79	8.59	329	-150
Minimum**	48	7.64	144	-299
Average	71	7.99	212	-232

E_h = Redox potential referring to the hydrogen standard electrode, consisting of redox potential (E_{obs}) as measured with reference electrode (Ag/AgCl) and by adding a fixed value of +197 mV for the potential of the reference electrode (E_{ref}) used, i.e. $E_h = E_{obs} + E_{ref.} E_{obs}$
* Average of values reported for each replicate
** Values for single replicates

Table 7.2.2.3- 35: Measurements of oxygen saturation, pH and redox potential in the [redacted] system

Sampling interval (day)	Water			Sediment
	Oxygen saturation (%)	pH	Redox E_h (mV)	Redox E_h (mV)
0.25*	72	8.15	305	-218
1*	75	8.39	150	-244
2*	74	8.39	243	-228
7*	78	8.25	239	-220
14*	63	8.24	253	-116
30*	75	8.47	128	-123
61*	58	8.13	159	-180
100*	73	8.25	251	-209
Maximum**	79	8.48	305	-260
Minimum**	56	8.08	108	-111
Average	71	8.28	216	-192

E_h = Redox potential referring to the hydrogen standard electrode, consisting of redox potential (E_{obs}) as measured with reference electrode (Ag/AgCl) and by adding a fixed value of +197 mV for the potential of the reference electrode (E_{ref}) used, i.e. $E_h = E_{obs} + E_{ref.} E_{obs}$
* Average of values reported for each replicate
** Values for single replicates

Table 7.2.2.3- 36: Degradation of [^{14}C]-fosetyl-Al in [redacted] water/sediment system under aerobic conditions at 20 °C

Compound	Source	Mean / SD	Incubation time (days)								
			0	0.25	1	2	7	14	30	61	100
Fosetyl-Al	Water	Mean	102.8	92.0	78.5	65.2	27.6	9.0	0.9	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Sediment	Mean	n.d.	0.5	0.6	0.6	0.3	n.d.	0.2	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Entire System		102.8	92.5	79.1	65.8	27.9	9.0	1.0	n.a.	n.a.
Ethanol	Water	Mean	n.d.	0.6	3.8	6.0	4.2	1.2	0.5	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Sediment	Mean	n.d.	2.0	2.5	1.9	0.8	0.1	0.4	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Entire System		n.d.	2.6	6.3	7.9	5.0	1.4	0.9	n.a.	n.a.
Metabolite A	Water	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Sediment	Mean	n.d.	4.1	3.7	3.3	2.5	2.1	0.5	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Entire System		n.d.	4.1	3.7	3.3	2.5	2.1	0.5	n.a.	n.a.
Total Extractable Residues	Water	Mean	102.8	92.6	82.3	71.2	31.8	10.3	1.4	0.5	0.3
		SD	±1.3	±2.4	±0.4	±1.1	±0.3	±0.6	±0.1	±0.0	±0.0
	Sediment	Mean	-	6.6	6.7	5.7	3.6	2.2	1.0	0.9	0.7
		SD	-	±0.1	±0.2	±0.5	±0.0	±0.0	±0.0	±0.1	±0.0
	Entire System	Mean	102.8	99.2	89.0	77.0	35.4	12.5	2.4	1.4	1.0
		SD	±1.3	±2.5	±0.2	±1.6	±0.3	±0.6	±0.1	±0.1	±0.0
^{14}C-Carbon dioxide and other volatiles		Mean	n.a.	0.2	2.3	6.4	30.6	53.5	68.4	71.4	75.9
		SD		±0.0	±0.0	±0.3	±0.7	±0.7	±0.4	±2.4	±0.1
Non-Extractable Residues		Mean	0.0	2.4	6.9	14.6	22.9	28.8	27.3	23.6	19.4
		SD	±0.0	±0.1	±0.3	±0.1	±0.2	±0.3	±0.5	±0.4	±0.3
Total Recovery		Mean	102.8	101.8	98.2	97.9	88.9	94.9	98.1	96.4	96.3
		SD	±1.3	±2.6	±0.2	±1.8	±0.2	±0.4	±0.0	±2.7	±0.4

All values expressed as percentages of total applied radioactivity
SD = standard deviation; n.d.: not detected; n.a.: not analyzed
[1] One replicate sample analysed and taken as mean thus resulting in no SD.

Table 7.2.2.3- 37: Degradation of [^{14}C]-fosetyl-Al in [redacted] water/sediment system under aerobic conditions at 20 °C

Compound	Source	Mean / SD	Incubation time (days)								
			0	0.25	1	2	7	14	30	61	100
Fosetyl-Al	Water	Mean	104.4	91.8	70.5	54.8	18.9	4.5	0.4	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Sediment	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Entire System		104.4	91.8	70.5	54.8	18.9	4.5	0.5	n.a.	n.a.
Ethanol	Water	Mean	n.d.	1.3	10.7	16.0	15.4	3.2	0.5	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Sediment	Mean	n.d.	4.2	n.d.	3.2	2.5	n.d.	0.9	n.a.	n.a.
		SD [1]	-	-	-		-	-	-	-	-
	Entire System		n.d.	5.5	10.7	19.2	17.9	3.2	1.3	n.a.	n.a.
Metabolite A	Water	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Sediment	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	n.a.	n.a.
		SD [1]	-	-	-	-	-	-	-	-	-
	Entire System		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	n.a.	n.a.
Total Extractable Residues [1]	Water	Mean	104.4	93.1	81.2	70.8	34.4	7.7	0.8	0.5	0.3
		SD	±5.1	±2.2	±2.1	±1.1	±0.2	±0.2	±0.0	±0.0	±0.0
	Sediment	Mean	-	4.2	3.4	3.2	2.5	2.5	1.2	1.3	1.0
		SD	-	±1.2	±0.7	±0.3	±0.0	±0.1	±0.2	±0.1	±0.1
	Entire System	Mean	104.4	97.3	84.6	74.0	36.8	10.2	2.1	1.8	1.3
		SD	±5.1	±1.1	±1.4	±1.5	±0.3	±0.3	±0.1	±0.1	±0.1
^{14}C-Carbon dioxide and other volatiles		Mean	n.a.	0.1	1.3	4.6	36.3	57.4	69.3	71.9	70.3
		SD	-	±0.0	±0.3	±0.5	±0.5	±1.5	±1.4	±0.3	±0.7
Non-Extractable Residues		Mean	0.0	2.0	5.4	10.6	18.9	22.7	24.0	22.5	20.8
		SD	±0.0	±0.1	±0.5	±0.6	±0.3	±0.8	±0.9	±0.7	±1.2
Total Recovery		Mean	104.5	99.4	91.3	89.2	92.0	90.3	95.5	96.2	92.4
		SD	±5.1	±1.0	±0.6	±2.6	±0.5	±0.3	±2.1	±1.0	±1.8

All values expressed as percentages of total applied radioactivity
SD = standard deviation; n.d.: not detected; n.a.: not analyzed
[1] One replicate sample analysed and taken as mean thus resulting in no SD.

B. MATERIAL BALANCE

For the [redacted] systems the total recovery of radioactivity in the individual test vessels ranged from 95.3 to 104.4% AR with an exception for samples of day 7 (replicate 1: 88.7% AR, replicate 2: 89.1% AR). Since the data for the total radioactivity in the water phase and the sediment were consistent, this lack in material balance is regarded to have no significant impact on the overall outcome of the study.

For the [redacted] systems the total recovery of radioactivity in the individual test vessels ranged from 90.6 to 109.6% AR with exceptions for samples of day 7 (i.e. 86.7% AR for one replicate) and of day 14 (89.9% AR for one replicate). Again, the data for the total radioactivity in the water phase and the sediment were consistent thus the lack in material balance not to have a significant impact on the overall outcome of the study.

C. DISTRIBUTION OF RESIDUES IN WATER AND SEDIMENT

In [redacted] systems, total [14]C-residues in water decreased from 102.8% AR by day zero to 0.3% AR after 100 days of incubation. For [redacted] systems, the corresponding values were 104.4% AR by day zero to 0.3% AR after 100 days.
Radioactive residues extractable from sediment decreased from 6.6% AR after 0.25 days to 0.7% AR after 100 days of incubation for systems [redacted] and from 4.2% AR (day 0.25) to 1.0% AR after 100 days for [redacted] systems.

Extractable radioactive residues in total system decreased from 102.8% AR by day zero to 1.0% AR after 100 days of incubation in system [redacted] and from 104.4% AR (day zero) to 1.3% AR after 100 days in [redacted] systems.

Non-extractable radioactive residues (NER) were 0.0% AR by day zero, peaked at 28.8% AR after 14 days to decrease to 19.4% AR after 100 days in system [redacted]. In [redacted] systems, NER were 0.0% AR (day zero), peaked at 24.0% AR after 30 days to decrease to 20.8% AR after 100 days. NER were associated with humic acids (approx. 4 to 10% AR) and humins (approx. 10 to 16% AR) while being little being associated with fulvic acids (approx 1 to 3% AR).

E. VOLATILES

Barium carbonate co-precipitation confirmed that the predominant portion of radioactivity (≥ 98%) collected in the traps was carbon dioxide. Other volatile radioactivity was detected to a negligible extent.
Maximum formation of [14]C-carbon dioxide was 75.9% AR for [redacted] systems after 100 days and 71.9% AR for [redacted] systems after 61 days of incubation.

F. TRANSFORMATION OF TEST SUBSTANCE

Fosetyl-Al was transformed by microbial-induced ester hydrolysis to its metabolites phosphonic acid and ethanol. Formation of ethanol was rapid to be rapidly mineralised in the following thus underlining its transient character. Values of ethanol were 7.9% AR ([redacted]) and 19.2% AR ([redacted]) in maximum each after two days of incubation. Other metabolites were observed at insignificant level (max. of 4.1% AR for Unknown metabolite A after 0.25 days in [redacted] systems) in all samples. This indicated again the transient character of [14]C-containing residues in the transformation of fosetyl-Al under conditions of water/sediment testing.

Values of fosetyl-Al extractable from sediment were at trace level for both test systems and for all sampling intervals (i.e. maximum of 0.6% AR by days 1 and 2 for [redacted] systems, 0.1% AR after 30 days for [redacted] systems).

For the total systems, values of fosetyl-Al decreased from 102.8% AR by day zero to 1.0% AR after 30 days in [redacted] and from 104.4% AR (day zero) to 0.5% AR after 30 days in [redacted] systems.

F. DEGRADATION KINETICS

The evaluation of degradation kinetics in the water phase and the total water/sediment systems was performed by use of the approach by Timme and Frehse and the software KIM (Thomae) each using the simple first order (SFO) kinetic model. The results were summarized in Table 7.2.2.3- 38.

Table 7.2.2.3- 38: Degradation kinetics of fosetyl-Al in two water/sediment systems under aerobic conditions at 20 °C

Compartment	Program (model)	[redacted] System		[redacted] System	
		DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)
Water Phase	Timme-Frehse (SFO)	4.3	14.2	3.8	12.5
	KIM (SFO)	3.3	13.8	2.1	10.3
Total System	Timme-Frehse (SFO)	4.5	14.8	3.9	12.9
	KIM (SFO)	3.4	13.9	2.1	10.3

The degradation times for the total systems were almost identical to that for the corresponding water phase since fosetyl-Al was rapidly broken down in the sediment as it transferred from the water. Owing to the fast degradation no reliable value for the DT_{50} value was estimated for the sediment.

III. CONCLUSIONS

Fosetyl-Al was rapidly degraded under conditions of water/sediment testing. Degradation of fosetyl-Al was found to proceed by mineralization of the ethyl carbon moiety to result predominantly in carbon dioxide formation. Ethanol was observed as a major intermediate, but transient product of biotransformation.

The study was designed, conducted and reported according to an important predecessor guideline thus following in its essential parts and fulfilling the actual guideline requirements of OECD 308.
A new study would therefore not contribute to a better understanding of the behaviour of fosetyl-Al residues in the aquatic environment.

CA 7.2.2.4 Irradiated water/sediment study

This point is regarded as a new optional data requirement in the EU. The degradation of fosetyl-aluminum (fosetyl-Al) is well understood under standard conditions of water/sediment testing. In view of the overall limited potential of the active substance and its residues for photolytic degradation (see KCA 7.2.1.2/01 and KCA 7.2.1.2/02) the conduct of an irradiated water/sediment study is not regarded to result in a significantly better understanding of the behaviour of fosetyl-Al and its residues in the aquatic environment.

An irradiated water/sediment study was therefore not performed or regarded as necessary.

CA 7.2.3 Degradation in the saturated zone

This data requirement had been addressed under Point 7.2.1.4 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

The evaluation revealed that the results of risk assessment in groundwater demonstrated no significant risk for a contamination of sub-soils or the saturated zone by fosetyl-aluminium and its metabolites, when applied according to good agricultural practice.
Therefore, the separate investigations on the degradation in the saturated zone are not regarded as necessary.

CA 7.3 Fate and behaviour in air

CA 7.3.1 Route and rate of degradation in air

Report:	KCA 7.3.1/01 [redacted]; 1995; M-163113-01-1
Title:	Fosetyl-aluminium: Estimation of the rate of photochemical transformation in the atmosphere under tropospheric conditions.
Report No.:	R002666
Document No.:	M-163113-01-1
Guideline(s):	OECD: No.61, (1992)
Guideline deviation(s):	none
GLP/GEP:	**yes**

This data requirement had been addressed under Point 7.2.2 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC as published in the corresponding DAR of RMS France and its Final Addendum (September 2005).

The estimation had been performed according to the OECD Monograph 61 reflecting the approach by Atkinson (KCA 7.3.1/01).

The evaluation revealed a half-life of 0.96 days (23 daylight hours). Due to the rapid degradation in the atmosphere, fosetyl-aluminium (fosetyl-Al) would not remain stable and thus not be available for long-range transport resulting from its susceptibility for reactions with photo-chemically produced hydroxyl radicals.

The value for the vapour pressure of fosetyl-Al had been determined to $< 10^{-7}$ Pa at 25 °C as submitted under Point 2.3.1 of the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC. Also in view of its ready solubility in water the value underlined the nature of the substance being a salt dissolving spontaneously into ions in contact with water.

By formation of non-volatile solids aluminium ions cannot exist in a free form in air.

In view of its fast degradation in soil and water being a ready biodegradable compound ethanol does not pose a risk for air.

Study summaries of existing studies and publications on route of degradation in air:

Following a request by the RMS, the photo-chemical life time of fosetyl-Al was re-calculated according to the method of Atkinson by use of the software AOPwin (study KCA 7.3.1/02). The data according to study KCA 7.3.1/01 were therefore regarded as outdated with no use in risk assessment for air. Consequently, there was no summary in detail in this document.

Report:	KCA 7.3.1/02 [redacted],; 2016; M-553106-01-1
Title:	Fosetyl-Al: Calculation of the chemical lifetime in the troposphere
Report No.:	EnSa-16-0345
Document No.:	M-553106-01-1
Guideline(s):	Regulation 1107/2009 of the European Parliament and of the Council as of October 21, 2009 concerning the placing of plant protection products on the market; Commission Regulation 283/2013 of March 01, 2013, setting out the data requirements for active substances, in accordance with Regulation 1107/2009 of the European Parliament and of the Council as of October 21, 2009 concerning the placing of plant protection products on the market
Guideline deviation(s):	none
GLP/GEP:	**no**

Executive Summary

Following the request, attempts were made to estimate the half-life of fosetyl-Al in air by the computer program AOPWIN™ (v 1.92), based on the approach by Atkinson.

However, this agreed standard for the estimation of photochemical transformation in air did not accept salts, in particular aluminium, as input for calculation of the photo-transformation half-life in air.

As a surrogate, the estimation of the photochemical transformation rate in air was provided for the corresponding monoethyl phosphonate ('fosetyl') to result in a DT_{50} in air of 0.55 days. The estimation was based on a hydroxyl radical concentration of 1.5×10^6 molecules/cm^3 and for a 12 hour day/night period.

I. Material and Methods

Based on a structure-activity relationship (SAR) developed by Atkinson and co-workers, the half-life time of monoethyl phosphonate ('fosetyl') in air was assessed by the computer program AOPWIN™ (version 1.92, Syracuse Research Corp.). Rate constants for the atmospheric gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals were estimated by the program. The software also estimates the rate constant for the gas-phase reaction between ozone and olefinic/acetylenic compounds. The rate constants estimated by the program were then used to calculate atmospheric half-lives for organic compounds based upon average atmospheric concentrations of hydroxyl radicals and ozone. AOPWIN™ required just the chemical structure and an estimated atmospheric concentrations of the potential reaction partners for the calculation.

An estimate for the maximum half-life in the air due to indirect photoreaction-oxidation could consequently be derived from the concentration of the hydroxyl radicals by the following formula:
$T_{1/2} = \ln 2 / (k_{OH} \times \text{concentration of OH radicals})$

Maximum chemical life-time in air is calculated similarly, using the below formula:
$\tau = 1 / (k_{OH} \times \text{concentration of OH radicals})$

A value of 1.5×10^6 OH radicals/cm^3 is generally regarded a typical concentration for daylight hours as a 12-hours-day-time concentration (12 hours period as an average daylight time for a whole year).

II. Results and Discussion

However, AOPwin as the agreed standard for the estimation of photochemical transformation in air did not accept salts, in particular aluminium, as input for calculation of the photo-transformation half-life in air.
A half-life time ($T_{1/2}$) of 0.55 days was therefore calculated for 'fosetyl' based on a typical atmospheric hydroxyl radical concentration of 1.5 × 10^6 OH radicals/cm^3. The corresponding chemical lifetime (τ) of 'fosetyl' in the troposphere was 0.79 days.

Table 7.3.1- 1: Half-life and chemical lifetime of fosetyl in air (AOPWIN, v. 1.92)

Daylight hours	(hours/day)	12
OH concentration	(radicals/cm^3)	1.5 x 10^6
OH rate constant	(cm^3 x $molecule^{-1}$ x s^{-1})	19.4543 x 10^{-12}
Half-life ($T_{1/2}$) due to reaction with OH	(hours) (days)	6.598 0.55
Chemical lifetime due to reaction with OH	(hours) (days)	- 0.79

'Fosetyl' can be considered susceptible for reactions with photochemically generated hydroxyl radicals to contribute significantly to the overall degradation of the substance in the atmosphere.

Further mechanisms of degradation, such as e.g. reaction with other radical species, gas-phase photolysis, or hydrolysis, are not considered in the employed model calculation, but may also contribute to the overall atmospheric elimination of 'fosetyl' from the atmosphere.

III. Conclusions

A half-life time ($T_{1/2}$) of 0.55 days was calculated for 'fosetyl' thus being considered susceptible for reactions with photochemically generated hydroxyl radicals. These potentially contribute significantly to the overall degradation of the substance in the atmosphere. In result, the compound cannot be transported in gaseous phase over long distances and cannot accumulate in the atmosphere.

CA 7.3.2 Transport via air

Being a new potential requirement this had not been addressed in the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC.

In view of values for vapour pressure measured being below the triggers of 10^{-4} Pa for soil and 10^{-5} Pa for plant, no study on transport of the active substance fosetyl-aluminium via air is regarded as necessary.

The combination of low half-life in the atmosphere (0.96 days) with a very low vapour pressure (< 10^{-7} Pa) results in a very low value for the Henry constant (< 3.2 x 10^{-10} Pa x m^3 x $mole^{-1}$ at 20°C), indicating non-volatility.
Consequently, fosetyl-aluminium is clearly not subject to transport via air.

CA 7.3.3 Local and global effects

Being a new potential requirement this had not been addressed in the Dossier submitted and evaluated for the Annex I inclusion of fosetyl under Directive 91/414/EEC.

Fosetyl-aluminium (fosetyl-Al) is applied to a limited number of crops. Following application residues are rapidly degraded. In combination with no potential for volatility these aspects indicate that residues are not present under outdoor conditions to form a risk for the environment short-term or long-term to set effects at local or global level.

The potential for local effects from use of fosetyl-Al has been considered in risk assessments performed following its use under field conditions in particular by considering factors like spray drift. The combination of exposure assessments with potential effects measured in soil and surface water do thus cover the environmental compartments of interest. In contrast and since there is no aerial application envisaged, air is not a compartment regarded to be major compartment of potential for fosetyl-Al occurrence following its intended use in the field.

The setting of global effects like contributions to global warming potential (GWP), ozone depleting potential (OPD), photochemical ozone creation potential (POCP) would require a high probability for the molecule assessed to evaporate and thus occur in the gas phase. This probability can be expressed by the volatility in terms of the vapour pressure and the Henry constant. The very low potential of fosetyl-Al residues to occur in the atmosphere has been addressed before in Section CA 7.3.2.

Any accumulation in the troposphere would require high volumes of fosetyl-Al applied and a significant volatility combined with persistence in the gas phase. The latter characteristic has been addressed in Section CA 7.3.1 to result in no long-term persistence of fosetyl-Al residues in the atmosphere.

An acidification potential (AP) would require the generation of acidifying gases like sulfur dioxide or nitrogen oxides in a free form. In comparison to ubiquitous occurring nutrients such as fertilizers the contribution from use as a plant protection agent to the overall eutrophication potential (EP) is expected to be low in particular when comparing seasonal application rates of phosphorous compounds applied as nutrients.
There were no indications that the degradation of fosetyl-Al residues in the environment via biological of physico-chemical processes would result in products that have a potential for acidification or eutrophication of the environment. Even when this would be the case and to set a potential effect this would require amounts of fosetyl-Al applied in the field being several orders of magnitude higher in comparison to the low seasonal application rates and from use in registered crops.

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The route and rate of degradation of fosetyl-aluminium (fosetyl-Al) had been investigated after application of radiolabeled fosetyl-Al to various soil, groundwater and surface water test systems in the laboratory. Following the observation of metabolites and transformation products above the trigger values set in the relevant tests, these are potential residues to occur in the environment thus to be considered in the corresponding environmental risk assessments.

Residue definition for soil:
Besides the parent compound fosetyl-Al, the metabolite phosphonic acid had been considered in the existing environmental risk assessments due to its estimated occurrence at more than 10% of AR in aerobic soil degradation tests.
Although formally triggered, metabolite ethanol was not included additionally to the compounds addressed in existing environmental risk assessments. This considered that ethanol showed clearly transient character in aerobic soil degradation and its nature being formed and clearly to undergo ready biodegradation by microbes.

Residue definition for groundwater:
The risk assessment for groundwater includes by default the components defined for the risk assessment in soil, i.e. the active substance fosetyl-Al and the metabolite phosphonic acid.

Residue definition for surface water and sediment:
The risk assessment for surface water includes by default the active substance fosetyl-Al and the compounds defined for risk assessment in soil and groundwater.
Apart from soil, ethanol was formed at >10% AR under the conditions of water/sediment testing as a transient metabolite. The reasons to exclude this compound from aquatic risk assessment were the same as given under the residue definition for soil.
Phosphonic acid is defined as residue in sediment based on its occurrence >10% AR in sediment of water/sediment tests.
No specific metabolites were observed in sterile buffer hydrolysis, sterile buffer photolysis or in tests on aerobic mineralisation beyond the triggers set for definition as residue for risk assessment.

Residue definition for air:
Fosetyl-Al is defined as the residue for air.

CA 7.4.2 Definition of the residue for monitoring

Following risk assessments in soil, groundwater and surface water according to the GAP defined, the environmental safety of all components under assessment could be demonstrated according to the requirements set.

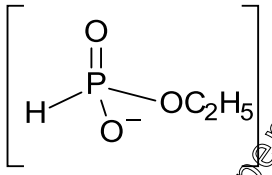
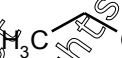
It is therefore justified to define the parent compound fosetyl-aluminium (fosetyl-Al) and phosphonic acid as the relevant residue for monitoring in soil, groundwater and surface water.
Fosetyl-Al is defined as the residue for air, while phosphonic acid is defined as the residue for sediment.

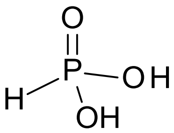
CA 7.5 Monitoring data

No formal monitoring program was requested or required to address this point for fosetyl-aluminium (fosetyl-Al) or its major residue phosphonic acid in soil and water in the EU.
Moreover, there are no published data from formal monitoring programs outside Bayer CropScience available that would indicate a specific concern or findings of residues of fosetyl-Al or phosphonic acid in remote environmental areas not being subject to the intended use.

List of metabolites observed in environmental fate testing

In the original study reports on biotic or abiotic transformation of fosetyl-aluminium the metabolites are denominated by different synonyms. In order to present a common system of nomenclature for the evaluation in the dossier a list of metabolites observed in environmental fate testing is included.

	Report name **Structure** **IUPAC name** **CAS name** **[CAS registry number]**	**Molecular formula** **molar mass** **Other names/ codes**	**Occurrence**
a.s.	**Fosetyl-aluminium (parent substance)**  Aluminium tris-O-ethylphosphonate (IUPAC) Ethyl hydrogen phosphonate, aluminium salt (IUPAC) Phosphonic acid monoethyl ester, aluminium salt (3:1) (CAS) CAS no: 39148-24-8	$C_6 H_{18} P_3 O_9 Al$ 354.1 g/mol **Fosetyl-aluminium** (common name) LS-74783 LS740783 RP 32545 RPA 095206 RPA 590540 AE F053616 BCS-AG74223 BCS-AV49868	Parent substance used as test material in all basic reports
M01	**Ethanol**  Ethyl alcohol, ethanol (IUPAC) Ethanol (CAS) CAS no: 64-17-5	$C_2 H_6 O$ 46.07 g/mol **Ethanol**	Soil, aerobic Water/sediment

	Report name **Structure** **IUPAC name** **CAS name** **[CAS registry number]**	**Molecular formula molar mass** **Other names / codes**	**Occurrence**
M02	**Phosphonic acid**  Phosphonic acid (IUPAC) Phosphonic acid (CAS) CAS no: 13598-36-2	$H_3 O_3 P$ 81.99 g/mol **Phosphonic acid** Phosphorous acid RP 37934 RP 037934 RPA 591409 AE 0540099 BCS-AT27878	Soil, aerobic Water/Sediment
	Salt forms: Disodium dioxido-oxophosphanium (IUPAC) Phosphonic acid, sodium salt (1:2) (CAS) Disodium phosphonate Disodium phosphite CAS no: 13708-85-5	Disodium phosphonate $H Na_2 O_3 P$ 125.96 g/mol	Used as test item or reference to represent metabolite phosphorous acid under pH conditions of the environment
	Pentahydrate: Disodium dioxido-oxophosphanium pentahydrate (IUPAC) Phosphonic acid, disodium salt, pentahydrate(CAS) Disodium phosphonate pentahydrate CAS no: 13517-23-2	Pentahydrate: $H Na_2 O_3 P \times 5 H_2O$ 216.02 g/mol LS741565 RPA Code: None AE 0618179 BCS-AX98334	
	Dipotassium dioxido-oxophosphanium (IUPAC) Phosphonic acid, potassium salt (1:2) (CAS) Dipotassium phosphonate Dipotassium phosphite CAS no: 13492-26-7	Dipotassium phosphonate $H K_2 O_3 P$ 158.17 g/mol LS 731384 RPA Code: None AE 0690030 BCS-AY41587	Used as test item or reference to represent metabolite phosphorous acid under pH conditions of the environment