



Document Title

Summary of the fate and behaviour in the environment for Propineb

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 40184/2013, for preparing dossiers for the approval of a chemical active substance

Date

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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

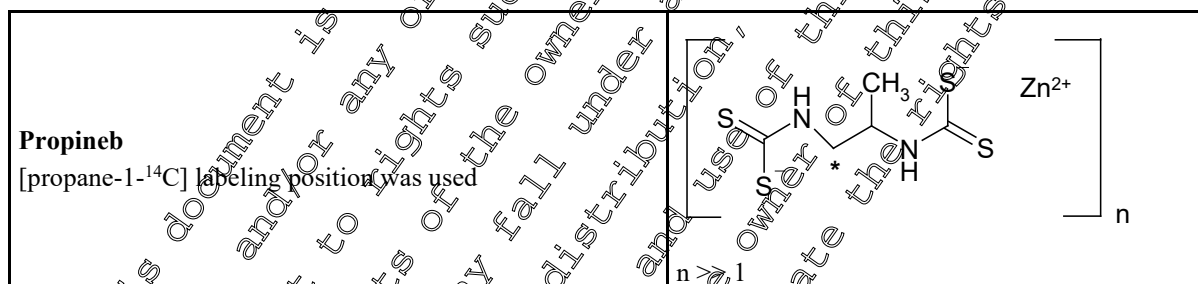
Data on the fate and behaviour of Propineb in soil, water, sediment and air were submitted within the EU Dossier (Baseline Dossier), which resulted in the Annex I inclusion under Directive 91/414/EEC in 2003. In the Supplemental Dossier for renewal of approval of Propineb presented here only those environmental fate studies are described in sections 7.1 to 7.5, which were not submitted within the Baseline Dossier. However, for a better understanding of the behaviour of Propineb in soil, water and sediment, and air, short summaries including the results of all environmental fate studies which were considered relevant during the first EU evaluation (compare EU Monograph Annex B7) are given additionally in this summary in sections [CA 7.1](#), [CA 7.2](#) and [CA 7.3](#). To differentiate between studies already evaluated during the last Annex I listing and new studies the references or author(s) given in tables are written in grey for studies already evaluated and in bold black for new studies.

The proposed residue definitions for each compartment are given in [CA 7.4](#).

Due to the intrinsic properties of Propineb no new studies were performed or were found in published literature with respect to monitoring of soil, surface water, ground/drinking water, sediment and air (see [CA 7.5](#)).

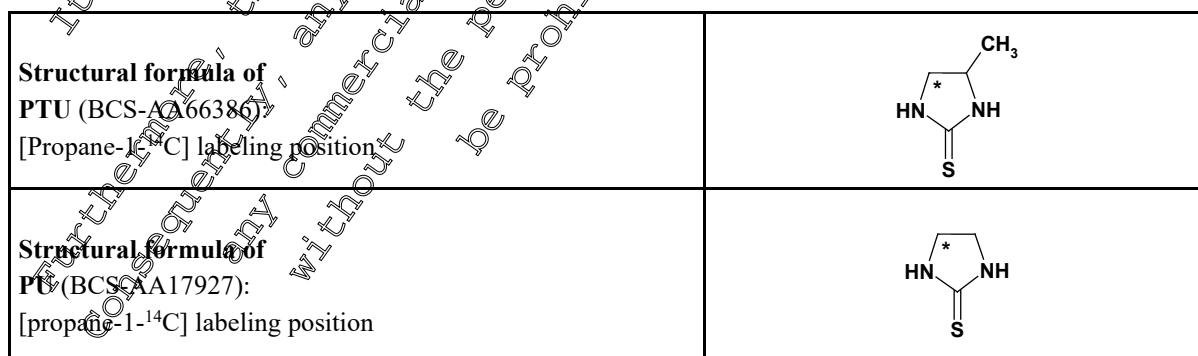
The studies concerning the fate and behaviour of Propineb in the environment were conducted using radiolabelled as well as unlabelled parent compound. The radiolabel position used is regarded adequate to define the route of degradation of Propineb.

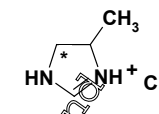
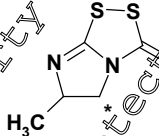
The structure of Propineb and the ¹⁴C-radiolabel (indicated by *) is as follows:



The results of studies are summarized in the following sections, the proposed degradation pathways in soil, water and sediment are given in [Figure 7.1- 1](#) and [Figure 7.2- 1](#), respectively.

In addition, studies have been performed with the following radiolabelled and/or unlabelled major degradation products: PTU (BCS-AA66386), PU (BCS-AA17927), 4-Methyl-imidazoline hydrochloride (BCS-CT29489) and Propineb-DIDT (BCS-CU99534). If ¹⁴C-test item was used the labeling position is indicated below by *:



<p>Structural formula of 4-Methyl-imidazoline hydrochloride (BCS-CT29489): [Propane-1-¹⁴C] labeling position was used</p>	
<p>Structural formula of Propineb-DIDT (BCS-CU99534) [Propane-1-¹⁴C] labeling position was used</p>	

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

CA 7.1 Fate and behaviour in soil

The chemical substance Propineb is different in comparison to most other active ingredients (e.g. fungicides) which are produced as pure chemical with a distinct chemical structure, purity, solubility and stability. Propineb is formed in one reaction step by mixing of propylenediamine, carbon disulfide, zinc sulfate and a small amount of formulation detergents. The resulting product is a polymeric zinc propylene bis(thiocarbamate) with not defined polymer length. The complexes in solid form are practically insoluble in water and after dissolution the polymer reacts immediately with water and other available surrounding substances. The reaction is likely at first a dissolution of the zinc salt forming the highly reactive dithiocarbamic acid with different chain length. The following decomposition can lead to propylenediamine and carbon disulfide as back-reaction. In the environment, bis(thiocarbamate) is likely to be easily oxidized and forms thioam disulfides followed by formation of isothiocyanates. The isothiocyanates are highly reactive and can react either with water, intramolecularly with other intermediates or with surrounding soil organic material (e.g. formation of non extractable residues NER).

The route of degradation of Propineb in soil has been investigated in a set of three laboratory studies using different soils. Due to its polymeric structure consisting of propylenedithiocarbamate units linked by zinc atoms as part of a stable complex Propineb does not exist in dissolved form. Brought in contact with humid soil after its application as suspension in water, the following distinct degradation products were found, since the transient first intermediates lead either to Propineb-DIDT, or by elimination of sulfur hydrogen and carbon disulfide to PTU and 4-Methyl-imidazoline, possibly via other transient degradation products. Propineb-DIDT, 4-Methyl-imidazoline and PTU are also quite short-living transients which are oxidised in several steps, partly via formation of PU or NER to the final degradation product ¹⁴C-O₂.

Anaerobic and photolytic experiments were performed with the degradate PU (M02) since it is the only one with a potential to persist for a longer time period in soil. Under anaerobic soil conditions this metabolite disappears slowly by the formation of bound residues. On soil surfaces under the influence of light it is well mineralised, however, it is obvious that photodecomposition is of minor importance for the dissipation of PU on and in soil.

The mean maximum occurrence of each major metabolite of Propineb in aerobic soil is summarised in [Table 7.1.1-1](#), the proposed degradation pathway in soil is shown in [Figure 7.1.1-1](#).

The DT₅₀ values and maximum occurrences in soil of Propineb and its major degradation products used as modelling input values for the calculation of PEC_{soil} values are summarized in [Table 7.1.2-1](#).

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The DT₅₀ values and relevant degradation fractions for Propineb-DIDT, PTU, PU and 4-Methyl-imidazoline used as modelling input parameter for the calculation of PEC_{gw} values are summarized in [Table 7.1.2-2](#).

For the assessment of surface water exposure maximum occurrences in soil were obtained from [redacted] 2014, and account for 25.8%, 33.7%, 42.5%, and 12.0%, respectively.

Propineb and its major degradation products are strongly to weakly adsorbed in soil, more details for the adsorption and desorption in soil of Propineb and its major degradation products are given in section [CA 7.1.3.1](#), and [Table 7.1.3.1-1](#) summarizes the adsorption constants $K_{oc(ads)}$ in soils to be used for modelling purposes.

CA 7.1.1 Route of degradation in soil

The route of degradation of Propineb in soil has been investigated in a set of three laboratory studies using different soils.

Due to its polymeric structure consisting of propylene dithiocarbamate units linked by zinc atoms as part of a stable complex Propineb does not exist in dissolved form. Brought in contact with humid soil after its application as suspension in water the zinc complex breaks down and unstable propylene dithiocarbaminic acid is formed. Degradation of the latter leads either to Propineb-DIDT, or by elimination of sulfur hydrogen and carbon disulfide to PTU and 4-Methyl-imidazoline, possibly via transient degradation products. Propineb-DIDT, 4-Methyl-imidazoline and PTU are also quite short-living transients which are oxidised in several steps, partly via formation of PU or NER to the final degradation product ¹⁴CO₂.

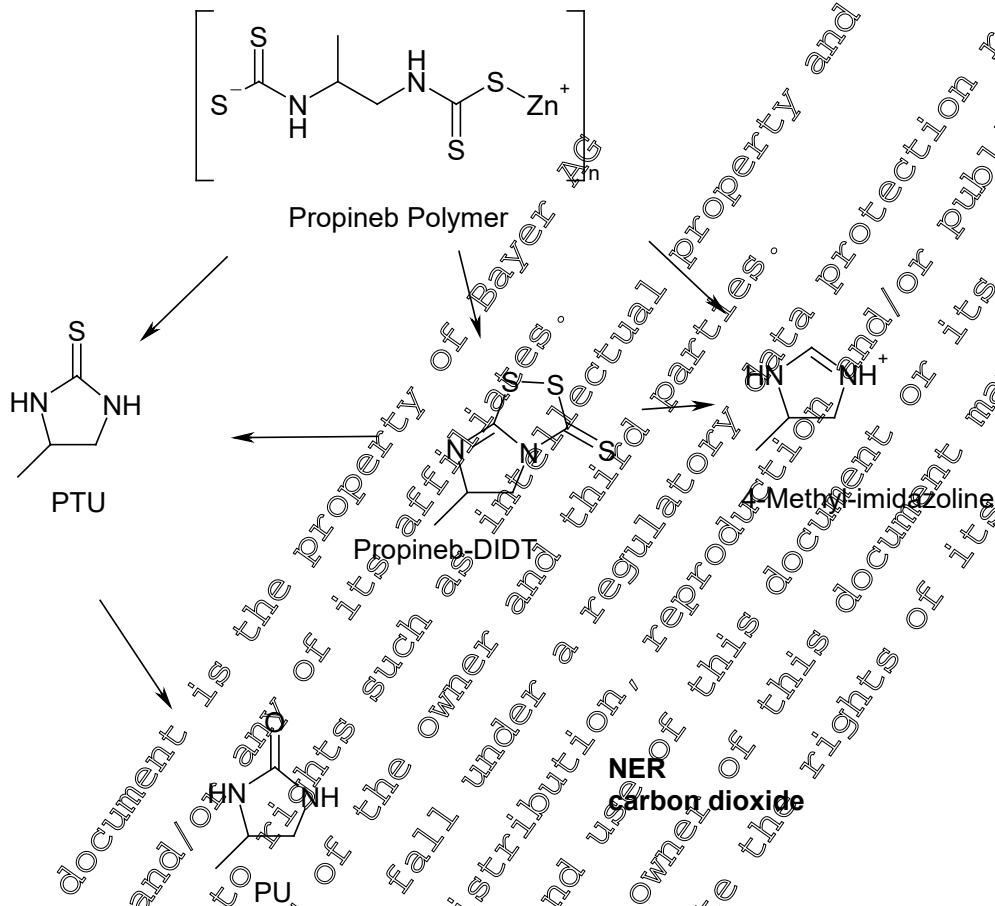
Anaerobic and photolytic experiments were performed just with the degradate PU (M02) since it is the only one with a potential to persist for a longer time period in soil. Under anaerobic soil conditions this metabolite disappears slowly by the formation of bound residues. On soil surfaces under the influence of light it is well mineralised, however, it is obvious that photodecomposition is of minor importance for the dissipation of PU on and in soil.

The mean maximum occurrence of each major metabolite of Propineb in aerobic soil is summarised in [Table 7.1.1-1](#), the proposed degradation pathway in soil is shown in [Figure 7.1.1-1](#).

The maximum occurrences in soil of Propineb and its major degradation products used as modelling input values for the calculation of PEC_{soil} values are summarized in [Table 7.1.2-1](#).

The relevant degradation fractions for Propineb-DIDT, PTU, PU and 4-Methyl-imidazoline used as modelling input parameter for the calculation of PEC values are summarized in [Table 7.1.2-2](#).

Figure 7.1.1- 1: Proposed degradation pathway of Propineb in soil



Remarks: NER and carbon dioxide formation can result from all structures shown (either directly or indirectly).

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CA 7.1.1.1 Aerobic degradation

The route of degradation of Propineb in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/7474/VI/97, 2003). The following two studies included in the Baseline Dossier (P-009496-01) were regarded as relevant during the Annex I inclusion:

Report:	[redacted]; 1976:M-102592-01
Title:	Metabolism of propineb, zineb, propylene thiourea and ethylene thiourea in soil (studies conducted in accordance with BBA Guideline no. 36)
Report No:	RA-726/76
Document No:	M-102592-01-2
Guidelines:	-/-, deviation not specified
GLP/GEP:	No

Report:	[redacted]; 1996:M-102675-02; Amended: 1996-12-16
Title:	Propineb - fate and behaviour in soil
Report No:	A&M 033/94
Document No:	M-102675-02-1
Guidelines:	-/-, deviation not specified
GLP/GEP:	Yes

Summary of study performed by [redacted] 1976

The metabolism of Propineb, Zineb, propylene thiourea (PTU) and ethylene thiourea (ETU) was studied. In two standard soils, in laboratory experiments (conducted in accordance with the experimental conditions specified in BBA Guideline No. 36), using ¹⁴C-labelled compounds. The principal metabolites of Propineb and Zineb detected after 3 and 23 days and after 28 days were propylene urea (PU) and ethylene urea (EU), respectively. CO₂ was also formed in very small amounts. The two thioureas PTU and ETU, which themselves were not detectable after 21 days, likewise degraded to PU and EU, respectively, and to CO₂. More CO₂ evolved from ETU than from PTU. In an experiment with radioactive EU, it was established that degradation to CO₂ proceeds via EU. Other metabolites that occurred accounted for less than 4% of the applied dose, and were not identified.

Summary of study performed by [redacted] 1996

The fate and behaviour of Propineb was investigated in 4 soils. As test substance [1-propane ¹⁴C-labelled] Propineb was used. Propineb was applied to the soil as a suspension in acetonitrile and incubated at 20° C in the dark for up to 105 days. Within this incubation time 8 samples were investigated: 0 (after application), 2, 8, 18, 30, 64, and 105 days. Since at each interval 2 samples were taken, 64 independent vessels were analysed for a. i. and metabolites.

In order to quantify the obtained metabolites, three extractions were performed. The first extraction with acetonitrile dissolved the main part of extractable substances (up to 62%). The following treatment performed with water did not extract more than 8 % of the initial radioactivity. The third step of the extraction procedure was performed with a solution of ethylenediaminetetracetic acid (EDTA) to complex the zinc and to solubilise the resulting monomers. The extracted part of radioactivity dropped to 8% during the course of the study. In parallel, the formation of carbon dioxide increased to 49% while the bound residue was < 50% at day 105 (mean values). The recoveries of single samples were between 90 and 110% except for one which exhibited a value of 112%.



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There was no evidence for unchanged Propineb at the sampling dates. The degradation and metabolism of Propineb revealed beside carbon dioxide one major metabolite: propylene urea (PU). The amount of PU formed was up to 40% 2 days after application of the test substance. Until the end of incubation propylene urea was nearly completely metabolised in all soils.

Immediately after application several further substances were detected in the chromatograms. One of them exhibited an abundance >10%. This substance has been identified as 4-Methyl-imidazoline by thin-layer chromatography (amended: The positive identification of 4-Methyl-imidazoline in the acetonitrile extract was performed with mass spectroscopy). It dropped to < 3% at day 4. Volatile substances others than carbon dioxide were not detected.

Before-mentioned two core studies were critically evaluated and then regarded not sufficient and adequate to describe the route of Propineb degradation. For such insoluble but reactive molecule any treatment of soils should have been performed by aqueous suspension, since just water is the base of any usual spray solution under practical conditions. Just doing so the true pattern of degradation, i.e. short-term after treatment, can be elaborated.

Therefore, a new core study is submitted within this Supplemental Dossier for the Propineb renewal of approval. Resulting from that, the degradation product Propineb-DIT (BCS: U99534) is newly addressed as major soil degradation product in this Supplemental Dossier because it was identified and quantified to occur short-term above the identification triggers in aerobic soil degradation study (see [Table 7.1.1.1- 1](#)).

Report:	[REDACTED];2014:M-484900-01
Title:	[Propane-1- ¹⁴ C]Propineb, Aerobic metabolism / Degradation in four soils
Report No:	EnSa-13-0746
Document No:	M-484900-01-1
Guidelines:	OECD Test Guideline No.307 Commission Regulation (EU) No 2835/2013 in accordance with Regulation (EC) No 107/2009; deviations not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The route and rate of [propane-1-¹⁴C]Propineb was studied in four soils under aerobic conditions in the dark in the laboratory for 42 days at 19.7 °C and 54.2% of respective maximum water holding capacity. A study application rate of 0.487 mg per 100 g soil dry weight was applied as solid polymer well suspended in water. The applied amount was based on the intended maximum single field application rate of 1.825 kg Antracol per hectare. The test was performed in static systems consisting of Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds. Duplicate samples were processed and analyzed 0.06, 0.21, 1, 3, 7, 14, 28 and 42 days after treatment (DAT). Due to the fast degradation of residues any longer interval was not regarded as necessary.

The following facts were considered for the processing of samples. Due to its polymeric nature Propineb is practically insoluble in water and in organic solvents. Since the polymeric Propineb shows decomposition, i.e. if water is present, any observed solubility is caused by degradation but not by dilution. In consequence, the parent compound propineb cannot be analyzed itself. In case valid values of its content are to be determined it must be guaranteed that the entire Propineb polymer still present in a sample is degraded to products which are soluble and can be measured.

At each sampling interval, the soil was extracted three times at ambient temperature, two times using acetonitrile / water 1/1 (v/v) and one time using acetonitrile. Further, two microwave-accelerated extraction steps were performed using acetonitrile / water 1/1 (v/v) at 70 °C and methanol / water 1/1

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(v/v) at 50 °C. This entire procedure was adequate to decompose all polymeric residues of [¹⁴C]-Propineb contained in a soil sample.

The amount of degradation products in soil extracts was determined by liquid scintillation counting (LSC) and by TLC/radiodetection analysis. The amount of volatiles and non-extractable residues was determined by LSC and combustion/LSC, respectively. Degradation products were identified by chromatography with reference compounds.

Investigation of the route of degradation showed that Propineb is well degraded and mineralised in soils incubated under standardised aerobic laboratory conditions in the dark. Complete material balances found at all sampling intervals for each soil demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. Mean material balance was 98.2% of AR (range from 95.7 to 100.6% of AR) for soil AX, 98.3% of AR (range from 95.1 to 100.6% of AR) for soil HF, 99.3% of AR (range from 96.6 to 101.4% of AR) for soil HN and 98.0% of AR (range from 95.7 to 100.6% AR) for soil DD.

The maximum amount of carbon dioxide was 44.6, 46.5, 28.5, and 39.9% of AR at study end (DAT-42) in soil AX, HF, HN and DD, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of ≤ 0.1% of AR at all sampling intervals for all soils.

Non-extractable residues (NER) quickly increased in all soils, slightly declining until DAT-42 (end of study). In soil AX the NER increased to max. 50.5% of AR at DAT-28, slightly declining to 49.2% of AR until DAT-42. In soil HF the NER increased to max. 49.8% of AR at DAT-28, declining to 44.8% of AR until DAT-42. In soil HN the NER increased to 60.5% of AR until DAT-42. In soil DD the NER increased to 53.7% of AR until DAT-28, slightly declining to 51.5% of AR at the end of study. Since high proportions of CO₂ and NER were observed in the metabolic degradation studies, also, this indicates that the NER formed from the parent is a major part of its entire route of degradation in soil, and NER formation is not caused by an inadequate extraction of parent from the soil matrix. Until study termination (DAT-42) extractable residues decreased to 5.1, 3.8, 9.4 and 4.3% of AR in soils AX, HF, HN and DD, respectively. The comparatively fast degradation leads to four major degradation products in soil with the following maximum amounts, all of them found at early sampling intervals:

Table 7.17.1- 1: Identified degradation products (mean maximum amounts, % of AR)

CO ₂ (46.5%) NER (60.5%)	
<p>Propineb-DIT (3.6%) (BCS-CU99074)</p>	<p>4-Methyl-imidazoline (11.7%) (BCS-AB78877)</p>
<p>PTH (31.3%) (BCS-AA66086)</p>	<p>PU (42.2%) (BCS-AA17927)</p>



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It is concluded from this study that Propineb and its residues will be well degraded in aerobic soils kept under normal moisture conditions. However, this study cannot be kinetically evaluated for parent degradation with the usual tools since the starting point of polymer degradation is not to be defined. Same holds true for the kinetics of Propineb-DIDT and PTU degradation which must be determined by metabolite soil degradation studies.

Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralisation of Propineb. Propineb and its degradation products have no potential for accumulation in the environment. Due to the fast degradation of Propineb and its metabolites no field dissipation or rotational crop studies are required.

I. MATERIALS AND METHODS

A. Test Item

[Propane-1- ¹⁴ C]Propineb:	MXM 7056-1-2 TK 83 (contains approx. 86.4% of Propineb)
Specific Radioactivity:	0.66 MBq (0.97 µCi) / mg
Radiochemical Purity:	Not to be determined
Chemical purity:	Not to be determined

B. Test System

The study was carried out using four different soils. The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. The plant protection product use history of the soils is known for at least 5 years. The characteristics of test soils are given in following table.

Table 7.1.1.1- 2 Physico-chemical characteristics of test soils

Parameter	Results/Units	
Soil Designation	AXX ¹ (AX)	(HF)
Soil Taxonomic Classification (USDA)	Sandy, mixed, mesic Typic Cambudoll	Loamy, mixed, mesic Typic Argudalf
Texture Class (USDA)	Sandy loam	Silt loam
Sand [50 µm – 200 µm]	73%	21%
Silt [2 µm – 50 µm]	18%	62%
Clay [< 2 µm]	9%	17%
pH (soil / 0.01 M CaCl ₂ 1/2)	6.3	6.1
pH (soil / water 1/1)	6.6	6.4
pH (saturated paste)	6.6	6.4
pH (soil / 1 N KCl 1/1)	6.1	5.8
Organic Carbon (combustion)	1.7%	2.0%
Organic Matter ¹	2.9%	3.4%
Cation Exchange Capacity	8.4 meq/100 g	11.9 meq/100 g
Water Holding Capacity maximum (MWHC) at 1/10 bar (pF 2.0)	49.7 g H ₂ O ad 100 g DW 13.9%	59.4 g H ₂ O ad 100 g DW 30.9%
Bulk Density (disturbed)	1.24 g/cm ³	1.12 g/cm ³

¹ % organic matter = % organic carbon x 1.724



Table 7.1.1.1- 2: Continued (Physico-chemical characteristics of test soils)

Parameter	Results/Units	
	(HN)	II (DD)
Soil Designation		
Soil Taxonomic Classification (USDA)	Loamy-skeletal, mixed, semiactive, mesic Dystric Eutrudept	Fine-loamy, mixed, active, frigid Typic Eutrudept
Texture Class (USDA)	Loam	Loam
Sand [50 µm – 2 mm]	31%	41%
Silt [2 µm – 50 µm]	50%	42%
Clay [< 2 µm]	19%	27%
pH (soil / 0.01 M CaCl ₂ 1/2)	5.1	5.3
pH (soil / water 1/1)	5.4	7.4
pH (saturated paste)	5.4	7.4
pH (soil / 1 N KCl 1/1)	4.7	7.3
Organic Carbon (combustion)	3.1%	4.9%
Organic Matter ¹	5.3%	8.4%
Cation Exchange Capacity	9.9 meq/100 g	19.8 meq/100 g
Water Holding Capacity maximum (MWHC) at 1/10 bar (pF 2.0)	62.2 g H ₂ O ad 100 g DW 34.4%	80.2 g H ₂ O ad 100 g DW 38.8%
Bulk Density (disturbed)	1.00 g/cm ³	0.98 g/cm ³

¹ % organic matter = % organic carbon x 1.724

II. STUDY DESIGN

A. Experimental conditions

The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Description of soil collection and storage is given in Appendix 3 of the report. The soil moisture [g H₂O ad 100 g soil dry weight] was determined using an automated halogen moisture analyzer by drying three aliquots of approximately 20 g of the sieved soils at 105 °C.

Static test systems (300-mL Erlenmeyer glass flasks) for degradation in soil under aerobic conditions were used as incubation vessels. Each flask was fitted with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to approx. 55 ± 5% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water, taken into account the water content of the application solution. The flasks were then fitted with above-mentioned trap attachments. The untreated test systems were equilibrated to study conditions for 7 days prior to application. For detailed information on experimental design see also Table 3 and Table 4 of report.

A study application rate of 0.487 µg per 100 g soil dry weight was applied as solid polymer well suspended in water. The applied amount was based on the intended maximum single field application rate of 1.825 kg Antracol per hectare. 400 µL of application suspension were applied dropwise onto the soil surface of the respective equilibrated test systems using a pipette. The application was performed with continuous stirring of the application suspension using a magnetic stirrer.

After application, the test vessels (except DAT-0.06 samples) were fitted with trap attachments and placed into a temperature-controlled walk-in climatic chamber for incubation. The soil moisture was maintained since water loss from evaporation (determined by re-weighing of flasks) was replaced after 28 and 35 days of incubation. Soil microbial biomass was determined at the beginning start and at end of the study in untreated test systems (DAT-0 and DAT-42),



B. Sampling

Duplicate treated flasks per soil were taken and processed completely for analyses at the following sampling dates: 0.06, 0.21, 1, 3, 7, 14, 28 and 42 days after treatment (DAT).

Due to the observed fast degradation of the residues any longer interval was not regarded as necessary.

C. Analytical Procedures

Prior to opening an incubated test system for processing of soil, volatiles possibly still present in the head space of the test system were purged into the trap attachment. Afterwards, the trap attachment was removed and the soil was extracted completely. The soil was extracted three times at ambient temperature, two times using acetonitrile / water 1/1 (v/v) and one time using acetonitrile. Further, two microwave-accelerated extraction steps were performed using acetonitrile / water 1/1 (v/v) at 70 °C and methanol / water 1/1 (v/v) at 70 °C. This entire procedure was adequate to destroy all polymeric residues of [¹⁴C]-Propineb contained in a soil sample.

The amount of degradation products in the combined soil extract was determined by liquid scintillation counting (LSC) and by TLC/radiodetection analysis.

The amount of volatiles and non-extractable residues was determined by LSC and combustion/LSC, respectively (for more details see section 3.6.2 of report). Degradation products were identified by co-chromatography with reference compounds and the methods described in more detail under section 3.6.2.4 of report.

III. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic laboratory conditions were maintained during the entire incubation period in the dark. The mean incubation temperature was 19.7 °C; the soil moisture was maintained on average at 54.2% of MWHC (min. 53.7%, max. 55.0%).

Determinations of microbial biomass demonstrated that the used soils were microbial viable. Under the conditions of a laboratory experiment a decrease of microbial biological activity is inevitable due to the absence of any further amendment of nutrients. Continued microbial respiration of nutrients in soil causes finally a lack of readily digestible organic matter.

A. Data

The amount of applied test item for the degradation samples was determined to be 359.55 kBq (equal to 470 µg of test item) with a RSD of 0.7%, and this was set to 100% of applied radioactivity [% of AR]. It was confirmed that the application suspension remained homogeneous during the application procedure.

All calculations for radioactivity (as % of applied radioactivity) in the four soil and the respective trap attachment for volatiles are listed in [Table 7.1.1.1- 3](#) to [Table 7.1.1.1- 10](#), the conclusive overview was presented in [Table 7.1.1.1- 1](#), already.

Complete material balances found at all sampling intervals for each soil demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. Mean material balance was 98.2% of AR (range from 95.7 to 100.6% of AR) for soil AX, 98.3% of AR (range from 95.1 to 100.6% of AR) for soil HF, 99.3% of AR (range from 96.6 to 101.4% of AR) for soil HN and 98.0% of AR (range from 95.7 to 100.6% AR) for soil DD.



Table 7.1.1.1- 3: Material balance of radioactivity in soil XXXXXXXXXX AXxa under aerobic conditions (expressed as percentage of applied radioactivity, % AR)

	Rep.	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Volatiles									
Carbon Dioxide	A	n.a.	0.1	0.7	3.4	9.6	22.6	39.0	44.3
	B	n.a.	0.1	0.8	3.3	9.3	22.6	40.0	43.6
	Mean	n.a.	0.1	0.8	3.3	9.5	22.6	39.5	44.0
Volatile Organic Compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Volatiles	A	n.a.	0.1	0.8	3.4	9.6	22.6	39.0	44.3
	B	n.a.	0.1	0.8	3.2	9.3	22.6	40.0	43.6
	Mean	n.a.	0.1	0.8	3.3	9.5	22.6	39.5	44.0
Extractable Residues									
Combined Extract Residues	A	82.4	77.0	65.8	55.5	44.0	26.2	7.3	5.0
	B	81.0	76.3	65.6	55.5	44.1	26.1	6.8	5.1
	Mean	81.5	76.9	65.7	55.6	44.1	26.6	6.9	5.1
Non-Extractable Residues	A	18.7	22.3	33.6	39.8	45.5	47.5	50.2	49.6
	B	19.6	22.4	34.9	38.5	38.8	49.3	50.8	48.8
	Mean	19.1	22.3	32.7	39.2	42.1	48.6	50.5	49.2
Material Balance	A	100.7	99.0	100.0	98.8	99.2	96.3	96.4	98.9
	B	100.6	98.8	98.4	97.2	92.2	99.4	97.4	97.5
	Mean	100.6	99.3	99.2	98.0	95.7	97.9	96.9	98.2

n.d.: not detected, n.a.: not analyzed

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Table 7.1.1.1- 4: Material balance of radioactivity in soil under aerobic conditions (expressed as percentage of applied radioactivity, % AR)

	Rep.	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Volatiles									
Carbon Dioxide	A	n.a.	0.1	0.7	3.6	10.0	23.2	42.4	46.2
	B	n.a.	0.1	0.8	3.4	10.3	23.3	43.3	46.2
	Mean	n.a.	0.1	0.7	3.4	10.1	23.2	42.9	46.5
Volatile Organic Compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Volatiles	A	n.a.	0.1	0.7	3.6	10.0	23.2	42.4	46.2
	B	n.a.	0.1	0.8	3.4	10.3	23.3	43.3	46.2
	Mean	n.a.	0.1	0.8	3.4	10.1	23.2	42.9	46.5
Extractable Residues									
Combined Extract Residues	A	78.9	72.2	63.4	53.6	42.2	25.6	5.6	3.8
	B	79.9	73.2	62.7	54.9	42.1	25.3	5.2	3.8
	Mean	79.2	73.0	63.0	54.2	42.3	25.4	5.1	3.8
Non-Extractable Residues	A	21.8	24.2	35.9	42.2	45.8	48.7	49.4	45.8
	B	21.2	24.6	35.5	41.6	45.8	50.0	50.2	44.5
	Mean	21.5	24.4	35.4	41.9	45.8	49.4	49.8	44.8
Material Balance	A	100.2	97.6	99.4	99.0	98.3	97.4	96.9	95.0
	B	101.1	97.9	99.0	99.7	98.2	98.5	98.7	95.1
	Mean	100.6	97.6	99.2	99.6	98.3	97.9	97.8	95.1

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Table 7.1.1.1- 5: Material balance of radioactivity in soil under aerobic conditions (expressed as percentage of applied radioactivity, % AR)

	Rep.	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Volatiles									
Carbon Dioxide	A	n.a.	0.1	0.3	1.4	4.5	10.3	21.2	28.3
	B	n.a.	0.1	0.3	1.5	4.4	10.0	21.4	28.6
	Mean	n.a.	0.1	0.3	1.5	4.4	10.6	21.3	28.5
Volatile Organic Compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Volatiles	A	n.a.	0.1	0.3	1.4	4.5	10.3	21.2	28.3
	B	n.a.	0.1	0.3	1.5	4.4	10.0	21.4	28.6
	Mean	n.a.	0.1	0.3	1.5	4.4	10.6	21.3	28.5
Extractable Residues									
Combined Extract Residues	A	58.9	61.7	58.0	49.8	42.1	31.3	16.1	9.4
	B	59.5	61.5	57.9	49.7	42.1	30.0	16.2	9.9
	Mean	58.9	61.7	58.0	49.8	42.1	31.3	16.1	9.4
Non-Extractable Residues	A	41.9	37.2	43.2	47.9	54.2	55.7	57.7	59.7
	B	41.0	37.4	43.0	49.1	52.9	58.5	60.9	61.3
	Mean	41.5	37.3	43.1	48.5	53.6	57.1	59.3	60.5
Material Balance	A	100.2	99.0	101.8	99.3	100.9	97.7	94.7	97.5
	B	100.5	98.9	102.2	100.3	99.4	100.3	98.4	99.2
	Mean	100.3	99.1	101.4	99.8	100.1	99.0	96.6	98.3

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Table 7.1.1.1- 6: Material balance of radioactivity in soil under aerobic conditions (expressed as percentage of applied radioactivity, % AR)

	Rep.	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Volatiles									
Carbon Dioxide	A	n.a.	0.1	0.3	2.4	5.8	22.7	34.0	40.1
	B	n.a.	0.1	0.3	2.5	5.4	21.4	35.5	39.6
	Mean	n.a.	0.1	0.3	2.5	5.6	22.1	34.7	39.9
Volatile Organic Compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Volatiles	A	n.a.	0.1	0.3	2.4	5.8	22.7	34.0	40.1
	B	n.a.	0.1	0.3	2.5	5.4	21.4	35.5	39.6
	Mean	n.a.	0.1	0.3	2.5	5.6	22.1	34.7	39.9
Extractable Residues									
Combined Extract Residues	A	69.8	65.7	60.8	53.9	47.1	20.6	7.8	4.4
	B	79.8	67.0	62.9	53.1	47.3	22.6	6.1	4.1
	Mean	70.1	63.5	61.9	53.5	47.3	21.6	7.3	4.3
Non-Extractable Residues	A	31.6	33.6	38.6	42.2	46.4	53.3	53.4	51.1
	B	29.3	35.1	37.8	40.7	46.6	53.2	54.9	52.0
	Mean	30.5	34.3	38.2	41.5	46.5	53.3	53.7	51.5
Material Balance	A	101.1	98.0	99.6	98.6	99.4	96.6	95.2	95.6
	B	100.1	97.1	100.0	96.3	99.3	97.4	96.3	95.8
	Mean	100.6	97.9	100.3	97.4	99.3	97.0	95.7	95.7

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Table 7.1.1.1- 7: Residues of ¹⁴C-Propineb in extract of soil [redacted] AXXa under aerobic conditions (expressed as % of AR; mean ± SD)

Compound	Mean SD	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Propineb	Mean SD	Not measurable							
ROI 1	Mean SD	1.1 ± 0.0	< LOD	1.0 ± 0.1	< LOD	0.7 ± 0.1	< LOD	< LOD	< LOD
ROI 2	Mean SD	< LOD	1.0 ± 0.0	1.0 ± 0.1	0.7 ± 0.0	1.3 ± 0.1	< LOD	< LOD	< LOD
PU (ROI 3)	Mean SD	7.1 ± 0.0	15.4 ± 0.4	30.0 ± 1.4	11.1 ± 0.4	2.5 ± 2.3	3.9 ± 2.2	1.4 ± 0.0	0.7 ± 0.1
ROI 4	Mean SD	0.8 ± 0.0	0.7 ± 0.0	1.0 ± 0.1	< LOD	< LOD	< LOD	< LOD	< LOD
PTU (ROI 5)	Mean SD	31.3 ± 2.4	26.0 ± 2.4	10.2 ± 1.0	8.8 ± 1.0	4.4 ± 0.3	3.4 ± 0.7	< LOD	< LOD
ROI 6	Mean SD	0.7 ± 0.0	1.0 ± 0.1	1.0 ± 0.3	0.0 ± 0.1	< LOD	< LOD	< LOD	< LOD
ROI 7	Mean SD	< LOD	1.3 ± 0.1	2.2 ± 0.0	0.0 ± 0.1	< LOD	< LOD	< LOD	< LOD
Propineb-DID (ROI 8)	Mean SD	23.3 ± 2.4	18.3 ± 1.0	8.0 ± 0.0	13.2 ± 1.2	0.8 ± 0.0	< LOD	< LOD	< LOD
ROI 9	Mean SD	1.0 ± 0.5	< LOD	< LOD	1.1 ± 0.0	< LOD	< LOD	< LOD	< LOD
ROI 10	Mean SD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
ROI 11	Mean SD	< LOD	1.0 ± 2.0	1.2 ± 0.8	1.2 ± 0.2	1.3 ± 0.3	< LOD	< LOD	< LOD
ROI 12	Mean SD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.4 ± 0.4
4-Methyl-imidazoline (ROI 13)	Mean SD	11.1 ± 0.2	7.0 ± 0.3	5.9 ± 0.1	4.2 ± 0.3	3.0 ± 0.2	3.1 ± 7.4	0.7 ± 0.1	< LOD

n.a.: not analyzed; SD: standard deviation; ROI: region of interest set for analysis
LOD = 0.6% of AR

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Table 7.1.1.1- 8: Residues of ¹⁴C-Propineb in extract of soil [redacted] under aerobic conditions (expressed as % of AR; mean ± SD)

Compound	Mean SD	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Propineb	Mean SD	Not measurable							
ROI 1	Mean SD	0.9 ± 0.1	< LOD	0.9 ± 0.0	< LOD	1.0 ± 0.1	< LOD	< LOD	< LOD
ROI 2	Mean SD	LOD ± 0.0	0.9 ± 0.0	1.1 ± 0.1	0.7 ± 0.0	1.2 ± 0.1	0.8 ± 0.0	< LOD	< LOD
PU (ROI 3)	Mean SD	7.9 ± 0.3	19.5 ± 0.4	34.1 ± 0.2	14.4 ± 0.5	21.1 ± 0.0	8.6 ± 0.3	1.0 ± 0.0	< LOD
ROI 4	Mean SD	0.7 ± 0.0	0.8 ± 0.1	1.1 ± 0.0	< LOD	< LOD	< LOD	< LOD	< LOD
PTU (ROI 5)	Mean SD	27.2 ± 0.2	20.8 ± 0.2	15.5 ± 0.0	5.4 ± 0.0	1.2 ± 0.1	0.8 ± 0.1	< LOD	< LOD
ROI 6	Mean SD	1.0 ± 0.0	1.1 ± 0.0	1.1 ± 0.0	0.3 ± 0.0	< LOD	LOD	< LOD	< LOD
ROI 7	Mean SD	LOD ± 0.0	1.6 ± 0.1	2.1 ± 0.1	1.2 ± 0.1	LOD	LOD	< LOD	< LOD
Propineb-DID (ROI 8)	Mean SD	15.6 ± 0.1	7.1 ± 0.0	6.7 ± 0.0	12.7 ± 0.1	< LOD	< LOD	< LOD	< LOD
ROI 9	Mean SD	2.0 ± 0.3	2.1 ± 0.1	0.8 ± 0.0	1.5 ± 0.1	< LOD	< LOD	< LOD	< LOD
ROI 10	Mean SD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
ROI 11	Mean SD	LOD ± 0.0	1.0 ± 0.1	0.9 ± 0.1	0.9 ± 0.7	1.0 ± 0.7	0.8 ± 0.4	LOD ± 0.0	< LOD
ROI 12	Mean SD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	1.1 ± 0.1
4-Methyl-imidazoline (ROI 13)	Mean SD	8.9 ± 0.3	4.5 ± 1.0	3.8 ± 0.1	2.7 ± 0.2	1.5 ± 0.9	< LOD	< LOD	< LOD

n.a.: not analyzed; SD: standard deviation; ROI = region of interest set for analysis
LOD = 0.6% of AR

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Document MCA: Section 7 Fate and behaviour in the environment
Propineb

Table 7.1.1.1- 9: Residues of ¹⁴C-Propineb in extract of soil [redacted] under aerobic conditions (expressed as % of AR; mean ± SD)

Compound	Mean SD	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Propineb	Mean SD	Not measurable							
ROI 1	Mean SD	0.9 ± 0.0	< LOD	< LOD	< LOD	0.7 ± 0.0	< LOD	< LOD	< LOD
ROI 2	Mean SD	0.7 ± 0.0	0.9 ± 0.0	1.0 ± 0.0	0.7 ± 0.0	1.2 ± 0.0	1.0 ± 0.1	< LOD	< LOD
PU (ROI 3)	Mean SD	10.4 ± 0.1	25.2 ± 0.9	32.0 ± 0.3	20.3 ± 0.7	30.8 ± 0.1	40.2 ± 0.5	40.2 ± 0.1	4.1 ± 0.1
ROI 4	Mean SD	0.7 ± 0.0	0.7 ± 0.1	1.2 ± 0.1	0.7 ± 0.0	< LOD	LOD	< LOD	LOD
PTU (ROI 5)	Mean SD	17.0 ± 0.3	17.5 ± 0.4	6.9 ± 0.1	9.1 ± 0.0	1.1 ± 0.1	0.7 ± 0.0	< LOD	< LOD
ROI 6	Mean SD	0.8 ± 0.0	1.0 ± 0.0	0.6 ± 0.0	0.9 ± 0.0	< LOD	LOD	< LOD	< LOD
ROI 7	Mean SD	LOD	< LOD	0.8 ± 0.0	< LOD	0.8 ± 0.1	0.7 ± 0.0	< LOD	< LOD
Propineb-DID (ROI 8)	Mean SD	10.0 ± 0.2	11.3 ± 0.1	5.9 ± 0.0	9.1 ± 0.4	1.0 ± 0.0	0.7 ± 0.0	< LOD	< LOD
ROI 9	Mean SD	4.2 ± 0.0	3.6 ± 0.1	1.8 ± 0.0	2.4 ± 0.0	LOD	< LOD	LOD	< LOD
ROI 10	Mean SD	LOD	LOD	< LOD	< LOD	0.7 ± 0.1	1.1 ± 0.0	1.1 ± 0.0	1.1 ± 0.0
ROI 11	Mean SD	LOD	LOD	< LOD	0.8 ± 0.6	1.0 ± 0.7	0.9 ± 0.2	0.8 ± 0.0	0.8 ± 0.0
ROI 12	Mean SD	< LOD	LOD	LOD	< LOD	LOD	< LOD	< LOD	< LOD
4-Methyl-imidazolinone (ROI 13)	Mean SD	7.9 ± 0.4	4.6 ± 0.3	4.1 ± 0.1	3.5 ± 0.1	2.6 ± 0.7	1.5 ± 0.2	< LOD	< LOD

n.a.: not analyzed; SD: standard deviation; ROI: region of interest set for analysis

LOD = 0.6% of AR

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Table 7.1.1.1- 10: Residues of ¹⁴C-Propineb in extract of soil under aerobic conditions (expressed as % of AR; mean ± SD)

Compound	Mean SD	DAT (Days after treatment)							
		0.06	0.21	1	3	7	14	28	42
Propineb	Mean SD	Not measurable							
ROI 1	Mean SD	< LOD	< LOD	< LOD	0.8 ± 0.0	< LOD	< LOD	< LOD	< LOD
ROI 2	Mean SD	< LOD	0.9 ± 0.0	< LOD	1.3 ± 0.0	1.3 ± 0.0	< LOD	< LOD	< LOD
PU (ROI 3)	Mean SD	17.6 ± 1.4	27.1 ± 0.7	15.5 ± 1.1	42.2 ± 0.3	25.9 ± 0.7	15.4 ± 0.5	1.0 ± 0.0	0.7 ± 0.0
ROI 4	Mean SD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PTU (ROI 5)	Mean SD	29.5 ± 1.9	17.4 ± 0.0	26.1 ± 1.9	1.3 ± 0.0	1.1 ± 0.0	1.8 ± 0.0	0.9 ± 0.0	< LOD
ROI 6	Mean SD	1.4 ± 0.0	0.0 ± 0.0	< LOD ± 0.1	< LOD	< LOD	< LOD	< LOD	< LOD
ROI 7	Mean SD	1.2 ± 0.0	2.3 ± 0.1	1.1 ± 0.2	2.7 ± 0.1	< LOD	< LOD	< LOD	< LOD
Propineb-DID (ROI 8)	Mean SD	0.3 ± 1.4	5.3 ± 0.0	8.2 ± 1.0	< LOD	< LOD	< LOD	< LOD	< LOD
ROI 9	Mean SD	1.0 ± 0.2	1.1 ± 0.1	1.4 ± 0.2	< LOD	< LOD	< LOD	< LOD	< LOD
ROI 10	Mean SD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
ROI 11	Mean SD	< LOD	1.1 ± 0.5	1.2 ± 1.0	0.8 ± 0.7	1.9 ± 0.2	4.4 ± 0.6	1.2 ± 0.1	0.9 ± 0.0
ROI 12	Mean SD	< LOD	0.6 ± 1.4	4.2 ± 0.0	1.1 ± 0.7	< LOD	< LOD	< LOD	0.7 ± 0.1
4-Methyl-imidazoline (ROI 13)	Mean SD	6.2 ± 0.8	3.0 ± 0.0	3.1 ± 0.2	1.9 ± 0.4	2.8 ± 0.1	< LOD	< LOD	< LOD

n.a.: not analyzed; SD: standard deviation; ROI: region of interest set for analysis
LOD = 0.6% of AR

B. Method Validation

Due to its polymeric nature, Propineb is practically insoluble in water and in organic solvents. Since the polymeric Propineb shows decomposition, i.e. if water is present, any observed solubility is caused by degradation but not by dilution. In consequence, the parent compound propineb cannot be analyzed itself. In case valid values of its content are to be determined it must be guaranteed that the entire Propineb polymer still present in a sample is degraded to products which are soluble and can be measured.



1. Verification of Sample Processing Method

For the test item investigated in the current study a recovery, even shortly after the treatment of soils, cannot be given. Therefore, the overall mass balance and the distribution pattern of products received during the study (based on LSC and radio-TLC analysis data) are regarded as the important quality parameter for this study. Those results demonstrated that the sample processing method (see Figure 3) was gentle enough to recover quite short living degradates for a distinct period of time.

Further, the method was adequate to destroy the total amount of polymeric Propineb still present in a soil sample at the respective sampling interval. However, since the primary degradates of polymeric Propineb are highly reactive species the quick formation of comparatively high portions of NER cannot be avoided in any natural soil environment containing water.

2. Verification of Chromatographic Procedures

A two-step radio-TLC method was used for data evaluation since experience was made that any concentration procedures (as needed prior to the use of radio-HPLC methods) did have an impact on the product pattern observed. A good selectivity and reproducibility demonstrated the suitability for separation and quantification of the major components of soil extracts. Representative TLC profiles showing the separation of degradation products can be found in Figure 4 to Figure 7 of the report.

The TLC limit of quantification (LOQ) for a single peak in the combined organic extracts was < 1% of applied radioactivity (0.6% of AR, see Section 3.7.4.2 of report).

Investigations were performed in order to confirm the results of the radio-TLC method with reversed phase radio-HPLC as second separation method. However, this was neither successful nor reproducible due to the need for concentrating the extract solutions. In principle, the metabolites itself could have been also analysed and verified by radio-HPLC, but for that a much higher concentration range of solutions and less content of matrix components would have been needed.

C. Degradation of Test Item

A synopsis on biotransformation of Propineb in aerobic soil is shown by [Table 7.1.1.1- 1](#), and the results were included in the proposed pathway of degradation in soil (see [Figure 7.1.1- 1](#)).

More detailed data (expressed as percent of applied radioactivity mean \pm SD) are summarized for soil [Table 7.1.1.1- 3](#) and [Table 7.1.1.1- 7](#), for soil [Table 7.1.1.1- 4](#) and [Table 7.1.1.1- 8](#), soil [Table 7.1.1.1- 5](#) and [Table 7.1.1.1- 9](#) and soil [Table 7.1.1.1- 6](#) and [Table 7.1.1.1- 10](#).

Volatiles, i.e. Mineralisation to $^{14}\text{CO}_2$

The maximum amount of carbon dioxide was 44.0, 46.5, 28.5, and 39.9% of AR at study end (DAT-42) in soil AX, HF, HN and DD, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of $\leq 0.1\%$ of AR at all sampling intervals for all soils.

Test Item and Degradation Products in Soil Extracts

Until study termination (DAT-42) extractable residues decreased to 5.1, 3.8, 9.4 and 4.3 of AR in soils AX, HF, HN and DD, respectively.

Degradation of Propineb was accompanied by the formation of four major degradation products with the following maximum amounts observed: PTU with 31.3% of AR in soil AX at DAT-0.06, PU with 42.2% of AR in soil DD at DAT-3, Propineb-DIDT with 25.6% of AR in soil HF at DAT-0.06, and 4-methyl-imidazole with 11.7% AR in soil AX at DAT-0.06. The compound propylene diamine (PDA) could not clearly be co-chromatographed with zones ROI 11 or ROI 12, a very polar peak area of chromatograms; if at all present it accounted for max. 1.6% of AR in soil DD at DAT-0.21, only.



Non-Extractable Residues

Non-extractable residues (NER) quickly increased in all soils, slightly declining until DAT-42 (end of study). In soil AX the NER increased to max. 50.5% of AR at DAT-28, slightly declining to 49.2% of AR until DAT-42. In soil HF the NER increased to max. 49.8% of AR at DAT-28, declining to 44.8% of AR until DAT-42. In soil HN the NER increased to 60.5% of AR until DAT-42. In soil DD the NER increased to 53.7% of AR until DAT-28, slightly declining to 51.5% of AR at the end of study.

Kinetic Analysis of Data

Propineb is very well degradable in soil, which is shown by the resulting data of study (i.e. compare [Table 7.1.1.1- 3](#) to [Table 7.1.1.1- 10](#)). However, in order to describe its metabolic pathway, a destruction method necessary for measuring the total residues of polymeric [propane-1-¹⁴C]Propineb (e.g. by the CS₂-method) could not be used for processing the treated soil samples. Therefore, since the starting point of the polymer degradation is not to be defined, this study cannot be kinetically evaluated with the usual tools for parent compound degradation and DT₅₀ and DT₉₀ values cannot be given for the test item Propineb.

Available Propineb DT₅₀ data (also considering literature data) result in a range between <0 to 6 days, highly depending on soil type, soil moisture and temperature. This range is well confirmed herein by comparatively high proportions of short living metabolites observed in the current study until day 3 in each soil (e.g. see for the findings of Propineb-DIDT and PTU). Obviously, this is caused by a fresh formation during the extraction procedure via destruction of Propineb polymer still present prior to sampling and extraction. Later on, the majority of polymeric [propane-1-¹⁴C]Propineb has been degraded until sampling time. Since Propineb-DIDT and PTU dissipated as fast as it is expected from their short DT₅₀ in soil. Those DT₅₀ in soil could be determined by metabolite degradation studies performed with the metabolites dosed as individual test items to soils (see later in section [CA 7.1.2.1.2](#)).

Degradation Pathway

Based on the results of current study, combined with findings from metabolite degradation studies described under section [CA 7.1.2.1.2](#), the proposed pathway for the degradation of [propane-1-¹⁴C]Propineb in soil under aerobic conditions presented by [Figure 7.1.1- 1](#). Thereby, the following processes are involved:

- Formation of Propineb-DIDT from Propineb
- Formation of 4-methyl-imidazoline from Propineb or from Propineb-DIDT. Now, it is not any longer regarded as a terminal metabolite proposed in an earlier pathway of degradation. This proposal is confirmed by the fact, that 4-Methyl-imidazoline was never found in the route of degradation studies performed with PTU and PU.
- Formation of PTU from Propineb or Propineb-DIDT
- Formation of PU from PTU
- Mineralization (¹⁴C-carbon dioxide formation)
- Formation of non-extractable residues (¹⁴C-NER).

IV. CONCLUSIONS

Investigation of the route of degradation showed that Propineb is well degraded and mineralized in soils incubated under standardized aerobic laboratory conditions in the dark. The quite fast degradation leads to four major degradation products in soil with the maximum amounts shown in [Table 7.1.1.1- 1](#), all of them found at rather early sampling intervals. Until study termination (DAT-42) extractable residues decreased to less than 10% of AR in all soils. ¹⁴CO₂ up to 46.5% of AR was



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trapped until the end of study. Non-extractable residues (NER) quickly increased in all soils up to 60.5% of AR, slightly declining until DAT-42. A quite similar behavior observed in the metabolite degradation studies indicates that the NER formed from the parent is a major part of its entire route of degradation in soil, thus NER formation is not caused by an inadequate extraction of parent from the soil matrix.

Propineb and its residues will be well degraded in aerobic soils if kept under usual moist conditions. Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralization of Propineb. From this study it is concluded that Propineb and its residues have no potential for accumulation in the environment. The outcome is included in the summary of the degradation rates of Propineb and its major degradation products in soil in the laboratory given in section [CA 7.1.1](#) and [Figure 7.1.1- 1](#).

Due to the fast degradation of Propineb and its metabolite observed under standardized laboratory conditions, no field dissipation or rotational crop studies are required.

Further new degradation studies performed with respective radiolabelled degradation products in soils were listed and summarized under Section [CA 7.1.2.1.2](#) (Aerobic degradation of metabolites, breakdown and reaction products). However, from their results on occurring degradates, valid information on the overall route of Propineb degradation in soil was received as well, and as such they were included in the proposed new route of degradation of Propineb in soil given in section [CA 7.1.1](#) and [Figure 7.1.1- 1](#).

CA 7.1.1.2 Anaerobic degradation

The route of degradation of Propineb in soil under anaerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7). In conclusion the following was stated:

The degradation of active substance in the saturated zone was not to be studied since Propineb is not expected to reach the saturated zone after its use according to good agricultural practices.

Just the following study on the terminal and well water soluble metabolite PU is included in the Baseline Dossier 009496-01 which was regarded as relevant during the Annex I inclusion:

Report:	[redacted];1999;M-006247-01
Title:	degradation of propineb use (PU) in soil under anaerobic conditions
Report No:	PM771
Document No:	M-006247-01-1
Guidelines:	-/- deviations not specified
GLP/GEP:	Yes

Summary of study performed by [redacted] 1999:

Under the experimental conditions used in this study PU disappeared slowly from the system with a DT₅₀ of 334 days from the sediment and with one of 130 days from the aqueous phase. A total of three radioactive zones along with that of the starting compound PU (M02) were detected on the TLC plates. None of the individual radioactive zones accounted for more than 6% of the applied amount of radioactivity. One metabolite accounting for 2.3 and 0.3% in the samples from day 121 was identified as PDA (M04).



No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval. A summary of the route of degradation of Propineb in soil is given in section [CA 7.1.1](#) and [Figure 7.1.1-1](#).

CA 7.1.1.3 Soil photolysis

The route of degradation of Propineb under soil photolysis conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7). In conclusion the following was stated:

The degradation of Propineb under soil photolysis conditions in the laboratory is not of relevance due to its rapid degradation in the dark. Therefore, sunlight is not expected to be a relevant route of degradation for Propineb after its use according to good agricultural practices.

Just the following study on the terminal metabolite PU is included in the Baseline Dossier which was regarded as relevant during the Annex I inclusion:

Report:	[redacted]; 1999; M-006235-01
Title:	Photolysis of propyleneurea (PU) on soil surfaces
Report No:	FM77
Document No:	M-006235-01-1
Guidelines:	-/-; deviation not specified
GLP/GEP:	Yes

Summary of study performed by [redacted] W. 1999:

Under the experimental conditions used in this study (15 days of irradiation in a Suntest apparatus corresponded to a total calculated maximum photo-period of 24.7 days under the extreme [redacted] solar conditions; soil moisture was maintained at 40 % of the MWHC) the test item PU disappeared with DT₅₀ value of 6 days, while the dark controls it was degraded with a DT₅₀ of 12 days.

During the test period of 15 days an amount equivalent to 13% of AR was mineralised to carbon dioxide in the irradiated samples. This proportion was similar with 11% in the case of the dark controls. The percentage of non-extracted radioactivity increased from 25% at the beginning and reached after 15 days 60 and 56% in the irradiated and dark control samples, respectively. The recovery of radioactivity of individual samples ranged from 90 to 107 %.

Based on these results it is obvious that photodecomposition is of minor importance for the dissipation of PU (M62) on soil.

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval. A summary of the route of degradation of Propineb in soil is given in section [CA 7.1.1](#) and [Figure 7.1.1-1](#).

CA 7.1.2 Rate of degradation in soil

Propineb was degraded in soil under aerobic conditions in the laboratory (see section [CA 7.1.1](#) before). Field dissipation studies were not performed and not required. The kinetic models and DT₅₀ values in soil of Propineb and its major degradation products used for modelling purpose and trigger



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evaluation (best-fit) as well as the formation fractions in soil for major degradation products are summarized in sections [CA 7.1.2.1](#) and [CA 7.1.2.2](#).

Modelling input values for the calculation of predicted environmental concentrations (PECs) of Propineb and its major degradation products in soil (PEC_{soil}), groundwater (PEC_{gw}) and surface water (PEC_{sw}) were derived from studies and kinetic evaluations (acc. to FOCUS kinetics (2006)¹ summarized in sections [CA 7.1.1](#), [CA 7.1.2](#) and [CA 7.2](#), and are submitted within this Supplemental Dossier for the Propineb renewal of approval.

Moisture normalization of degradation half-lives (DT_{50}) in aerobic soil was performed for Propineb and degradation products Propineb-DIDT, PTU, PU and 4-Methyl-imidazoline, respectively following the recommendations by FOCUS (2000).

- Propineb degrades fast with DT_{50} values of 0.5 and 8.1 days.
- The DT_{50} values for degradation product Propineb-DIDT were derived from the second, slow rate constant of double first order in parallel fits and account for 0.5 days (geometric mean).
- PTU shows very fast degradation with a geometric mean value of 0.2 days.
- The DT_{50} values for PU were derived from a number of relevant studies and the geometric mean value after normalization accounts for 5.6 days.
- The degradation product 4-Methyl-imidazoline also shows very fast degradation in soil and its geometric mean value after normalization accounts for 2.3 days.

The DT_{50} values and maximum occurrences in soil of Propineb and its major degradation products used as modelling input values for the calculation of PEC_{soil} values are summarized in [Table 7.1.2- 1](#) (data taken from [redacted] 2014).

Table 7.1.2- 1: DT_{50} values and max. occurrences in soil of Propineb and its major degradation products used as modelling input values for calculation of PEC_{soil}

Modelling Input Parameter	Endpoint	Comment
Propineb		
DT_{50} in soil [days]	8.1	laboratory, worst case
Maximum occurrence in soil [%]	100	worst case
Propineb-DIDT		
DT_{50} in soil [days]	0.0846	laboratory, worst case
Maximum occurrence in soil [%]	25.8	laboratory, worst case
PTU		
DT_{50} in soil [days]	3.7	laboratory, worst case
Maximum occurrence in soil [%]	33	laboratory, worst case
PU		
DT_{50} in soil [days]	46.5	laboratory, worst case
Maximum occurrence in soil [%]	42.5	laboratory, worst case
4-Methyl-imidazoline		
DT_{50} in soil [days]	2.8	laboratory, worst case
Maximum occurrence in soil [%]	17.5	laboratory, worst case

¹ FOCUS kinetics (2006): "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration", Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.



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The DT₅₀ values and relevant degradation fractions for Propineb-DIDT, PTU, PU and 4-Methylimidazolin used as modelling input parameter for the calculation of PEC_{GW} values are summarized in [Table 7.1.2-2](#). The data were taken from [redacted] 2014, which modelled all the related experimental data.

Table 7.1.2-2: DT₅₀ values and degradation fractions in soil of Propineb and its major degradates used as modelling input values for calculation of PEC_{GW}

Modelling Input Parameter	Endpoint	Comment
Propineb		
DT ₅₀ in soil [days]	0.5	The shorter of the normalised laboratory values is used to account for a fast formation of leaching metabolites; this is regarded as worst case
Maximum occurrence in soil [%]	100	worst case
Propineb-DIDT		
DT ₅₀ in soil [days]	0.5	Laboratory, normalised, the second slow rate constant of the bi-phasic fit for the pathway description may be regarded as appropriate to conduct exposure assessments for groundwater leaching
Degradation fraction from → to (FOCUS PEARL)	0.214 PPB → DIDT	Laboratory, average
PTU		
DT ₅₀ in soil [days]	9	Laboratory, normalised, GEOMean
Degradation fraction from → to (FOCUS PEARL)	0.327 PPB → PTU 0.233 DIDT → PTU	Laboratory, average
PU		
DT ₅₀ in soil [days]	5.7	Laboratory, normalised, GEOMean
Degradation fraction from → to (FOCUS PEARL)	0.88 PTU → PU	Laboratory, average
4-Methylimidazolin		
DT ₅₀ in soil [days]	2.7	Laboratory, normalised, GEOMean
Degradation fraction from → to (FOCUS PEARL)	0.106 PPB → 4-MI 0.088 DIDT → 4-MI	Laboratory, average

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CA 7.1.2.1 Laboratory studies

CA 7.1.2.1.1 Aerobic degradation of the active substance

The rate of degradation of Propineb in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/7474/VI/97, 2003). The following two studies included in the Baseline Dossier (P-009496-01) were regarded as relevant during the Annex I inclusion:

Report:	[redacted]; 1976; M-102592-01
Title:	Mertabolism of propineb, [redacted] and ethylene thio[redacted] in soil)
Report No:	RA-726/76
Document No:	M-102592-01-2
Guidelines:	Studies conducted in accordance with [redacted] guidelines no. 36 deviations not specified
GLP/GEP:	No

Report:	[redacted]; 1996; M-102675-02; Amended: 1996-12-19
Title:	Propineb - fate and behaviour in soil
Report No:	A&M 033/94
Document No:	M-102675-02-1
Guidelines:	-, degradation not specified
GLP/GEP:	Yes

In the study by [redacted] 1976 the degradation of Propineb was investigated in two soils by a colourimetric and method, which was regarded best practice that time. The method used is not Propineb specific and, therefore, does not quantify the Propineb polymere itself but fragments immediately formed in soil. The results were summarized by a short notice, only, and the description of the soils was different from current standards; only the content of the organic carbon (2.58 and 0.57% for standard soil 1 and standard soil 2, respectively) and the pH value (6.8 and 5.5, respectively) were reported. The soils were incubated in dark in at a temperature of 20°C. Soils were incubated at approximately 11% gravimetric water content. In general the recovery rate was just 24.2 and 66.7%, and the dissipation was fast (see [Table 7.1.2.1.1- 1](#)). The half-lives for the residues were estimated to be about 0.5 days (standard soil 1) and about 9 days (standard soil 2).

Table 7.1.2.1.1-1: Degradation of Propineb (% of applied determined with non-specific colourimetric method, by [redacted] 1976)

Soil	DAT (days)						
	0	1	2	4	8	15	22
Standard soil 1	100	24.3	5.0	n.m.	n.m.	n.m.	n.m.
Standard soil 2	100	94.5	n.m	65.3	52.8	37.1	5.0

It is known from other experiments that Propineb as polymere is not stable and decomposes in case of contact to water or soil immediately. This was well confirmed in the above EU listed study by [redacted] 1996, and the new study by [redacted] 2014. However, both studies were



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designed as route of degradation studies, thus not adequate to derive degradation kinetics for the parent compound Propineb. Altogether, available Propineb DT₅₀ data (also considering literature data) result in a range between <0.7 to 8 days, highly depending on soil type, soil moisture and temperature. This range is well confirmed by comparatively high proportions of short living metabolites observed in the study by [redacted] 2014, until day 3 in each soil (compare [Table 7.1.1.1.3](#) to [Table 7.1.1.1- 10](#)). Obviously, this is caused by a fresh formation during the extraction procedure via destruction of Propineb polymer still present prior to sampling and extraction. Later on, the majority of polymeric [propane-1-¹⁴C]Propineb has been degraded until sampling time, since Propineb-DIDT and PTU dissipated as fast as it is expected from their short DT₅₀ in soil.

No additional “rate of degradation study for the active substance” is submitted within this Supplemental Dossier for the Propineb renewal of approval.

However, updated kinetic evaluations of the degradation behaviour of Propineb in soil under aerobic conditions in the dark in the laboratory have been performed according to FOCUS kinetics (2006)¹ to derive kinetic parameters suitable for modelling purpose and environmental risk assessment (see [redacted] 2014, below, and [redacted] 2014, thereafter). The listed study by [redacted] 1996 and the new study by [redacted] 2014 are route of degradation studies. Therefore, degradation half-lives to be used in exposure calculations cannot be derived from that.

A summary of the degradation rates of Propineb and its major degradation products in soil in the laboratory is given in [Table 7.1.2- 1](#) and [Table 7.1.2- 2](#).

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Report:	[REDACTED];2014;M-486677-01
Title:	Kinetic evaluation of aerobic degradation of propineb and its degradation products in aerobic soil according to Focus Kinetics
Report No:	EnSa-14-0472
Document No:	M-486677-01-1
Guidelines:	FOCUS (2011): Generic guidance for estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 1.0, 23 November 2011
GLP/GEP:	No

EXECUTIVE SUMMARY

A kinetics evaluation of the relevant aerobic soil degradation studies with the fungicide Propineb and its degradation products in soil Propineb-DIDT, PTU, PU and 4-Methyl-imidazoline has been conducted according to FOCUS kinetics guidance (FOCUS, 2011) using the computer program KinGUI2. The modelling endpoints of Propineb and its soil degradation products can be used in environmental exposure assessments. The DT₅₀ values obtained for Propineb from [REDACTED] (1976) are summarized in the following table. Propineb degrades fast with DT₅₀ values of 0.5 and 8.1 days.

Table 7.1.2.1.1- 2: Summary of DT₅₀ values for Propineb

Soil	Kinetic model	Chi ² error-%	DT ₅₀ [days]
Standard soil 1	SFO	0.9635	0.5
Standard soil 2	SFO	8.474	8.1

The formation fractions of the three primary degradation products in soil Propineb-DIDT, PTU, and 4-Methyl-imidazoline were derived by means of proportional calculation from data presented [REDACTED] 2014, taking into account the substantial formation of non-extractable residues. The respective formation fractions were derived by a simple approach using the maximum occurrence of the individual compound proportional to the sum of all primary degradation products (i.e. Propineb-DIDT, PTU and 4-Methyl-imidazoline) including the NER at the first sampling point. The results are summarized in following Table 7.1.2.1.1-3. It shows that a substantial amount of Propineb is converted to the primary degradation products accounting for a mass fraction of 0.214, 0.327, and 0.106, for Propineb-DIDT, PTU, and 4-Methyl-imidazoline, respectively.

Table 7.1.2.1.1- 3: Formation fractions of Propineb-DIDT, PTU, and 4-Methyl-imidazoline (4-MI) in aerobic soil

Soil	Formation fraction Propineb-DIDT [-]	Formation fraction PTU [-]	Formation fraction 4-MI [-]
[REDACTED] XXa	0.273	0.366	0.137
[REDACTED]	0.308	0.327	0.107
[REDACTED]	0.152	0.224	0.099
[REDACTED]	0.123	0.391	0.082
Average value	0.214	0.327	0.106



Report:	[REDACTED];2014;M-487355-01
Title:	Normalization of degradation half-lives in aerobic soil according to FOCUS
Report No:	EnSa-14-0582
Document No:	M-487355-01-1
Guidelines:	FOCUS (2011): Generic guidance for estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 1.0, 23 November 2011
GLP/GEP:	No

EXECUTIVE SUMMARY

Moisture normalization of degradation half-lives (DT₅₀) in aerobic soil was performed for Propineb and degradation products Propineb-DIAT, PTO, PUC and 4-Methyl-imidazole, respectively, following the recommendations by FOCUS (2000). Propineb degrades fast with DT₅₀ values of 0.5 and 8.1 days. For data on other the degradation products see respective section [CA 7.2.1.1](#) later.

The following study was not yet submitted within the EU, since it was not performed with EU soils, however, it was submitted in Brazil and contains supportive information well confirming the data presented in earlier [Table 7.1.2.1.1.2](#).

Report:	[REDACTED];1999;M-023467-01
Title:	Soil biodegradability of Antracol Tecnico
Report No:	M10214
Document No:	M-023467-01
Guidelines:	Instituto Brasileiro de Meio Ambiente e dos Recursos Naturais Renovaveis – IBAMA. Portaria Normativa no. 84, of October 15, 1996
GLP/GEP:	Yes

EXECUTIVE SUMMARY

This study was conducted to determine the biodegradability of ANTRACOL TECNICO (Propineb) when applied to LE (Typic Hapludox), LR (Rhodic Hapludox) and GH (Cumulic Humaquept) soils. This assay was carried out in Biotin biometric flasks containing 100 g of soil. Two concentrations of the active ingredient were added in four replicates, resulting in concentrations of 1.0 and 10.0 µg/g of soil. The biometric flasks were incubated at 24±2°C in dark room for 28 days. Propineb was analyzed with the CS₂-method, which determines Propineb itself as well as its metabolites which are transformed to CS₂ (CS₂-residue). Every week the soil was sampled and the CS₂-residue was analyzed. According to the results, for the concentrations 1.0 and 10.0 µg/g, the extracted CS₂-residues after 28 days were 40.0 and 56.3% for GH soil, and less than 10% for LR and LE soils. The DT₅₀ for the CS₂-residue was 3.3 days for LE soil, 9.4 days for LR soil, and 27.8 days for GH soil. It means that the DT₅₀ of Propineb itself is much shorter than the DT₅₀ of the total CS₂-residue.

The resulting data from these Brazilian soils were not included into the data set used for further EU risk assessment since the influence of taking acetone as solvent medium for stock solution and as solvent for



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the treatment of soils is highly uncertain. As mentioned earlier just taking water suspensions of Propineb can actually simulate the behavior after treatment of soil under normal use conditions.

The following study was found in the public literature. It was not performed with EU soils, however, contains supportive information well confirming the data presented in earlier [Table 7.1.2.1.1-2](#).

Report:	[REDACTED];2005/M-455833-00
Title:	Persistence of mancozeb and propineb in soil as affected by moisture regimes
Report No:	M-455833-01-1
Document No:	M-455833-01-1
Guidelines:	-/-
GLP/GEP:	No

EXECUTIVE SUMMARY

The effect of moisture level on the persistence of Mancozeb and Propineb in sandy clay soil was studied over a period of 60 days. As the purpose of this review was to identify information on the active substance Propineb, the details in the study related to Mancozeb are not discussed further. The authors did not state any specific guidelines that were followed. Soil moisture levels were maintained at 20, 50 and 80% of field capacity. However, the incubation conditions of soil samples were not stated in adequate detail.

Residues of propineb dissipated according to first order kinetics with a half-life of 6.5 to 7.3 days. The rate of degradation increased with increasing moisture content (DT₅₀ values of 7.3 and 6.5 days at 20 and 80% field capacity moisture, respectively).

I. MATERIAL AND METHODS

Details of material and methods used are provided below:

1. Test material

Test item:	Propineb 70 WP.
Active substance(s):	Propineb (no CAS no or IUPAC name or any other identifiers specified).
Chemical state and description:	No details specified.
Source of test item:	No details specified.
Batch number:	No details specified.
Purity:	No details specified.
Storage conditions:	No details specified.
Water solubility:	No details specified.

2. Soil:

Name / Classification	[REDACTED] soil.
Source, sampling date and storage conditions	Soil was collected from a cultivated field of [REDACTED] area with no history of pesticide use. Soil was air dried and sieved (2 mm) prior to use. No storage details provided.
Soil type:	Sandy clay.
Particle size:	No details specified.
pH:	7.9
Organic carbon content:	0.28% (calculated from the quoted organic matter content of 0.48% by division with 0.1724).



Other specifications: Moisture content (%) at field capacity: 26.9%
Cation exchange capacity (no units specified): 14.28

3. Soil application

Propineb 70 WP (27.14 mg) was dissolved in water (108 ml) and added to soil (2 kg). The resulting application level was equivalent to 5 µg/g CS₂ (carbon disulfide) and a moisture content of 20% field capacity. The bulk soil sample was divided into 20 g sub-samples which were stored in 50 ml beakers.

4. Sampling

Sampling technique: Separate whole samples of 20 g soil taken at each sampling interval.

Sampling frequency: 0, 5, 10, 15, 20, 25, 30, 40, 50, 60 days.

Number of samples per site/soil type: Triplicate samples were taken for each treatment type (i.e. moisture level).

Storage of samples: Soil samples (20 g) were added to incubation vessels (50 ml) and following treatment were incubated. Soils were stored at either 20, 50 or 80% field capacity moisture.

Other information: Lost moisture was replaced every day by addition of water (by weight).

5. Measurements

Temperature: No details specified.

Soil moisture: 20, 50 or 80% field capacity.

pH: No details specified (on how measurements performed).

Organic carbon: No details specified (on how measurements performed).

6. Chemical analysis

Guideline/protocol: Keppel, 1969², 1971³.

Method: The test substance was converted to carbon disulphide, trapped and quantified according to the standard method of Keppel (1969, 1971).

Pre-treatment of samples: Not required.

Conduction: Not required.

Reference item: The absorbance of the prepared sample versus a blank solution made up of 15 ml colour reagent and 10 ml ethanol was measured at 435 nm on spectrophotometer.

Recovery: No details specified.

Limit of detection: The limit of detection was quoted as 0.1 µg/g of carbon disulphide in soil.

Limit of quantification: No details specified.

² Keppel, GE. 1969. Modification of carbon disulphide evolution method for dithiocarbamate residues. J AOAC 52(1):162-167.

³ Keppel, GE. 1971. Collaboration study of the determination of dithiocarbamate residues by a modified carbon disulphide evolution method for dithiocarbamate residues. J AOAC 54(3):528-532.



II RESULTS

1. Validity criteria: Not stated.

2. Analytical findings:

The analysis of the residue levels determined in the soil samples is presented in [Table 7.1.2.1.1-4](#)

Table 7.1.2.1.1- 4: Effect of soil moisture content on the dissipation of propineb

Days after treatment	Recovered residue (µg/g) as CS ₂		
	Moisture 20% of field capacity	Moisture 50% of field capacity	Moisture 80% of field capacity
0	4.62	4.66	4.72
5	3.44 (25.5)	3.00 (34.8)	2.86 (39.4)
10	2.35 (49.1)	2.16 (53.7)	1.92 (59.3)
15	1.73 (62.6)	1.38 (70.4)	1.02 (78.4)
20	0.84 (81.8)	0.88 (81.1)	0.75 (84.1)
25	0.51 (89.0)	0.30 (93.6)	0.28 (94.1)
30	0.27 (94.2)	BDL	BDL
Half-life (days)	7.3	6.8	6.5

Residue levels are a mean of triplicate samples. Parentheses denotes % dissipation. BDL: below detectable limit (<0.1 µg/g as CS₂).

Initial residues were 4.62, 4.66 and 4.72 µg/g (expressed as CS₂) in soils maintained at 20, 50 and 80% of field capacity, respectively. Detectable residues persisted for 25 to 30 days.

3. Degradation kinetics

The degradation of propineb followed first order kinetics with half-lives ranging from 6.5 to 7.3 days.

III CONCLUSIONS

The degradation of propineb in soil followed first order kinetics. The half-lives determined were 7.3, 6.8 and 6.5 days in soils maintained at 20, 50 and 80% of field capacity, respectively. The rate of degradation increased with increasing moisture content. DT₅₀ values of 7.3 and 6.5 days at 20 and 80% field capacity moisture, respectively.

This study, not performed with EU soils and running at a non-defined temperature, contains supportive information since the general study design is comparable to that normally expected. However, it is not used for deriving EU endpoints since reporting details are somewhat lacking and reliability (i.e. suitable for inclusion in risk assessment) cannot be clearly demonstrated.

In general, valuable information about the non-persistence of Propineb in soil can be drawn; a reasonable range of DT₅₀ of approx. one week can be given for Propineb, very well confirming the data presented in [Table 7.1.2.1.1-2](#), earlier.

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Report:	[REDACTED];2005;M-459460-01
Title:	Persistence of mancozeb and propineb in different soils
Report No:	M-459460-01-1
Document No:	M-459460-01-1
Guidelines:	not applicable
GLP/GEP:	No

EXECUTIVE SUMMARY

The persistence of mancozeb and propineb in 4 varying soil types was studied over a period of 60 days at 100% field capacity moisture level. As the purpose of this review was to identify information on the active substance propineb, the details in the study related to mancozeb are not discussed further. The authors did not state any specific guidelines that were followed. Residues of propineb dissipated according to first order kinetics with a half-life of 19 to 60 days. However, the incubation conditions of soil samples were not stated in adequate detail.

I. MATERIAL AND METHODS

Details of material and methods used are provided below.

1. Test material

Test item: Propineb 90 WP
Active substance(s): Propineb (no CAS no or IUPAC name or any other identifiers specified).
Chemical state and description: No details specified.
Source of test item: No details specified.
Batch number: No details specified.
Purity: No details specified.
Storage conditions: No details specified.
Water solubility: No details specified.

2. Soil:

For data see table below.
Name / Classification: 4 soils, [REDACTED] (clay), [REDACTED] (sandy clay), [REDACTED] (Loamy sand), [REDACTED] (sandy loam).
Source, sampling date and storage conditions: Soil samples were collected from the places listed in table below.
Soil samples were ground in order to break the clods without any damage to the physical, chemical and biological characteristics and moisten to field capacity to encourage growth of unwanted plants which were removed. Soils were air dried and sieved (2 mm) prior to use.

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Table 7.1.2.1.1- 5: Properties of different types of soil used for persistence studies

Soil no.	Soil type	Place	Soil pH	Sand (%)	Silt (%)	Clay (%)	Organic matter (%)	CEC	Field capacity (%)
1	Clay (Inceptisol)	██████████	7.6	26	29	45	0.26	15.58	38.1
2	Sandy clay (Inceptisol)	██████████	7.9	59	11	30	0.48	14.22	26.9
3	Loamy sand (Afisol)	██████████	8.2	86	9	5	0.25	10.72	9.1
4	Sandy loamsand (Afisol)	██████████	8.6	86	10	4	0.51	11.34	12.4

3. Soil application

Propineb 70 WP (27.14 mg) was dissolved in water (108 ml) and added to soil (2 kg). The resulting application level was equivalent to 5 µg/g CS2 and a moisture content of 20% field capacity. The bulk soil sample was divided into 20 g sub-samples which were stored in 50 ml beakers.

4. Sampling

Sampling technique: Separate whole samples of 20 g soil taken at each sampling interval.

Sampling frequency: 0, 5, 10, 15, 20, 25, 30, 40, 50, 60 days.

Number of samples per site/soil type: Triplicate samples were taken for each soil type.

Storage of samples: Soil samples (20 g) were added to incubation vessels (50 ml) and following treatment were incubated. Soils were incubated at field capacity moisture by addition of water (13.5 ml).

Other information: Loss moisture was replaced every day by addition of water (by weight).

5. Measurements

Temperature: No details specified.

Soil moisture: 100 % field capacity.

pH: No details specified (on how measurements performed).

Organic carbon: No details specified (on how measurements performed).

6. Chemical analysis

Guideline/protocol: Keppel, 1971⁴.

Method: The test substance was converted to carbon disulfide, trapped and quantified according to the standard method of Keppel (1971).

Pre-treatment of samples: Not required.

Conductivity: Not required.

Reference item: The absorbance of the prepared sample transferred to 25 mL volumetric flask and made up to volume with ethanol was measured at 435 nm.

⁴ Keppel, GE. 1971. Collaboration study of the determination of dithiocarbamate residues by a modified carbon disulphide evolution method for dithiocarbamate residues. J AOAC 54(3):528-532.



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Recovery: No independent methodology recovery samples mentioned. Mass balance from the soil samples was not monitored.
Limit of detection: The limit of detection was quoted as 0.1 µg/g of carbon disulfide in soil.
Limit of quantification: No details specified.

II RESULTS

1. Validity criteria: Not stated.

2. Analytical findings:

The analysis of the residue levels determined in the soil samples is presented in [Table 7.1.2.1-6](#).

Initial residues were 4.84, 4.88, 4.80 and 4.86 µg/g (expressed as CS₂ average 4.8 µg/g in soils maintained at 100% of field capacity (97% of nominal). Detectable residues persisted for 30 days.

Table 7.1.2.1.1- 6: Persistence of Propineb residues in different types of soil

Sampling interval (days)	Recovered residues as CS ₂ in µg/g soil			
	Clay	Sandy clay	Loamy sand	Sandy loam
0	4.84	4.88	4.80	4.86
5	2.36	2.40	2.44	2.38
10	2.02	1.82	1.76	1.74
15	1.24	1.16	1.12	1.10
20	0.86	0.69	0.66	0.62
25	0.38	0.35	0.32	0.28
30	0.14	0.14	0.13	0.12
40	BDL	BDL	BDL	BDL
50	-	-	-	-
60	-	-	-	-

BDL: below detectable limit (<0.1 µg/g as CS₂).

3. Degradation kinetics:

Residues of Propineb persisted beyond 30 days (around 99 to 97.5% dissipation was recorded after 30 days). The dissipation of propineb in different soils followed first order kinetics with half-live values varying from 5.9 to 6.3 days (incubated at 100% field capacity moisture).

III CONCLUSIONS

The degradation of Propineb in different soil followed first order kinetics. The half-lives determined were in a range of 5.9 to 6.3 days in soils maintained at 100% of field capacity.

This study, not performed with EU soils and running at a non-defined temperature, contains supportive information since the general study design is comparable to that normally expected. However, it is not used for deriving EU endpoints since reporting details are somewhat lacking and reliability (i.e. suitable for inclusion in risk assessment) cannot be clearly demonstrated.

In general, valuable information about the non-persistence of Propineb in soil can be drawn; a reasonable range of DT₅₀ of approx. 6 days can be given for Propineb, very well confirming the data presented in [Table 7.1.2.1.1- 2](#), earlier.



Report:	[REDACTED]
Title:	[REDACTED];2012;M-459499-01 Persistence and degradation of propineb in different soils and moisture regimes.
Report No:	M-459499-01-1
Document No:	M-459499-01-1
Guidelines:	-/-
GLP/GEP:	No

EXECUTIVE SUMMARY

A study was undertaken under laboratory conditions to determine the persistence and degradation of propineb residues in two soils ([REDACTED] and [REDACTED]) following application at two different treatment rates (10 and 25 µg/g) and at two different moisture regimes (field capacity and submergence). The authors did not state any specific guidelines that were followed. Persistence of propineb was slightly increased with a higher rate of application and residues persisted more in [REDACTED] soil than [REDACTED] soil irrespective of application rate. The propineb residues persisted up to 21 to 60 days and 30 to 60 days at field capacity moisture and submergence respectively. The half-life of propineb ranged from 5.3 to 7.3 days under both moisture and application rates in [REDACTED] soil whereas in [REDACTED] soil it ranged from 6.0 to 13.0 days. The degradation half-life of propineb residues was quicker under field capacity moisture than under submergence. However, the incubation conditions of soil samples were not stated in adequate detail.

I. MATERIAL AND METHODS

Details of material and methods used are provided below.

1. Test material

Test item:	Technical grade propineb (non radiolabelled)
Active substance(s):	Propineb (no CAS no or IUPAC name or any other identifiers specified)
Chemical state and description:	No details specified
Source of test item:	Bayer India Ltd.
Batch number:	No details specified
Purity:	82.1%
Storage conditions:	No details specified
Water solubility:	No details specified

2. Soil:

Name / Classification	For data see table below. 2 soils, [REDACTED] and [REDACTED] soil
Source, sampling date and storage conditions	Surface soil samples were collected from top 15 cm depth from areas with no history of propineb application. Soil samples were air dried, ground using a mortar and sieved (2 mm). The soil was moistened to field capacity for 8 to 10 days before use to bring to uniformity and unwanted weed seedlings were removed. No further details specified.
Soil type	[REDACTED]: Sandy clay loam. [REDACTED]: sandy loam
Particle size	[REDACTED]: Sand 53.6%, silt 16.1%, clay 30.3%. [REDACTED]: Sand 76.8%, silt 8.2%, clay 15.0%
pH:	(1:2.5) [REDACTED]: 8.1. [REDACTED]: 6.4
Organic carbon content:	[REDACTED]: 9.6 g/kg. [REDACTED]: 6.4 g/kg
Other specifications:	Moisture content (%) at field capacity: [REDACTED]: 36.5%. [REDACTED]: 25.0%



Cation exchange capacity (cmol/kg soil): [redacted]: 22.3
[redacted]: 8.8

3. Study design and methods

Soil application

Technical grade propineb was added to individual soil samples at an application rate of either 10 or 25 µg/g. After mixing thoroughly, the soils were made up to either field capacity moisture or submerged under a 2 cm layer of water.

Sampling

Sampling technique:

Separate whole samples of 50 g soil taken at each sampling interval.

Sampling frequency:

0, 3, 7, 14, 20, 30, 60, 90 days.

Number of samples per site/soil type:

Two samples were taken for each treatment type.

Storage of samples:

Soil samples were added to incubation vessels (300 ml) and following treatment were incubated (temperature, whether soil samples were open or enclosed or whether they were exposed to light was not specified). Soils were either stored at field capacity moisture or submerged by 2 cm water layer. Lost moisture was replaced every day by addition of de-ionised water.

Other information:

Measurements

Temperature

No details specified

Soil moisture

Soil samples were maintained at field capacity or submerged under 2 cm water layer

pH:

No details specified (on how measurements performed)

Organic carbon:

No details specified (on how measurements performed)

Other measurements/observations:

Recovery samples: To determine the recovery of propineb from the soil, separate soil samples (50 g) treated with 50 and 1250 µg propineb (equivalent to 1 and 25 µg/g) were analysed immediately after treatment (1 hr).

Chemical analysis

Guideline/protocol

Keppel 1969⁵, 1971⁶

Method:

The test substance was converted to carbon disulphide, trapped and quantified according to the standard method of Keppel (1969, 1971).

Pre-treatment of samples

Not required

Conduction:

Not required

Reference item:

A calibration line of absorbance versus concentration of carbon disulphide was prepared using the methodology of Keppel² and Weeren and Brennecke⁷.

Recovery:

No independent methodology recovery samples mentioned. Mass balance from the soil samples was not monitored.

Limit of detection:

The limit of detection of carbon disulphide in soil was found to be 0.1 µg/g which is equivalent to 0.19 µg/g of propineb.

Limit of quantification:

No details specified

⁵ Keppel, GE. 1969. Modification of carbon disulphide evolution method for dithiocarbamate residues. J AOAC 52:162-167.

⁶ Keppel, GE. 1971. Collaboration study of the determination of dithiocarbamate residues by a modified carbon disulphide evolution method for dithiocarbamate residues. J AOAC 54:528-532.

⁷ Weeren, GD and Brennecke, R. 1996. Method for the determination of propineb residues in sample materials of plant and animal origin. Pflanzenschutz Nachrichten Bayer Eng Edn, 49:239-290.



II RESULTS

1. Validity criteria: Not stated.

2. Recovery information:

The analysis of the soil samples treated for recovery determination showed recovery was 95 to 89.1%.

3. Analytical findings:

The analysis of the residue levels determined in the soil samples is presented in [Table 7.1.2.1.1-7](#) and [Table 7.1.2.1.1-8](#) for the [redacted] and [redacted] soils, respectively.

Table 7.1.2.1.1- 7: Persistence of Propineb in [redacted] soil as influenced by application rate and moisture

Time interval (days)	Propineb-residue (µg/g) at different intervals			
	Field capacity		Submergence	
	Treated at 10 µg/g	Treated at 25 µg/g	Field capacity 10 µg/g	Submergence 25 µg/g
0	8.41	20.74	8.03	20.66
3	8.02 (1.1)	20.55 (0.9)	7.91 (1.5)	20.52 (0.7)
7	7.01 (62.9)	9.58 (53.8)	3.71 (53.7)	10.42 (49.6)
14	2.19 (73.0)	6.85 (67.0)	2.62 (66.4)	8.26 (60.0)
21	0.94 (88.4)	3.78 (81.8)	0.98 (87.5)	4.49 (78.3)
30	n.d.	0.35 (98.3)	0.46 (94.3)	1.24 (94.0)
60	n.d.	n.d.	n.d.	n.d.
90	n.d.	n.d.	n.d.	n.d.

n.d.: not detectable.

Table 7.1.2.1.1- 8: Persistence of Propineb in [redacted] soil as influenced by application rate and moisture

Time interval (days)	Propineb residue (µg/g) at different intervals			
	Field capacity		Submergence	
	Treated at 10 µg/g	Treated at 25 µg/g	Field capacity 10 µg/g	Submergence 25 µg/g
0	8.26	21.80	8.23	21.71
3	8.18 (0.9)	21.74 (0.3)	8.18 (0.6)	21.64 (0.3)
7	4.13 (50.0)	12.97 (40.5)	4.82 (41.4)	13.38 (38.4)
14	2.91 (64.8)	8.42 (61.4)	3.13 (61.9)	10.50 (51.7)
21	1.81 (78.1)	6.23 (71.4)	2.16 (73.7)	7.78 (64.2)
30	0.23 (97.3)	0.93 (95.7)	0.68 (91.8)	2.02 (90.7)
60	n.d.	0.42 (98.1)	n.d.	1.19 (94.5)
90	n.d.	n.d.	n.d.	n.d.

n.d.: not detectable.

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Initial levels determined in samples treated at a nominal levels of 10 and 25 µg/g ranged from 8.03 to 8.26 µg/g (average 8.16 µg/g, 82% nominal) and 8.03 to 8.26 µg/g (average 21.23 µg/g, 85% nominal). Generally, propineb was more quickly degraded at lower treatment rates (except for the [redacted] soil incubated at field capacity) and at field capacity moisture level rather than under submergence. Residue levels were detectable up to 21-60 at field capacity moisture and 36-60 under submergence. The paper proposed that the lower persistence of propineb in [redacted] soil compared to [redacted] soil maybe be due to higher soil pH (8.1 vs 6.4), however the paper also acknowledged that the lower persistence could also be due to the higher organic matter and/or clay content. The paper made comparison to a previous paper on the degradation rate of propineb in soil (i.e. [redacted] and [redacted], 2005⁸) and to other papers related to the degradation of mancozeb in soil.

4. Degradation kinetics:

The determination coefficient (R^2) values were more than 0.814 and this was taken by the authors to indicate that degradation followed first order kinetics. Overall half-lives ranged from 5.3 to 9.6 days at field capacity moisture level and 6.7 to 13.0 days under submergence. The rate constants (k_{deg}) were higher at lower dose of application (10 µg/g) when compared to higher rate of application (25 µg/g) in both soils except in the treatment receiving 25 µg/g propineb at field capacity in [redacted] soil. The authors concluded that, in general, Propineb was found to follow two different phases of degradation in all the treatments. The first phase of degradation was up to seven days of incubation and the second phase seven days onwards. Degradation over the 1st phase (0-7 days) was quicker than over the 2nd phase (7-60 days) with half lives in the range 4.0 to 7.2 days and 5.7 to 10.7 days, respectively at field capacity moisture level and 4.8 to 7.6 days and 7.8 to 14.9 days, respectively under submergence. The half-lives of the degradation of Propineb were longer under submergence (6.7-13.0 days) compared to field capacity moisture (5.3-9.6 days) at all application rates.

CONCLUSIONS

The degradation of Propineb in soil follows an overall first order degradation rate of 5.3 to 9.6 days at field capacity moisture level and 6.7 to 13.0 days under submergence.

This study, not performed with EU soils and running at a non-defined temperature, contains supportive information since the general study design is comparable to that normally expected. However, it is not used for deriving EU endpoints since reporting details are somewhat lacking and reliability (i.e. suitable for inclusion in risk assessment) cannot be clearly demonstrated.

In general, valuable information about the non-persistence of Propineb in soil can be drawn; a reasonable DT_{50} of approx 1 week for soil at FC and max 13 days under submerged conditions can be given for Propineb, very well confirming the data presented in [Table 7.1.2.1.1-2](#), earlier.

⁸ [redacted] A.K., [redacted] B.N. 2005. Persistence of mancozeb and propineb in different soils. *Pestic Res J* 17 : 94-96.



CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

Formation of the major degradates PTU and PU and their rates of degradation in soil under aerobic conditions in the laboratory were evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and were accepted by the European Commission (SANCO/74/VI/97, 2003). The following studies included in the Baseline Dossier (P-009496-01) and regarded as relevant during the Annex I inclusion and are still used in this Supplemental Dossier for the Propineb renewal of approval:

Report:	[redacted]; 1983; M-102886-02; Amended: 1988-05-18
Title:	Degradation of PTU (metabolite of propineb) in soil - Behaviour of pesticides in soil - propylenethiourea/propineb
Report No:	RR8013/83
Document No:	M-102886-02-1
Guidelines:	-/-
GLP/GEP:	No

Report:	[redacted]; 1996; M-102675-02; Amended: 1996-12-19
Title:	Propineb - fate and behaviour in soil
Report No:	A&M 033/94
Document No:	M-102675-02-1
Guidelines:	n.a.
GLP/GEP:	Yes

Report:	[redacted]; 1993; M-105176-01
Title:	Degradation and metabolism of propineb urea (PU) in soil under aerobic conditions
Report No:	PF-3884
Document No:	M-105176-01-2
Guidelines:	- deviation not specified
GLP/GEP:	Yes

For these old studies, new kinetics evaluations were performed which are described in the following.

Further, in order to fill data gaps and to mirror the proposed new pathway of Propineb degradation in aerobic soil study a plenty of new rate of degradation studies have been performed for all four major degradation products Propineb, DIDT, PTU, PU and 4-Methyl-imidazoline. They are submitted within this Supplemental Dossier for the Propineb renewal of approval, together with an updated kinetics evaluation of their degradation kinetics considering all respective relevant data ([redacted] 2014) order to derive kinetic parameters suitable for modelling purpose and environmental risk assessment (a summary of the respective final data is given in [Table 7.1.2- 1](#) and [Table 7.1.2-2](#)).

Degradation of Propineb-DIDT

Justification for inclusion into the Supplemental Dossier for Propineb renewal of approval Annex I:

The metabolite Propineb-DIDT was identified as a primary metabolite in the new aerobic soil metabolism study by [redacted] 2014, and exceeded the trigger for consideration in risk assessments. Therefore, the degradation rate was investigated.



Report:	[REDACTED];2014;M-484906-01
Title:	[Propane-1-14C]Propineb-DIDT: Aerobic degradation in four soils
Report No:	EnSa-14-1129
Document No:	M-484906-01-1
Guidelines:	OECD Test Guideline No. 307 Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009 US EPA OCSPP Test Guideline No. 835.4100; deviations not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The rate of degradation of [propane-1-¹⁴C]Propineb-DIDT, a primary metabolite of the fungicide Propineb, was determined under aerobic laboratory conditions in the dark for 14 days at 19.4 °C and 54.2% of the maximum water holding capacity in the following four soils:

Table 7.1.2.1.2- 1: Test soils used in study by [REDACTED] 2014

Soil	Soil ID	Source	Texture (USDA)	pH*	OC [%]
[REDACTED] AXXa	AX	[REDACTED] Germany	Sandy loam	5.8	1.7
[REDACTED]	HF	[REDACTED] Germany	Silt loam	5.8	2.0
[REDACTED]	HN	[REDACTED] Germany	Silt loam	4.9	2.6
[REDACTED]	DD	[REDACTED] Germany	Loam	7.0	6.1

* pH values were derived from aqueous 0.01 M CaCl₂ suspensions.

A study application rate of 139 mg/100 g soil-dry weight was applied based on a maximum single field application rate of the parent active substance Propineb of 1575 g/ha and a maximum occurrence of Propineb-DIDT of approximately 50% of the applied amount, implying a possible worst case soil contamination to be in the same order of magnitude.

The test was performed in static systems consisting of Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds but permeable for oxygen.

Duplicate samples were processed and analyzed 0, 0.24, 1, 2, 5, 9, and 14 days after treatment (DAT). At each sampling interval, the soil was extracted three times at ambient temperature using acetonitrile/water 1/1 (v/v). Furthermore, two microwave-accelerated extraction steps were performed at 70 °C using acetonitrile/water 1/1 (v/v) and methanol/water 1/1 (v/v). The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by TLC/radiodetection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. Test item identity was confirmed by HPLC-MS(/MS) including accurate mass determination and/or by co-chromatography with reference item.

Mean material balance was 99.3% AR for soil AX (range from 96.6 to 101.6% AR), 99.8% AR for soil HF (range from 98.3 to 101.0% AR), 88.0% AR for soil HN (range from 77.1 to 99.2% AR) and 98.7% AR for soil DD (range from 97.7 to 99.8% AR).

The maximum amount of trapped carbon dioxide was 25.3, 22.4, 13.9 and 26.5% AR at study end (DAT-14) in soil AX, HF, HN and DD, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals for all soils.

Extractable residues decreased from DAT-0 to DAT-14 from 77.3 to 11.1% AR in soil AX, from 73.6 to 11.7% AR in soil HF, from 64.9 to 11.3% AR in soil HN and from 45.3 to 7.9% AR in soil [REDACTED].

Non-extractable residues (NER) increased to 63.2% AR at DAT-9 and slightly declined to 62.8% AR until DAT-14 in soil AX. In soil HF, NER increased to 65.4% AR at DAT-9 and slightly declined to 64.2% AR until DAT-14. In soil HN, the amount of NER increased to 55.4% AR at DAT-1 and



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remained almost constant until study end (DAT-14). In soil DD, NER increased to 65.0% AR at DAT-9 and slightly declined to 64.0% AR until DAT-14.

The amount of Propineb-DIDT in the soil extracts decreased very fast from 50.7% (soil AX), 47.4% (soil HF), 36.9% (soil HN) and 20.3% (soil DD) of AR to non-detectable amounts at DAT-29 in three soils, at DAT-5 in soil AX.

According to the lowest chi² error values and visual assessments the degradation of Propineb-DIDT followed double first order in parallel (DFOP) kinetics in three soils, and first order multi-compartment kinetics (FOMC) in soil [redacted].

The maximum DT₅₀ for Propineb-DIDT was 0.02 days (0.5 h), and the maximum DT₉₀ was 1.1 days in the soils tested under standardized aerobic laboratory conditions at 20 °C in the dark.

Table 7.1.2.1.2- 2: Degradation kinetics of Propineb-DIDT in soils under aerobic conditions

Soil	Best Fit Kinetic Model ¹	DT ₅₀ [days]	DT ₉₀ [days]	Chi ² Error [%]	Visual Assessment ²
[redacted] AXXa	DFOP	0.0109	1.09	1.881	+
[redacted]	DFOP	0.0848	0.97	0.6337	+
[redacted]	DFOP	0.0056	0.59	1.00	+
[redacted]	FOMC	0.0183	0.18	1.711	+

¹ SFO: Single first order, FOMC: First order multi compartment, DFOP: Double first order in parallel

² Visual assessment: + = good, o = moderate, - = poor

Besides the formation of carbon dioxide, three degradation products were identified with the following maximum occurrence: PU with 23.4% AR at DAT-2 in soil DD, PTU with 14.7% AR at DAT-0.21 in soil HN, and 4-methylimidazole with 7.7% AR at DAT-1 in soil AX. It is concluded from this study that Propineb-DIDT and its residues will be fast degraded in soil under aerobic conditions. Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil.

The short half-lives in soil combined with the determined K_{oc} values indicate that Propineb-DIDT and its major metabolite PTU do not have a potential to accumulate and leach in soil.

I. MATERIALS AND METHODS

1. Test Item

- Test item: Propane-1-¹⁴C Propineb-DIDT
- Sample ID: KML 9670
- Specific Activity: 3.40 MBq/mg (9.80 µCi/mg)
- Radiochemical Purity: > 98% (HPLC with radioactivity detector)
- Chemical Purity: > 99% (HPLC with UV-detector, 280 nm)

2. Test Soils

Four soils were used (see Table 7.1.2.1.2-3). The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. No plant protection products were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Soil collection and handling were in accordance to ISO 10381-6.



B. STUDY DESIGN

1. Experimental Conditions

The rate of degradation of [propane-1-¹⁴C]Propineb-DIDT was determined under aerobic laboratory conditions in the dark for 14 days at 19.4 °C and 54.2% of the maximum water holding capacity in the following four soils:

A study application rate of 139 µg /100 g soil dry weight was applied based on a maximum single field application rate of the parent active substance Propineb of 1575 g/ha and a maximum occurrence of Propineb-DIDT of approximately 50% of the applied amount, implying a possible worst case soil contamination to be in the same order of magnitude.

The test was performed in static systems consisting of Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds but permeable for oxygen.

Duplicate samples were processed and analyzed 0, 0.2, 1, 2, 5, 9, and 14 days after treatment (DAT). At each sampling interval, the soil was extracted three times at ambient temperature using acetonitrile/water 1/1 (v/v). Furthermore, two microwave-accelerated extraction steps were performed at 70 °C using acetonitrile/water 1/1 (v/v) and methanol/water 1/1 (v/v). The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by TLC/radiodetection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. Test item identity was confirmed by HPLC-MS(/MS) including accurate mass determination and/or by co-chromatography with reference item.

2. Sampling

Duplicate samples were processed and analyzed 0, 0.2, 1, 2, 5, 9, and 14 days after treatment (DAT).

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Table 7.1.2.1.2- 3: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	[REDACTED]	AXXa	[REDACTED] 4a	[REDACTED] II
Geographic Location	[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
City	[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany	Germany
GPS Coordinates	[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
Soil Taxonomic Classification (USDA)	loamy-skeletal, mixed, semiarid, mesic dystic Eutrudept	sandy, mixed, mesic Typic Cambudoll	loamy, mixed, mesic Typic Argudalf	fine-loamy, mixed, active, frigid Typic Eutrudept
Textural Class (USDA)	silt loam	sandy loam	silt loam	loam
Sand [50 µm – 2 mm]	33%	75%	19%	31%
Silt [2 µm – 50 µm]	53%	17%	65%	43%
Clay [< 2 µm]	14%	8%	16%	26%
pH (soil/0.01 M CaCl ₂ 1/2)	4.9	5.8	5.8	7.0
pH (soil/water 1/1)	5.2	6.1	6.1	7.2
pH (saturated paste)	5.1	6.0	6.1	7.1
pH (soil/1 N KCl 1/1)	4.5	5.6	5.6	6.8
Organic Carbon	2.6%	2.7%	2.0%	6.1%
Organic Matter ¹	4.5%	2.9%	3.4%	10.5%
Cation Exchange Capacity [meq/100 g]	9.9	8.4	11.5	20.6
Water Holding Capacity maximum [g H ₂ O/100 g soil DW] at 0.1 bar (pF 2.0)	39.7 31.6%	27.7 14.5%	32.0 31.7%	53.9 39.5%
Bulk Density (disturbed) [g/cm ³]	1.06	1.20	1.08	0.89
Microbial Biomass [mg microbial carbon per kg soil DW]				
DAT-0 (BIO)	1028	876	1411	3208
DAT-14 (BIO)	116	644	1211	2662

¹ % organic matter = % organic carbon x 1.24

DAT: days after treatment

DW: dry weight

GPS: global positioning system

USDA: United States Department of Agriculture



3. Analytical Procedures

At each sampling interval, the soil was extracted three times at ambient temperature using acetonitrile/water 1/1 (v/v). Furthermore, two microwave-accelerated extraction steps were performed at 70 °C using acetonitrile/water 1/1 (v/v) and methanol/water 1/1 (v/v). The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by TLC/radiodetection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. Test item identity was confirmed by HPLC-MS(/MS) including accurate mass determination and/or by co-chromatography with reference item.

The degradation kinetics of the test item was determined according to FOCUS kinetics (2006) using the software KinGUI2 with three different kinetic models: single first order, first-order multi-compartment and double first order in parallel. Model input datasets were the residual amounts found in each replicate test system at each sampling interval. The initial recovery at DAT-0 was included in the parameter optimization procedure, but for optimal goodness of fit, the value was allowed to be estimated by the model. The best-fit kinetic model was selected on the basis of the χ^2 scaled-error criterion and on the basis of a visual assessment of the goodness of the fits. DT₅₀ and DT₉₀ values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic conditions were maintained and that the soils were microbially active over the duration of the laboratory study.

A. DATA

All calculations for radioactivity (as % of applied radioactivity) in the four soil and the respective trap attachment for volatiles are listed in [Table 7.1.2.2- 4](#) to [Table 7.1.2.2- 7](#), the conclusive overview was presented in [Table 7.1.2.2- 9](#) already.

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Table 7.1.2.1.2- 4: Degradation of Propineb-DIDT in soil [redacted] AXXa under aerobic conditions (mean values and SD expressed as % AR)

Compound	Mean SD	DAT (days)						
		0	0.21	1	2	5	9	14
Test Item	Mean SD	50.7 ± 3.5	31.3 ± 0.9	10.7 ± 0.7	3.9 ± 0.3	LOD	< LOD	< LOD
PU	Mean SD	2.1 ± 0.1	7.1 ± 0.2	4.2 ± 0.0	18.5 ± 0.0	14.9 ± 0.3	7.4 ± 0.1	1.0 ± 0.0
PTU	Mean SD	6.6 ± 0.6	10.8 ± 0.1	5.3 ± 0.3	1.9 ± 0.1	< LOD	< LOD	< LOD
ROI 12	Mean SD	1.8 ± 0.0	2.6 ± 0.1	< LOD	< LOD	< LOD	< LOD	< LOD
4-methyl-imidazoline	Mean SD	5.2 ± 0.1	6.8 ± 0.1	7.7 ± 0.1	5.5 ± 0.2	3.0 ± 0.3	< LOD	< LOD
Sum of Unid./Diff. Residues ¹	Mean SD	10.3 ± 2.0	8.0 ± 0.1	2.1 ± 0.5	8.5 ± 0.6	9.7 ± 0.5	9.9 ± 0.4	8.0 ± 0.2
Total Extractable Residues	Mean SD	76.7 ± 0.7	66.6 ± 0.2	48.8 ± 0.9	39.0 ± 0.8	27.7 ± 0.5	16.3 ± 0.4	10.0 ± 0.3
Carbon Dioxide ³	Mean SD	n.a. ± 0.0	< 0.1 ± 0.0	0.6 ± 0.0	1.9 ± 0.1	2.2 ± 0.1	16.3 ± 0.3	25.3 ± 0.0
Volatile Organic Compounds ³	Mean SD	n.a. ± 0.0	< 0.1 ± 0.0	0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0
Non-Extractable Residues	Mean SD	27.5 ± 0.3	32.4 ± 0.4	49.3 ± 0.3	38.0 ± 0.8	58.4 ± 2.6	63.2 ± 2.6	62.8 ± 1.1
Total Recovery ²	Mean SD	99.2 ± 0.3	99.1 ± 0.2	98.8 ± 0.6	98.9 ± 0.0	93.3 ± 3.1	96.2 ± 3.3	98.1 ± 0.8

n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

¹ Minor degradates are framed up to sum of unidentified / diffuse residues

² Difference of Material Balance values due to rounding errors as well as clean up and chromatographic losses

³ Values taken from Material Balance

ROI 12 (Region of Interest #12) is a very polar zone, probably containing proportions of PDA

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Table 7.1.2.1.2- 5: Degradation of Propineb-DIDT in soil [redacted] under aerobic conditions (mean values and SD expressed as % AR)

Compound	Mean SD	DAT (days)						
		0	0.21	1	2	5	9	14
Test Item	Mean SD	47.4 ± 0.5	27.4 ± 0.9	9.8 ± 0.9	3.4 ± 0.1	< LOD	< LOD	< LOD
PU	Mean SD	2.6 ± 0.1	7.6 ± 0.0	14.4 ± 0.4	18.1 ± 0.0	17.1	22.0 ± 0.0	4.2 ± 0.1
PTU	Mean SD	8.1 ± 0.2	11.5 ± 0.0	6.1 ± 0.5	2.2 ± 0.0	< LOD	< LOD	< LOD
ROI 12	Mean SD	2.2 ± 0.1	2.2 ± 0.0	< LOD	< LOD	< LOD	< LOD	< LOD
4-methyl-imidazoline	Mean SD	5.6 ± 0.0	6.6 ± 0.3	6.6 ± 0.7	4.9 ± 0.1	2.0	< LOD	< LOD
Sum of Unid./Diff. Residues ¹	Mean SD	7.1 ± 0.0	7.6 ± 0.1	8.8 ± 0.9	8.4 ± 0.0	8.0	6.5 ± 0.2	6.4 ± 0.1
Total Extractable Residues ²	Mean SD	72.3 ± 0.0	62.6 ± 1.1	46.7 ± 1.9	3.0 ± 0.0	27.6	26.5 ± 0.2	10.6 ± 0.1
Carbon Dioxide ³	Mean SD	n.a.	0.1 ± 0.0	0.6 ± 0.0	1.6 ± 0.1	7.8	12.9 ± 0.1	22.4 ± 0.1
Volatile Organic Compounds ³	Mean SD	n.a.	0.1 ± 0.0	0.1 ± 0.0	< 0.1 ± 0.0	< 0.1	< 0.1 ± 0.0	< 0.1 ± 0.0
Non-Extractable Residues ³	Mean SD	27.0 ± 0.3	36.3 ± 0.4	51.0 ± 0.0	59.9 ± 0.0	62.1	65.4 ± 0.7	64.2 ± 0.5
Total Recovery ²	Mean SD	99.2 ± 0.5	98.9 ± 1.0	98.2 ± 1.8	98.5 ± 0.2	95.5 n.d.	98.8 ± 0.5	97.2 ± 0.3

n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

¹ Minor degradates are summed up to sum of unidentified / diffuse residues

² Difference to Material Balance values due to rounding errors as well as clean up and chromatographic losses

³ Values taken from Material Balance

⁴ Replicate 2 was accidentally applied twice with application solution. Therefore, only the results of replicate 1 were considered for this report

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Table 7.1.2.1.2- 6: Degradation of Propineb-DIDT in soil [redacted] under aerobic conditions (mean values and SD expressed as % AR)

Compound	Mean SD	DAT (days)						
		0	0.21	1	2	9	14	
Test Item	Mean SD	36.9 ± 1.7	17.5 ± 0.2	5.3 ± 0.4	1.2 ± 0.1	< LOD ± 0.1	< LOD ± 0.1	< LOD ± 0.1
PU	Mean SD	2.3 ± 0.2	7.3 ± 0.0	14.9 ± 0.3	14.0 ± 0.4	13.8 ± 0.4	5.1 ± 0.1	5.6 ± 0.1
PTU	Mean SD	11.8 ± 0.0	14.7 ± 0.3	6.8 ± 0.3	1.4 ± 0.1	< LOD ± 0.1	< LOD ± 0.1	< LOD ± 0.1
ROI 12	Mean SD	< LOD ± 0.0	< LOD ± 0.0	< LOD ± 0.0	< LOD ± 0.0	< LOD ± 0.0	< LOD ± 0.0	< LOD ± 0.0
4-methyl-imidazoline	Mean SD	5.9 ± 0.9	6.1 ± 0.1	5.4 ± 0.1	3.5 ± 0.2	3.3 ± 0.1	< LOD ± 0.1	< LOD ± 0.1
Sum of Unid./Diff. Residues ¹	Mean SD	6.2 ± 0.3	5.9 ± 0.0	5.1 ± 0.0	3.0 ± 0.3	5.0 ± 0.2	2.2 ± 0.0	4.8 ± 0.2
Total Extractable Residues ²	Mean SD	63.7 ± 0.8	53.0 ± 0.4	31.1 ± 1.8	24.4 ± 1.1	21.6 ± 0.7	14.3 ± 0.4	10.4 ± 0.2
Carbon Dioxide ³	Mean SD	n.a. ± 0.0	< 0.1 ± 0.0	0.4 ± 0.0	1.0 ± 0.0	5.2 ± 0.1	8.2 ± 0.1	13.9 ± 0.6
Volatile Organic Compounds ³	Mean SD	n.a. ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0
Non-Extractable Residues ³	Mean SD	34.0 ± 0.1	44.1 ± 0.1	55.4 ± 0.1	50.7 ± 0.3	55.0 ± 2.1	53.1 ± 1.6	54.7 ± 3.0
Total Recovery ²	Mean SD	98.0 ± 0.9	97.6 ± 0.5	96.9 ± 2.5	96.1 ± 1.4	79.9 ± 2.7	75.6 ± 1.3	79.0 ± 3.8

n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

¹ Minor degradates are summed up to sum of unidentified / diffuse residues

² Difference to Material Balance values due to rounding errors as well as clean up and chromatographic losses

³ Values taken from Material Balance

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Table 7.1.2.1.2- 7: Degradation of Propineb-DIDT in soil under aerobic conditions (mean values and SD expressed as % AR)

Compound	Mean SD	DAT (days)						
		0	0.21	1	2	5	9	14
Test Item	Mean SD	20.3 ± 0.7	8.4 ± 0.2	2.4 ± 0.3	< LOD	LOD	< LOD	< LOD
PU	Mean SD	3.6 ± 0.2	10.8 ± 0.3	20.0 ± 0.2	23.4 ± 0.3	17.3 ± 0.1	5.9 ± 0.1	1.9 ± 0.1
PTU	Mean SD	6.4 ± 0.2	6.6 ± 0.4	3.3 ± 0.4	1.3 ± 0.1	< LOD	< LOD	< LOD
ROI 12	Mean SD	2.5 ± 0.0	2.7 ± 0.5	< LOD	< LOD	< LOD	< LOD	< LOD
4-methyl-imidazoline	Mean SD	4.1 ± 0.1	5.3 ± 1.0	5.5 ± 0.1	4.4 ± 0.0	1.0 ± 0.1	< LOD	< LOD
Sum of Unid./Diff. Residues ¹	Mean SD	6.2 ± 0.3	6.2 ± 0.2	6.5 ± 0.1	6.0 ± 0.0	6.4 ± 0.3	6.0 ± 0.0	5.5 ± 0.0
Total Extractable Residues	Mean SD	45.0 ± 1.1	39.0 ± 1.2	37.0 ± 0.7	33.0 ± 0.7	25.4 ± 0.0	11.6 ± 0.1	7.4 ± 0.1
Carbon Dioxide ³	Mean SD	n.a. ± 0.0	< 0.1 ± 0.0	0.7 ± 0.0	1.8 ± 0.0	2.2 ± 0.1	19.4 ± 0.6	26.5 ± 0.0
Volatile Organic Compounds ³	Mean SD	n.a. ± 0.0	< 0.1 ± 0.0	0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0
Non-Extractable Residues	Mean SD	52.7 ± 1.1	56.6 ± 0.4	59.6 ± 0.6	61.0 ± 0.1	63.6 ± 0.0	65.0 ± 0.7	64.0 ± 1.1
Total Recovery ²	Mean SD	97.8 ± 0.0	96.5 ± 0.7	97.0 ± 0.0	97.8 ± 0.8	97.2 ± 0.3	96.1 ± 1.1	97.9 ± 1.2

n.a.: not analyzed; DAT: days after treatment; SD: standard deviation

¹ Minor degradates are summed up to sum of unidentified / diffuse residues

² Difference to Material Balance values due to rounding errors as well as clean up and chromatographic losses

³ Values taken from Material Balance

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B. METHOD VALIDATION

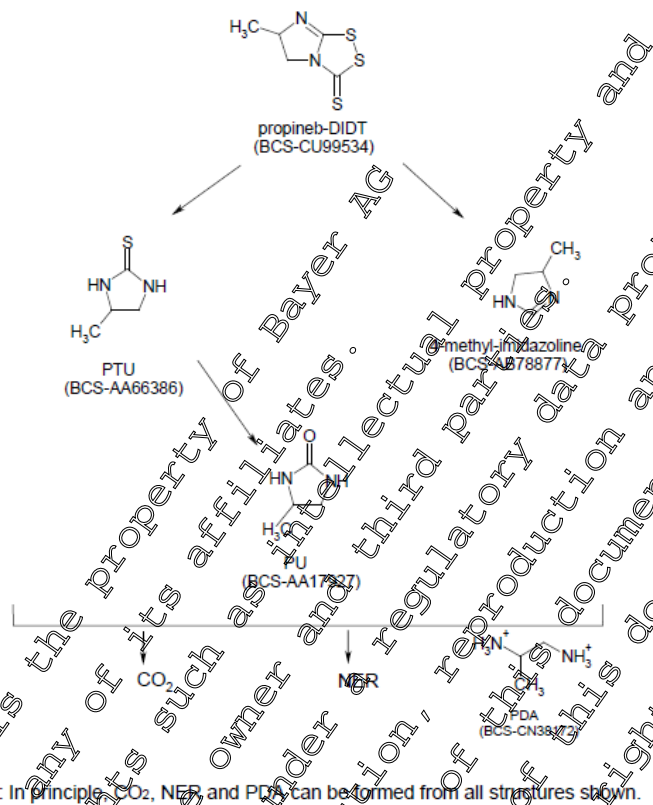
The TLC method was used for data evaluation. A good selectivity and reproducibility demonstrated the suitability for separation and quantification. The TLC limit of quantification (LOQ) for a single peak in the combined organic extracts was 1% of applied radioactivity.

C. DEGRADATION OF PROPINEB-DIDT

The maximum DT₅₀ for Propineb-DIDT was 0.02 days (0.5 h), and the maximum DT₉₀ was 1.1 days in the soils tested under standardized aerobic laboratory conditions at 20 °C in the dark (see [Table 7.1.2.1.2- 2](#)).

Besides the formation of carbon dioxide, three degradation products were identified with the following maximum occurrence: PU with 23.4% AR at DAT-2 in soil DD, PTU with 14.7% AR at DAT-0.21 in soil HN, and 4-Methyl-imidazoline with 7.7% AR at DAT-1 in soil AX. The proposed pathway of degradation of Propineb-DIDT is shown in the following [Figure 7.1.2.1.2- 1](#).

Figure 7.1.2.1.2- 1: Proposed degradation pathway of Propineb-DIDT in soil

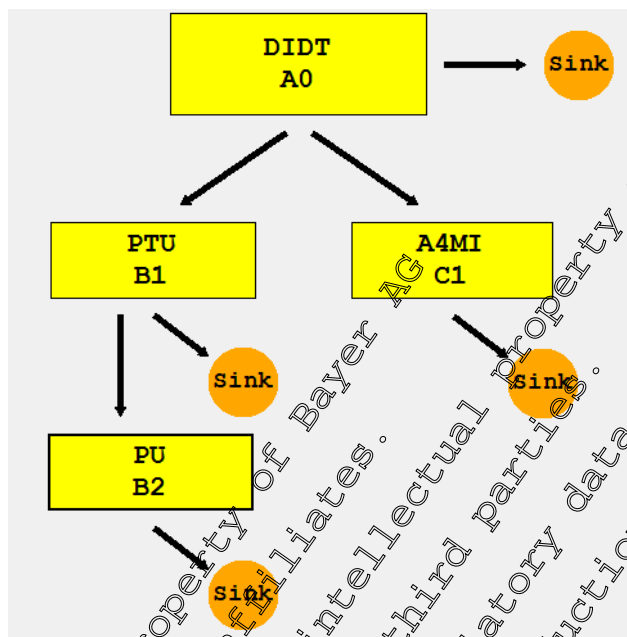


III. CONCLUSIONS

It is concluded from this study that Propineb-DIDT and its residues will be fast degraded in soil under aerobic conditions. Formation of significant amounts of non-extractable residues and carbon dioxide indicates participation in the natural carbon cycle of soil. The short half-lives in soil combined with the determined K_{oc} values indicate that Propineb-DIDT and its major metabolite PTU do not have a potential to accumulate and leach in soil.

The summary of evaluation is compiled by the kinetics report of [redacted] 2014, and the respective results are included in the summary of the degradation rates of Propineb and its major degradation products in soil in the laboratory given in section [CA 7.1.2](#).

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Two systems of kinetics were evaluated. At first all the degradation kinetics were described by SFO. Secondly the degradation of Propineb-DIDT was described with the bi-phasic DFOP model while the degradation of the remaining compounds was still described by SFO kinetics.

Results

The first system, i.e. SFO kinetics for all compounds, resulted in overall reasonable Chi² error values ranging from 14.2 – 23.0 for the entire pathway fit and 3.78 – 13.7 for Propineb-DIDT (Table 7.1.2.1.2- 5).

The visual assessment however indicates rather poor description of the Propineb-DIDT residue data by the SFO model and suggests the system with DFOP kinetics for Propineb-DIDT degradation is a better representation of the data. While the fast first rate constant of the DFOP model is seemingly relevant to also describe the observed fast formation of 4-methyl-imidazoline, propylene-thiourea and propylene-urea values for its t-probability indicate an uncertainty for all four investigated data sets (Table 7.1.2.1.2- 8). Given by the small t-probabilities the corresponding second rate constant was determined at high level of statistical certainty and the split factor “g” as well. The choice of the DFOP approach has only little effect on the fits for the degradation products. Their Chi² error values either improve (e.g. propylene-thiourea and propylene-urea) or deteriorate slightly (e.g. for 4-methyl-imidazoline Table 7.1.2.1.2- 8). In general also the data for the degradation products were best described by using DFOP kinetics for Propineb-DIDT.



Table 7.1.2.1.2- 8: Summary of the kinetic evaluation for Propineb-DIDT degradation in soil ([redacted] 2014)

Soil	Kinetic model ¹	Chi ² error-% ²	Model parameters ³	Visual assessment ⁴	Details in report sect.
AXXa	SFO	DIDT: 13.7	k(DIDT): 5.78***	-	11.4.1.1
	SFO	PTU: 7.73	k(PTU): 1.525***	o	
	SFO	PU: 21.5	k(PU): 0.1060***	-	
	SFO	4-MI: 5.40	k(4-MI): 0.2789***	+	
		system: 23.0			
	DFOP	DIDT: 1.93	k1(DIDT): 7.03# k2(DIDT): 1.308*** g(DIDT): 0.585***	+	
	SFO	PTU: 5.79	k(PTU): 1.717***	o	
	SFO	PU: 11.3	k(PU): 0.0343***	o	
	SFO	4-MI: 6.37	k(4-MI): 0.3055***	+	
		system: 7.87			
[redacted]	SFO	DIDT: 12.8	k(DIDT): 6.08***	o/+	11.4.2.1
	SFO	PTU: 5.96	k(PTU): 1.352***	o/+	
	SFO	PU: 20.7	k(PU): 0.0741***	-	
	SFO	4-MI: 2.91	k(4-MI): 0.3962***	+	
		system: 21.9			
	DFOP	DIDT: 1.75	k1(DIDT): 1.65# k2(DIDT): 1.274*** g(DIDT): 0.643***	+	
	SFO	PTU: 4.16	k(PTU): 1.401***	+	
	SFO	PU: 15.8	k(PU): 0.0867***	o	
	SFO	4-MI: 2.88	k(4-MI): 0.3868***	+	
		system: 11.1			
[redacted]	SFO	DIDT: 7.85	k(DIDT): 8.298***	o	11.4.3.1
	SFO	PTU: 4.24	k(PTU): 1.355***	+	
	SFO	PU: 15.1	k(PU): 0.1043***	+	
	SFO	4-MI: 9.37	k(4-MI): 0.2867***	+	
		system: 14.2			
	DFOP	DIDT: 1.91	k1(DIDT): 1.984# k2(DIDT): 1.518*** g(DIDT): 0.757***	+	
	SFO	PTU: 6.7	k(PTU): 1.450***	+	
	SFO	PU: 11.1	k(PU): 0.1064***	+	
	SFO	4-MI: 2.25	k(4-MI): 0.3054***	+	
		system: 8.04			

¹ SFO: Single first order, DFOP: Double first order in parallel

² for DIDT, PTU, PU, 4-MI and the whole system respectively.

³ k = degradation rate constant, g = split factor for DFOP model, alpha = FOMC parameter, beta = FOMC parameter

⁴ Visual assessment: + = good, o = moderate, - = poor

t-prop: *** < 0.001, ** < 0.01, * < 0.05, # > 0.05

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Table 7.1.2.1.2- 8: (Continued) Summary of the kinetic evaluation for Propineb-DIDT degradation in soil (██████████ 2014)

Soil	Kinetic model ¹	Chi ² error-% ²	Model parameters ³	Visual assessment ⁴	Details in report section	
██████████	SFO	DIDT:	3.78	k(DIDT): 11.54***	-	11.4.4.1
	SFO	PTU:	52.1	k(PTU): 1.505***	o	
	SFO	PU:	18.8	k(PU): 0.0839**	-	
	SFO	4-MI:	6.69	k(4-MI): 0.2774**	+	
		system:	17.5			
	DFOP	DIDT:	n.a.	k(DIDT): 210		
				k(DIDT): 1.560***		
				g(DIDT): 0.882***		
	SFO	PTU:	49.2	k(PTU): 5.00*	o	
	SFO	PU:	18.1	k(PU): 0.1224***	o	
SFO	4-MI:	7.70	k(4-MI): 0.2449***	+		
	system:	7.4				

¹ SFO: Single first order, DFOP: Double first order in parallel
² for DIDT, PTU, PU, 4-MI and the whole system respectively, n.a.: not available
³ k = degradation rate constant, g = split factor for DFOP model, alpha = FQMC parameter, beta = FQMC parameter
⁴ Visual assessment: + = good, o = moderate, - = poor
 t-prop: ***<0.001, **<0.01, *<0.05, o<0.05

In combination with the higher formation fraction for the degradation products of Propineb-DIDT resulting from the DFOP approach (c.f. [Table 7.1.2.1.2- 9](#)), the slow rate of the DFOP model appears to be the best choice for the calculation of half-lives for Propineb-DIDT to be used in pesticide fate models for exposure assessment. It has to be noted that in case of the AXXa soil and the DFOP approach the starting values for the compound Propineb-DIDT were set to a parameter fit resulted from a solo DFOP optimization of Propineb-DIDT data conducted prior to the pathway fit. The procedure was necessary to come to a meaningful result for the pathway fit.

Table 7.1.2.1.2- 9: Comparison of the formation fractions for the degradation products of Propineb-DIDT by two different kinetic model for its degradation

Soil	Path	Formation fraction [-] (SFO, all)	Formation fraction [-] (DFOP and SFO)
██████████ AXXa	DIDT → PTU	0.189	0.229
	DIDT → 4-MI	0.097	0.107
	PTU → PU	1.0	1.0
██████████	DIDT → PTU	0.189	0.210
	DIDT → 4-MI	0.093	0.099
	PTU → PU	1.0	1.0
██████████	DIDT → PTU	0.215	0.243
	DIDT → 4-MI	0.073	0.076
	PTU → PU	0.982	0.885
██████████	DIDT → PTU	0.242	0.246
	DIDT → 4-MI	0.066	0.068
	PTU → PU	1.0	1.0

According to the modelling report by 03!ヤ4.ケ1.pl;(2!uy SI: 2014, the normalized DT₅₀ values for degradation product propineb-DIDT were derived from the second, slow rate constant of double first order in parallel fits and account for 0.5 days (geometric mean). Individual values are listed in the following table.



Table 7.1.2.1.2- 9a: Summary of the DT₅₀ values for propineb-DIDT degradation in soil

Soil	Moisture [% MWHC]	Corr. factor [-]	DT ₅₀ [days]	DT _{50ref} [days]
AXXa	54.2	1	0.5	0.5
	54.2	1	0.5	0.5
	54.2	1	0.5	0.5
	54.2	1	0.5	0.5
Geometric mean			0.5	0.5
Median			0.5	0.5

Degradation of PTU

The degradation of major metabolite PTU was just evaluated on base of a weak experimental data set using two soils by an old not rather detailed reported study (██████████ 1988) which was not any longer regarded sufficient for the Supplemental Dossier for Propineb renewal of approval Annex I.

Therefore, its degradation rate was investigated in a new ¹⁴C-PTU degradation study performed on four soils by ██████████ 2012. In addition further evaluated data (compare [Table 7.1.2.1.2- 4](#) to [Table 7.1.2.1.2- 7](#)) were received within the new Propineb-DIDT aerobic soil degradation study by ██████████ 2014. The overall summary of evaluation is compiled by the report of da ██████████ 2014. The following tables summarise the respective results.

Table 7.1.2.1.2- 10: Kinetic evaluation for degradation of PTU in soil (██████████ 1988)

Soil	Kinetic model ¹	Chi ² error	Model parameters ²	Visual assessment ³
Soil 1	SFO	7.79	k: 0.3433**	+
	FOMC	10.5	alpha: 1469#, beta: 3250#	o
	DFOP	9.25	k1: 0.3433***, k2: 0.0109#, g: 1.0	+
Soil 2	SFO	7.12	k: 0.1866**	+
	FOMC	7.5	alpha: 3396#, beta: 18550#	+
	DFOP	8.48	k1: 0.1438**, k2: 0.1866**, g: 0.001#	+

¹ SFO: Single first order, FOMC: First order multi compartment, DFOP: Double first order in parallel

² k = degradation rate constant, g split factor for DFOP model, alpha = FOMC parameter, beta = FOMC parameter

³ Visual assessment: + = good, o = moderate, - = poor

t-prop: *** < 0.001, ** < 0.01, * < 0.05, # < 0.05; bold letters indicate the model of choice

In [Table 7.1.2.1.2- 10](#) the DT₅₀ for PTU degradation received in soil are summarized. All DT₅₀ values were derived from SFO fits and their corresponding rate constants. The summary shows that PTU is very short living in aerobic soil and degrades with a geometric half-life of 0.2 days, only. A dependence of the DT₅₀ on soil properties was not revealed. In general, the newer studies resulted in shorter half-lives than the older study by ██████████ 1988, and substantiated the very fast degradation of PTU in soil. Longer DT₅₀ values may be an effect of the moisture content as in older studies typically the optimum moisture was not adjusted. However, the information on the soil moisture content used by ██████████ 1988, is not available and therefore a moisture normalisation to scrutinize that hypothesis is not possible.



Table 7.1.2.1.2- 11: Summary of the DT₅₀ for PTU degradation in soil

Soil	Study	Kinetic	DT50
	2014	SFO	0.1
	2012	SFO	0.06
	2014	SFO	0.5
	2014	SFO	0.5
	2012	SFO	0.04
AXXa	2014	SFO	0.4
	2012	SFO	0.04
	2012	SFO	0.03
Soil 1	1988	SFO	2.0
Soil 2	1988	SFO	3.7
Geometric mean			0.2
Median			0.3
max			3.7

PTU is formed from Propineb-DIDT and Propineb. The formation fractions were derived from pathway fits in the case of Propineb-DIDT or by simple means of proportional calculation in the case of Propineb (c.f. section 5.1.4 or section 4.1 of report by [redacted] 2014) and are summarized in Table 7.1.2.1.2- 12. The formation of propylene-thiothrea from Propineb-DIDT and Propineb accounts on average for 0.232 and 0.510, respectively.

Table 7.1.2.1.2- 12: Formation fractions (ff) for the formation of PTU from degradation of Propineb-DIDT and Propineb

Soil	Path	ff	Path	ff
AXXa	DIDT → PTU	0.229	PPB → PTU	0.472
	DIDT → PTU	0.243	PPB → PTU	0.440
	DIDT → PTU	0.243	PPB → PTU	0.470
	DIDT → PTU	0.246	PPB → PTU	0.656
Mean		0.232		0.510

Report:	[redacted];2012;M-426863-01
Title:	Degradation of [14C]BCS-AA66386 in four soils under aerobic conditions at 20 centigrade degrees in the dark
Report No:	S1102562
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Guidelines:	OECD Test Guideline No. 307 Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009; deviations not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The aim of this study was to investigate the degradation of [5-¹⁴C]BCS-AA66386 (= [¹⁴C]PTU) and to follow the formation and disappearance of metabolites in four soils under aerobic conditions at 20°C in the dark. The study was performed with BCS-AA66386 over a period of 14 days.

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The average soil moisture content was maintained at 55% of the maximum water holding capacity (MWHC) over the entire period of the study. The biomass of each soil was determined at the start and 15 days after treatment. No significant difference was observed during the incubation period.

The application rate of [5-¹⁴C]PTU was 45.78 µg (0.16 MBq) per vessel (100 g dry weight of soil), which was equivalent to 0.46 mg BCS-AA66386 /kg at a soil density of 1 g/cm³ and 10 cm depth.

The mass balance was between 90.0 and 99.7% of applied radioactivity (AR) for all soils at all sampling intervals. The amount of extractable radioactivity decreased in soil AX from 84.4% of AR directly after application to 9.6% of AR at the end of the study (day 14). In soil HH the amount of extractable radioactivity decreased from 83.9 to 11.8% of AR, in soil DD from 80.4 to 5.7% and in soil WW from 73.3 to 12.2% of AR. The cold extraction procedure was quite efficient, already since accelerated extraction revealed values always below 5% AR, except for one interval in soil HH (5.4% of AR, day 3) and one interval in soil DD (5.9% of AR, day 1).

The amount of non-extracted (bound) residues increased in soil AX from 14.4% of AR at the start of the study to maximum 51.3% of AR after 7 days decreasing slightly thereafter, in soil HH from 14.2% (day 0) to approx. 41.5% of AR after 10 and 14 days, in soil DD from 18.3% (day 0) to 53.9% of AR after 10 days decreasing thereafter, and in soil WW from 24.8% (day 0) to 50.2% of AR after 14 days. The formation of CO₂ increased steadily to maximum values of 36.0% of AR in soil AX, 37.1% of AR in soil HH, 37.6% of AR in soil DD and 29.6% of AR in soil WW. The amount of organic volatiles was below 0.1% of AR in all soils during the complete study.

One major metabolite was found in the extracts of all four soils showing a maximal occurrence of 64.6% of AR in soil AX (1 day), 67.7% of AR in soil HH (1 day), 36.8% of AR in soil DD (day 2) and 66.8% of AR in soil WW (day 0.125). It was identified as [5-¹⁴C]PU (i.e. BCS-AA17927).

In conclusion, [14C]PTU was degraded rapidly in all four soils and was not detectable at all one day after treatment. The DT₅₀ for degradation was not to be calculated. However, less than 50% AR was contributed to the test item at the first sampling interval three hours after application.

I. MATERIALS AND METHODS**1. Test Item**

Test item [14C]PTU:	[5- ¹⁴ C]BCS-AA66386
Sample ID:	KML 9263
Specific Activity:	9.52 MBq/mg
Radiochemical Purity:	100%
Chemical Purity:	n.a.

2. Test Soils

Four soils were used (see [Table 7.1.2.1.2, 3](#)). The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. No plant protection products were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Soil collection and handling were in accordance to ISO 10381-6.



Table 7.1.2.1.2- 13: Physico-chemical properties of test soils

Parameter	Results/Units	Results/Units	Results/Units	Results/Units
Soil (Soil ID)	AXXa (AX)	4a (HH)	II (DD)	(WW)
Texture Class ¹⁾	Loamy sand	Silt Loam	Loam	Sandy loam
Soil Taxonomic Classification ¹⁾	Sandy, mixed, mesic typic Cambudolls	Loamy, mixed, mesic typic Argudalfs	Fine-loamy, mixed, active, frigid Typic Eutrudept	Loamy, mixed, mesic typic Argudalfs
Sand ¹⁾	77 %	19 %	37 %	57 %
Silt ¹⁾	17 %	64 %	36 %	27 %
Clay ¹⁾	6 %	17 %	27 %	16 %
pH (water)	6.3	6.6	7.5	5.5
pH (saturated paste)	6.5	6.7	7.4	5.6
pH (0.01 M CaCl ₂)	6.1	6.4	7.3	5.3
pH (1 N KCl)	5.9	6.1	7.0	5.0
Organic Matter ²⁾	3.3 %	2.8 %	3.8 %	3.3 %
Organic Carbon	1.9 %	1.6 %	5.1 %	1.9 %
Cation Exchange Capacity	9.6 meq/100 g	11.1 meq/100 g	20.0 meq/100 g	10.7 meq/100 g
Maximum Water Holding Capacity	47.9 g H ₂ O ad 100 g DW	55.0 g H ₂ O ad 100 g DW	78.1 g H ₂ O ad 100 g DW	56.5 g H ₂ O ad 100 g DW
Water Holding Capacity at 0.33 bar (pF 2.5)	11.5 %	19.0 %	34.9 %	17.1 %
at 0.1 bar (pF 2.0)	21.5 %	30.9 %	45.8 %	28.5 %
Bulk Density (disturbed)	1.24 g/cm ³	1.14 g/cm ³	1.00 g/cm ³	1.15 g/cm ³

¹⁾ according to USDA classification²⁾ % organic matter = % organic carbon × 1.724**Biomass of untreated samples [mg C/100 g soils]**

Date of sampling	Days after application	Soil AX	Soil HH	Soil DD	Soil WW
01/08/2011	0	457.8	389.9	520.2	327.9
15/08/2011	14	489.4	346.1	439.3	280.6

B. STUDY DESIGN**1. Experimental Conditions**

The rate of degradation of radiolabelled PTU (BCS-AA66386) was determined under aerobic laboratory conditions in the dark for 14 days at 20 °C and 55% of the maximum water holding capacity in the following four soils:

The application rate of [¹⁴C]-BCS-AA66386 was 45.78 µg (0.16 MBq) per vessel (100 g dry weight of soil), which was equivalent to 0.46 mg BCS-AA66386 /kg at a soil density of 1 g/cm³ and 10 cm depth. The test was performed in static systems consisting of Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds but permeable for oxygen.

2. Sampling

Duplicate samples were processed and analyzed 0, 0.125, 1, 2, 3, 7, 10 and 14 days after treatment (DAT).



3. Analytical Procedures

Duplicate samples were processed and analyzed 0, 0.125, 1, 2, 3, 7, 10 and 14 days after treatment (DAT). At each sampling interval, the soil was extracted three times at ambient temperature using acetonitrile/water 1/1 (v/v). Furthermore, an microwave-accelerated extraction step was performed at 65-70 °C using acetonitrile/water 1/1 (v/v) for 10 minutes. The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC), and by HPLC/radiodetection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. Metabolite identification was performed by co-chromatography. The degradation rates were not evaluated by kinetic models due to very fast observed degradation.

II. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic conditions were maintained and that the soils were microbially active over the duration of the laboratory study.

A. DATA

All calculations for radioactivity (as % of applied radioactivity) in the four soil and the respective trap attachment for volatiles are listed in [Table 7.1.2.1.2- 10](#) to [Table 7.1.2.1.2- 11](#).

Table 7.1.2.1.2- 14: Characterisation of the extractable radioactivity in soil AX in % AR

Sampling interval [days]	0 *	0.125	1	2	3	7	10	14
Test item	57.2 61.8	14.5 11.1	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.
Mean	59.5	12.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
[¹⁴ C]BCS-AA1792 (PU)	24.7 20.7	61.0 64.6	65.3 69.9	60.4 60.9	51.4 50.9	25.8 23.6	16.8 16.3	7.3 8.0
Mean	22.7	62.8	64.6	60.7	51.1	24.7	16.5	7.7

n.d.: not detected; * at time zero interaction with viable soil matrix up to 30 minutes is quite reasonable.

Table 7.1.2.1.2- 15: Characterisation of the extractable radioactivity in soil HH in % AR

Sampling interval [days]	0 *	0.125	1	2	3	7	10	14
Test item	53.6 68.6	18.5 20.0	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.
Mean	61.1	14.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
[¹⁴ C]BCS-AA1792 (PU)	26.5 13.8	56.1 64.8	65.8 69.6	59.3 63.7	50.3 47.1	34.2 35.8	22.5 22.7	8.6 11.1
Mean	20.1	60.4	67.7	61.5	48.7	35.0	22.6	9.9

n.d.: not detected; * at time zero interaction with viable soil matrix up to 30 minutes is quite reasonable.



Table 7.1.2.1.2- 16: Characterisation of the extractable radioactivity in soil DD in % AR

Sampling interval [days]	0 *	0.125	1	2	3	7	10	14
Test item	59.0 68.1	18.2 26.8	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.
Mean	63.6	22.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
[¹⁴ C]BCS-AA17927 (PU)	19.7 7.8	56.2 51.2	56.6 55.5	58.6 55.1	40.4 49.5	19.3 24.0	19.6 17.6	n.d. n.d.
Mean	13.8	53.7	56.0	56.8	40.4	21.6	8.5	n.d.

n.d. not detected; *: at time zero interaction with viable soil matrix up to 30 minutes is quite reasonable.

Table 7.1.2.1.2- 17: Characterisation of the extractable radioactivity in soil WW in % AR

Sampling interval [days]	0 *	0.125	1	2	3	7	10	14
Test item	36.2 46.7	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.
Mean	40.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
[¹⁴ C]BCS-AA17927 (PU)	33.6 24.2	66.6 67.0	61.6 64.8	57.1 59.9	48.7 51.9	32.8 35.4	22.0 21.9	10.8 9.1
Mean	28.5	66.8	63.2	58.5	50.3	34.1	21.9	10.0

n.d. not detected; *: at time zero interaction with viable soil matrix up to 30 minutes is quite reasonable.

B. METHOD VALIDATION

The total recovery of the applied radioactivity (AR) ranged between 90.0 % AR and 99.7 % AR for all soils during the complete study. The material balances shown for all sampling intervals demonstrate that no significant RA dissipated from the flasks or was lost during processing. The analytical limits were obtained from blank samples containing no radioactivity. Typical blanks contained 15 dpm/ sample (dpm = decays per minute).

C. DEGRADATION OF PTU

Due to the very fast degradation a kinetic analysis was not to be performed within the report. However, DT₅₀ was shown to be less than 3 hours.

III. CONCLUSIONS

[¹⁴C]BCS-AA66386 (PTU) decreased rapidly. At day 0 analysis, the amounts of [¹⁴C]PTU were between 63.6 and 59.5 % AR. One day after application BCS-AA66386 was not detectable in any of the soils already.

From this study it is concluded that PTU has no potential for accumulation in the environment. The results are included in the summary of the degradation rates of Propineb and its major degradation products in soil in the laboratory given in section [CA 7.1.2](#).

In [Table 7.1.2.1.2-11](#) the DT₅₀ for PTU degradation received in various soils and studies soil are summarized. All DT₅₀ values were derived from SFO fits and their corresponding rate constants. The summary shows that PTU is very short living in aerobic soil and degrades with a geometric half-life of 0.2 days, only.



According to the modelling report by [redacted] 2014, the normalized DT₅₀ values for degradation product PTU are short with a geometric mean value of 0.2 days (c.f. table below).

Table 7.1.2.1.2- 17a: Summary of the DT₅₀ values for PTU degradation in soil

Soil	Study	Moisture [%MWHC]	Corr. factor [1]	DT ₅₀ [days]	DT _{50,corr} [days]
[redacted]	[redacted] 2014	54.2	1	0.1	
[redacted]	[redacted] 2012	55	1	0.06	0.06
[redacted]	[redacted] 2014	54.2	1	0.5	0.5
[redacted] am	[redacted] 2014	54.2	1	0.5	0.5
[redacted]	[redacted] 2012	55	1	0.04	0.04
[redacted]	[redacted] 2014	54.2	1	0.4	0.4
AXXa	[redacted] 2012	55	1	0.04	0.04
[redacted]	[redacted] 2012	55	1	0.03	0.03
Soil 1	[redacted] (1988)	n.a.	n.a.	2.0	2.0
Soil 2	[redacted] (1988)	n.a.	n.a.	3.7	3.7
Geometric mean				0.3	0.2
Median				0.3	0.3
Maximum				3.7	3.7

n.a.: not applicable

Degradation of PU

Propylene-urea was identified as a degradation product of Propineb by [redacted] 2014, and [redacted] (1996). It is proposed to be a primary degradation product of PTU. This is confirmed by [redacted] 2012, where PU was identified as degradation product of PTU degradation in aerobic soil. Rate of degradation studies for PU itself are available from [redacted] (2008a, 2008b) (for study summaries see later in this chapter) and [redacted] (1993). Furthermore, PU was also detected in the study by [redacted] 2014, where the degradation of Propineb-DIDT was investigated.

The degradation of major terminal metabolite PU is now evaluated on base of a large experimental data set for the Supplemental Dossier for Propineb renewal of approval Annex I.

The evaluation of PU degradation values from study by [redacted] 2014, was contained in the earlier PTU section (see [redacted] 2014) already. Initial values for the metabolites, 4-Methyl-imidazoline, PTU and PU were set to zero. First values at the limit of detection (LOD) or below LOD were set to 0.5 × LOD. The LOD accounted for 1.0 % AR. The pre-processed data is shown in section 5.1.2 (Table 10) of report, and the proposed degradation pathway indicated by Figure 7.1.2.1.2- 2 was used. The resulting data for PU were in Table 7.1.2.1.2- 8 and Table 7.1.2.1.2- 9, already.

As well the evaluation of PU degradation values from study by [redacted] 2012, was contained in the earlier PTU section (see [redacted] 2014) already. Initial values for the metabolites, 4-Methyl-imidazoline, PTU and PU were set to zero. First values at the limit of detection (LOD) or below LOD were set to 0.5 × LOD. The LOD accounted for 1.0 % AR. The pre-processed data is shown in section 5.1.2 (Table 10) of report, and the proposed degradation pathway indicated by Figure 7.1.2.1.2- 2 was used. The resulting data for PU were in Table 7.1.2.1.2- 8 and Table 7.1.2.1.2- 9, already.

The evaluation of all PU degradation data is compiled by the report of [redacted] 2014.



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The following [Table 7.1.2.1.2- 18](#) and [Table 7.1.2.1.2- 19](#) summarise the respective results.

All DT₅₀ values were derived from SFO fits and their corresponding rate constants. The summary shows that PU is short living in aerobic soil and degrades with a geometric non-normalized half life of 5.9 days and a median of 5.7 days, respectively. A dependence of the DT₅₀ on soil properties was not detected, however, a dependency of concentration is soil (the lower the faster). In general the newer studies with more realistic lower concentrations in soil resulted in shorter half-lives than the older ones, i.e. the study by [redacted] 1993, which includes the maximum DT₅₀ value of 45.9 days. In order to use the DT₅₀ values for modelling purposes in exposure predictions the values derived from [redacted] 1993, may be normalized to optimum soil moisture content and a geometric mean or median value may then be calculated.

Table 7.1.2.1.2- 18: Overall Summary of the DT₅₀ for PU degradation in soil

Soil	Study	Study conditions ¹	Kinetic model	DT ₅₀
BBA soil 2.2	[redacted] 1993	14.4 %	SFO	17.0
BBA soil 2.3	[redacted] 1993	24.0 %	SFO	9.6
[redacted]	[redacted] 2014		SFO	5.7
[redacted]	[redacted] 2012		SFO	3.7
[redacted]	[redacted] (2008a)		SFO	4.4
[redacted]	[redacted] (2008b)		SFO	1.9
[redacted]	[redacted] 2014		SFO	6.5
[redacted]	[redacted] (2008a)		SFO	6.9
[redacted]	[redacted] (2008b)		SFO	5.4
[redacted]	[redacted] 1993	14.4 %	SFO	7.7
[redacted] am	[redacted] 2014		SFO	8.1
[redacted]	[redacted] 2012		SFO	5.7
[redacted]	[redacted] (2008a)		SFO	5.4
[redacted]	[redacted] (2008b)		SFO	2.3
[redacted]	[redacted] 1993	10.3 %	SFO	45.9
[redacted] AIIIa	[redacted] (2008a)		SFO	6.8
[redacted]	[redacted] (2008b)		SFO	3.0
[redacted]	[redacted]		SFO	5.2
AXXa	[redacted] 2014		SFO	5.2
[redacted]	[redacted] 2012		SFO	4.6
[redacted]	[redacted] (2008a)		SFO	5.9
[redacted]	[redacted] (2008b)		SFO	3.4
[redacted]	[redacted] 2012		SFO	5.9
Geometric mean				5.9
Median				5.7
Max				45.9

¹ moisture content (grav. %) and temperature if deviating from optimum (i.e. 55% MWHC, 20°C)

Table 7.1.2.1.2- 19: Formation fractions (ff) for the formation of PU from degradation studies of Propineb-DIDT and PTU

Soil	Study	ff
[redacted]	[redacted] 2014	1.0



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		2012	0.767
		2014	0.885
		2014	1.0
		2012	0.798
	AXXa	2014	1.0
		2012	0.815
		2012	0.775
		Mean	0.880

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The following new experimental study was performed in order to broaden (i.e. for soil pH) the data set for PU, the terminal degradate of Propineb.

Report:	[REDACTED];2008-M-311730-01
Title:	[5- ¹⁴ C]BCS-AA17927 (propylene-urea): Aerobic degradation in five European soils
Report No:	MEF-08/443
Document No:	M-311730-01-1
Guidelines:	OECD 307; EU 95/36/EC amending 91/414/EEC, Annex II and III
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The biotransformation of [5-¹⁴C]BCS-AA17927, (¹⁴C-propylene-urea, PU) was studied in [REDACTED] AXXa (LX), sandy loam soil (pH 6.1, organic carbon 2.0%, [REDACTED] Germany), [REDACTED] II (DDII), silty clay (pH 7.1, organic carbon 4.1%, [REDACTED] Germany, [REDACTED] AIIIa (LA), loam soil (pH 6.3, organic carbon 1.3%, [REDACTED] Germany), [REDACTED] HaH, silt loam soil (pH 6.5, organic carbon 2.5%, [REDACTED] Germany), [REDACTED] (HH), loam soil (pH 4.8, organic carbon 3.3%, [REDACTED] Germany) for 20 days under aerobic conditions in the dark at 20°C and 55% WHC_{max} (max. water holding capacity). [5-¹⁴C]BCS-AA17927 (PU) was applied at the nominal rate of 515 µg/kg soil (DM). This value is based on maximum PEC values of 655 and 375 µg/kg for PU in soil for the two intended uses in field crops and grapes. The PEC values were determined for field application rates of 4 x 2100 g Propineb/ha (field crops) and 4 x 1348.6 g Propineb / ha (grapes).

The test system consisted of Erlenmeyer flasks equipped with traps for the collection of CO₂ and volatile organic compounds. Samples were analyzed at 0, 2, 4, 7, 10, 14, 21 days after treatment (DAT). At each sampling date the soil samples were extracted five times by shaking at ambient temperature and once with microwave assistance at 70°C with methanol/water mixtures. The [5-¹⁴C]BCS-AA17927 (PU) residues were analyzed and quantified by HPLC. TLC was used as confirmation method. The identification of the test item was accomplished by LC-MS/MS and LC-1H-NMR spectroscopy and was confirmed by co-chromatography using a non-labeled reference. Only trace amounts of other residues were detected in the extracts.

The test conditions outlined in the study protocol were maintained throughout the study. Material balances were 96.8 ± 3.1% (94.4 to 99.2%, soil LX), 92.7 ± 4.0% (89.2 to 99.4%, soil DDII), 95.9 ± 2.6% (93.1 to 100.1%, soil LA), 95.4 ± 2.9% (92.6 to 100.4, soil HaH) and 96.4 ± 1.8% (94.6 to 99.4%, soil HH) of the applied amount.

The test item was declining from 94.0, 90.3, 94.4, 94.2% and 93.0% AR at DAT-0 to 1.1, 0.5, 4.7, 1.8 and 12.0% in the soils LX, DDII, LA, HaH and HH, respectively, at the end of the study. For kinetics evaluations see [Table 7.1.2.1.2, 20](#).

The half-life (SFO, GEOMean) for [¹⁴C]PU in the tested soils kept at 20°C under aerobic conditions was 6.1 days.

Non-extractable ¹⁴C-residues increased from 3.2, 4.7, 2.7, 3.6 and 4.4% AR at DAT-0 to 35.8, 35.8, 35.1, 39.2 and 47.9% AR at the end of the study period, respectively.

Considerable amounts of ¹⁴CO₂ were produced amounting to 53.2, 51.3, 50.5, 49.7 and 32.4% of AR in the soils LX, DDII, LA, HaH and HH, respectively, at the end of the study. No volatile organic compounds were measured at values > 0.1% AR at all sampling dates.



Table 7.1.2.1.2- 20: Degradation kinetics calculations for [¹⁴C]PU in soil (best fits indicated bold typed)

Soil	Kinetic Model	DT ₅₀ [d]	DT ₉₀ [d]	Chi ² error
[redacted] AXXa	SFO	6.1	20.4	7.2723
	FOMC	6.1	20.5	7.9397
	DFOP	6.1	20.4	8.6556
[redacted] II	SFO	4.7	15.5	11.2532
	FOMC	4.6	15.5	12.2701
	DFOP	4.7	15.5	13.3933
[redacted] AIIIa	SFO	7.1	23.7	6.4198
	FOMC	7.1	23.8	7.0465
	DFOP	7.1	23.7	7.6410
[redacted]	SFO	5.2	18.8	5.7411
	FOMC	5.6	18.9	6.3244
	DFOP	5.7	18.8	6.8931
[redacted]	SFO	7.3	24.3	4.0113
	FOMC	7.7	24.9	4.1588
	DFOP	7.3	24.4	4.2025
SFO-Mean	Arithmetic	6.2	20.5	
	Geometric	6.1	20.3	

I. MATERIALS AND METHODS

1. Test Item

Test item: [¹⁴C]BCS-A017927 (¹⁴C-PU)
 Sample ID: KATH 6556
 Specific Activity: 4.20 MBq/mg (115.41 µCi/mg)
 Radiochemical Purity: 97.5% (HPLC radiodetection)
 Chemical Purity: > 99% (HPLC UV det., 192 nm)

2. Test Soils

Five soils were used (see Table 7.1.2.1.2-21). The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. No plant protection products were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm.

B. STUDY DESIGN

1. Experimental Conditions

The biotransformation of [¹⁴C]BCS-A017927 (¹⁴C-PU) was studied in 5 soils for 21 days under aerobic conditions in the dark at 20°C and 55% WHCmax (max. water holding capacity).

The test was performed in static systems consisting of Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds but permeable for oxygen.

2. Sampling

Samples were analyzed at 0, 2, 4, 7, 10, 14, 21 days after treatment (DAT) Duplicate samples were processed at each sampling date.



Table 7.1.2.1.2- 21: Physico-chemical properties of test soils

Parameter	Results/Units	Results/Units	Results/Units	Results/Units	Results/Units
Soil	AXXa	II	AIIIa		
Soil Taxonomic Classification (USDA)	Sandy floodplain deposits of the lower terrace of the Rhine river, material from the Pleistocene Ice Age	Not available	Finer fluvial sediment above coarse floodplain deposits of the lower terrace of the Rhine river, material from the Pleistocene Ice Age	Loess or loess colluvium (Pleistocene, Holocene)	Not available
Soil Series	Sandy, mixed, mesic Typic Cambudolls	Not available	Loamy, mixed, mesic Typic Argudalfs	Loamy, mixed, mesic Typic Argudalfs	Not available
Texture Class (USDA)	Sandy Loam	Silty Clay	Loam	Silt Loam	Silt Loam
Sand	67%	17%	43%	21%	27%
Silt	19%	41%	33%	59%	35%
Clay	14%	42%	22%	20%	20%
pH in Water	6.3	7.2	6.1	6.6	5.1
pH in saturated paste	6.2	7.7	6.5	6.6	5.0
pH in KCl	5.9	8.8	6.1	6.2	4.4
pH in CaCl ₂	6.1	7.1	6.6	6.5	4.8
Organic Matter ¹⁾	3.4%	7.1%	2.2%	4.3%	5.7%
Organic Carbon	2.0%	4.6%	1.3%	2.5%	3.3%
Soil Biomass ²⁾ (DAT-0 and DAT-42)	492/473	233/1819	176/198	113/701	723/483
Cation Exchange Capacity (CEC)	9.6 meq/100 g	19.2 meq/100 g	9.6 meq/100 g	13.4 meq/100 g	10.5 meq/100 g
55% of WHC _{max}	28.4 g water ad 100 g soil DM	42.7 g water ad 100 g soil DM	27.4 g water ad 100 g soil DM	36.5 g water ad 100 g soil DM	41.4 g water ad 100 g soil DM

1) % organic matter = % organic carbon x 1.24

2) mg microbial carbon per kg of soil [dry weight]

3. Analytical Procedures

The soil samples were extracted five times by shaking at ambient temperature and once with microwave assistance at 70°C with methanol/water mixtures. The [5-¹⁴C]BCS-AA17927 residues were analyzed and quantified by HPLC. TLC was used as confirmation method. The identification of the test item was accomplished by LC-MS/MS and LC-1H-NMR spectroscopy and was confirmed by co-chromatography using a non-labeled reference.



II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.2.1.2- 22: Biotransformation of [¹⁴C]PU in soil [redacted] AXx under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)						
		0	2	4	7	10	14	21
BCS-AA17927 (¹⁴ C-PU)	Mean	94.0	80.6	66.5	47.4	33.0	17.8	11.1
	SD	±0.6	±0.4	±0.3	±0.6	±0.0	±0.2	±0.3
Unidentified RA	Mean	2.0	1.0	1.8	3.2	3.1	3.3	4.3
	SD	±0.1	±0.2	±0.2	±0.6	±0.0	±0.2	±0.2
Total extractable residues	Mean	96.0	81.6	68.3	49.0	32.1	19.0	5.4
	SD	±0.7	±0.2	±0.4	±0.0	±1.9	±0.0	±0.0
¹⁴ CO ₂	Mean	n.a.	1.5	1.3	20.6	22.5	40.5	53.2
	SD		±0.1	±0.2	±0.0	±0.9	±0.3	±0.1
Volatile organics	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	SD							
Non-extractable residues	Mean	3.2	11.1	17.9	25.0	32.9	36.3	35.8
	SD	±0.2	±0.3	±0.5	±0.2	±5.0	±0.2	±0.1
Total Recovery	Mean	99.2	97.2	97.5	95.5	98.4	95.8	94.4
	SD	±0.9	±0.4	±0.3	±0.2	±6.2	±0.1	±0.0

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

Table 7.1.2.1.2- 23: Biotransformation of [¹⁴C]PU in soil [redacted] under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)						
		0	2	4	7	10	14	21
BCS-AA17927 (¹⁴ C-PU)	Mean	92.0	75.9	60.0	38.8	18.8	1.4	0.5
	SD	±0.6	±1.0	±0.1	±0.2	±0.7	±0.6	±0.1
Unidentified RA	Mean	2.4	2.1	2.7	2.0	2.6	3.7	2.9
	SD	±0.6	±0.5	±0.2	±0.0	±0.1	±0.5	±0.0
Total extractable residues	Mean	94.6	78.0	62.6	40.8	21.4	5.1	3.4
	SD	±0.1	±0.5	±0.3	±0.2	±0.7	±0.0	±0.1
¹⁴ CO ₂	Mean	n.a.	3.3	8.8	19.4	30.3	45.5	51.3
	SD		±0.1	±0.2	±0.1	±0.6	±0.0	±0.0
Volatile organics	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	SD							
Non-extractable residues	Mean	4.7	15.0	21.7	30.5	37.5	39.1	35.8
	SD	±0.3	±0.7	±0.1	±0.4	±0.1	±0.1	±0.0
Total Recovery	Mean	99.4	96.3	93.1	90.6	89.2	89.7	90.5
	SD	±0.2	±1.3	±0.2	±0.7	±0.1	±0.0	±0.0

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation



Table 7.1.2.1.2- 24: Biotransformation of [¹⁴C]PU in soil [redacted] AIIIa under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)						
		0	2	4	7	10	14	21
BCS-AA17927 (¹⁴ C-PU)	Mean	94.4	83.2	71.6	53.1	38.9	23.3	4.7
	SD	±0.7	±0.2	±0.9	±0.5	±0.3	±0.5	±0.2
Unidentified RA	Mean	3.0	1.7	2.1	2.8	2.5	2.8	2.8
	SD	±0.4	±0.1	±0.5	±0.2	±0.1	±0.2	±0.3
Total extractable residues	Mean	97.4	84.9	73.7	55.9	41.4	26.1	7.5
	SD	±0.3	±0.3	±0.4	±0.3	±0.2	±0.1	±0.1
¹⁴ CO ₂	Mean	n.a.	23	9.0	18.3	26.6	36.4	50.5
	SD		±0.1	±0.0	±0.1	±0.1	±0.2	±0.5
Volatile organics	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	SD							
Non-extractable residues	Mean	2.7	9.7	14.4	21.3	25.5	31.4	35.1
	SD	±0.4	±0.2	±0.2	±0.4	±0.4	±0.2	±0.2
Total Recovery	Mean	100.1	97.9	97.0	95.5	93.5	93.9	93.1
	SD	±0.1	±0.0	±0.5	±0.1	±0.4	±0.3	±0.3

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

Table 7.1.2.1.2- 25: Biotransformation of [¹⁴C]PU in soil [redacted] under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)						
		0	2	4	7	10	14	21
BCS-AA17927 (¹⁴ C-PU)	Mean	94.2	78.0	63.2	43.8	28.9	13.7	1.8
	SD	±1.2	±0.5	±0.0	±0.3	±1.5	±0.0	±0.3
Unidentified RA	Mean	2.5	1.6	4.8	2.0	2.4	2.3	2.7
	SD	±0.4	±0.4	±0.5	±0.2	±0.2	±0.1	±0.1
Total extractable residues	Mean	96.7	79.5	65.0	45.8	31.3	16.0	4.5
	SD	±0.8	±0.1	±0.0	±0.4	±1.3	±0.0	±0.2
¹⁴ CO ₂	Mean	n.a.	4.4	11.3	20.7	29.0	38.8	49.7
	SD		±0.1	±0.1	±0.2	±0.2	±0.1	±0.3
Volatile organics	Mean	n.d.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	SD							
Non-extractable residues	Mean	3.6	13.5	20.2	27.8	32.2	38.5	39.2
	SD	±0.1	±0.0	±0.1	±0.3	±0.5	±0.6	±0.3
Total Recovery	Mean	100.4	97.5	96.5	94.3	92.6	93.4	93.5
	SD	±0.7	±0.3	±0.3	±0.1	±0.5	±0.7	±0.1

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

Table 7.1.2.1.2- 26: Biotransformation of [¹⁴C]PU in soil under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)						
		0	2	4	7	10	14	21
BCS-AA17927 (¹⁴ C-PU)	Mean	93.0	75.6	62.5	48.2	36.1	25.1	12.0
	SD	±0.1	±0.8	±0.6	±0.7	±0.1	±0.8	±0.1
Unidentified RA	Mean	2.0	1.5	1.6	1.6	1.9	1.9	3.5
	SD	±0.2	±0.0	±0.4	±0.2	±0.3	±0.4	±0.2
Total extractable residues	Mean	95.0	77.2	64.1	49.9	38.1	27.0	14.6
	SD	±0.3	±0.8	±0.1	±0.6	±0.3	±0.4	±0.1
¹⁴ CO ₂	Mean	n.d.	2.2	7.2	12.9	17.5	23.5	32.4
	SD		±0.1	±0.1	±0.1	±0.1	±0.1	±0.0
Volatile organics	Mean	n.a.	0.1	0.1	0.1	0.1	0.1	0.1
	SD		±0.1	±0.1	±0.1	±0.1	±0.1	±0.1
Non-extractable residues	Mean	4.4	17.7	25.7	33.7	39.5	44.9	47.9
	SD	±0.2	±0.2	±0.5	±0.1	±0.1	±0.1	±0.1
Total Recovery	Mean	99.4	98.1	96.4	95.8	95.1	95.4	94.6
	SD	±0.5	±1.0	±0.3	±0.6	±0.2	±0.1	±0.3

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

B. METHOD VALIDATION

The DAT-0 extraction efficiency was 94.6 to 97.4% AR. The stability of the test item was verified by a DAT-0 recovery of 92.3 to 94.4% AR for the organic and microwave extracts. These results indicated that the extraction method was well suited to extract the applied [¹⁴C]-labeled test item from the soil matrix.

The HPLC method (reversed phase RP-18) was used for data evaluation. A good selectivity and reproducibility demonstrated the suitability of the separation and quantitation.

The limit of quantitation values (LOQ) of HPLC for a single peak in the organic soil extracts was approximately 0.8% AR. The HPLC mean recovery for this method was approximately 102.0 and 102.5% for the two types of extracts indicating that no significant losses of radioactivity occurred on column, tubing or detectors.

Normal phase Si-60 TLC was used to confirm the results.

C. DEGRADATION OF ¹⁴C-PU

The test item was declining from 94.0, 92.3, 94.4, 94.2% and 93.0% AR at DAT-0 to 1.1, 0.5, 4.7, 1.8 and 12.0% in the soils LX, DD, LA, HaH and HH, respectively, at the end of the study. Thereby, not any other major metabolite could be observed.

For kinetics evaluation see [Table 7.1.2.1.2- 20](#). The half-life (SFO, GEOmean) for [¹⁴C]PU in the tested soils kept at 20°C under aerobic conditions was 6.1 days.

III. CONCLUSIONS

The data gathered in the current laboratory investigation demonstrate that the test item is degraded well in the five soils. For [¹⁴C]PU a DT₅₀ of 6.1 days (GEOmean over the five soils) was calculated. High amounts of ¹⁴CO₂ (up to 53.2% AR) were measured at the end of the study indicating that relatively quick mineralization occurred once metabolism of [¹⁴C]PU is initiated.



The following new experimental study (quite similar to the study described before) was performed with a lower treatment dose since there were some hints that the degradation of PU is depended on the test concentration in soil.

Report:	[REDACTED];2008;M-312784-01
Title:	[5- ¹⁴ C]BCS-AA17927 (propylene-urea): Aerobic degradation at low rate in five European soils
Report No:	MEF-08/473
Document No:	M-312784-01-1
Guidelines:	OECD 307; EU 95/36/EC amending 91/414/EEC, Annexes II and III
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The biotransformation of [5-¹⁴C]BCS-AA17927 ([¹⁴C]PU) at low application rate was studied in the same five soils as mentioned in the study before [REDACTED] AXXa (LX), [REDACTED] D (DD), [REDACTED] AIIIa (LA), [REDACTED] (HH), and [REDACTED] (HS) for 14 days under aerobic conditions in the dark at 20 °C and 55% WHC_{max} (max. water holding capacity). [¹⁴C]PU was applied at the nominal rate of 50 µg/kg soil (DM) corresponding to 10 µg on an environmentally relevant maximum soil concentration used in an earlier study. Due to e.g. translocation of PU in soil its concentration will decrease to lower values in deeper soil layers. This effect was simulated for the investigation in the present study.

Again, the test system consisted of Erlenmeyer flasks equipped with traps for the collection of CO₂ and volatile organic compounds. Samples were analyzed at 0, 1, 2, 3, 4, 10 and 14 days after treatment (DAT). At each sampling date the soil samples were extracted five times by shaking at ambient temperature and once with microwave assistance at 70 °C with methanol/water mixtures. The [5-¹⁴C]BCS-AA17927 residues were analyzed and quantified by HPLC. TLC was used as confirmation method. The identity of the test item in the application solution was verified by LC-MS/MS and was confirmed throughout the experiment by co-chromatography using a non-labeled reference. Only trace amounts of other residues were detected in the extracts.

The test conditions outlined in the study protocol were maintained throughout the study. Material balances were 95.6 ± 2.3% (92.2 to 99.1%, soil LX), 92.5 ± 3.7% (89.4 to 99.9%, soil DD), 95.7 ± 2.5% (93.1 to 99.9%, soil LA), 95.8 ± 3.1% (92.7 to 101%, soil HH) and 95.8 ± 2.0% (93.8 to 99.0%, soil HS) of the applied amount.

The test item was declining from 94.8, 92.8, 94.2, 92.7% and 92.1% AR at DAT-0 to 0.9, 0.4, 0.6, 0.6 and 1.2% in the soils LX, DD, LA, HH and HS, respectively, at the end of the study. For kinetics evaluations see [Table 1.1.2.1.2- 27](#)

The half-life (SFO, GEO_{mean}) for [¹⁴C]PU in the tested soils kept at 20 °C under aerobic conditions was just 2.7 days, and this significantly lower, as that determined for the higher test concentrations. As it was indicated a concentration dependency of the degradation rate for PU was shown. In a supplementary non-GLP experiment it was demonstrated that this effect was not caused by scattering activities of different soil batches taken from the same field, but rather is a genuine property of the metabolite PU.

Non-extractable ¹⁴C residues increased from 2.3, 3.8, 2.2, 5.4 and 3.7% AR at DAT-0 to 40.6, 40.4, 39.4, 44.6 and 46.5% AR at the end of the study period, respectively.

Considerable amounts of ¹⁴CO₂ were formed amounting to 44.9, 49.4, 48.1, 45.9 and 42.2% of AR in the soils LX, DD, LA, HH and HS, respectively, at the end of the study.

No volatile organic compounds were measured at values > 0.1% AR at all sampling dates.



Table 7.1.2.1.2- 27: Degradation kinetics calculations for [5-¹⁴C]PU in soil (best fits indicated bold typed)

Soil	Kinetic Model	DT ₅₀ [d]	DT ₉₀ [d]	Chi ² error
[REDACTED] AXXa	SFO	3.5	11.8	5.5879
	FOMC	3.5	11.8	6.2427
	DFOP	3.5	11.8	6.4374
[REDACTED] II	SFO	2.0	6.8	7.6685
	FOMC	2.0	6.8	8.4598
	DFOP	2.0	6.8	8.8695
[REDACTED] AIIIa	SFO	3.2	10.5	7.6954
	FOMC	3.2	10.6	8.4452
	DFOP	3.2	10.5	8.9678
[REDACTED]	SFO	2.5	8.2	6.5303
	FOMC	2.5	8.2	7.0688
	DFOP	2.5	8.2	7.5281
[REDACTED]	SFO	2.7	8.9	5.2965
	FOMC	2.7	8.9	5.7010
	DFOP	2.7	8.9	6.0322
SFO-Mean	Arithmetic	2.8	9.2	
	Geometric	2.7	9.1	

SFO, single first order
FOMC, first order multi compartment
DFOP, double first order in parallel

I. MATERIALS AND METHODS

1. Test Item

Test item: [5-¹⁴C]BCS-AA17927 (¹⁴C)PU
 Sample ID: KATH 6556
 Specific Activity: 4.27 MBq/mg (115.4 μCi/mg)
 Radiochemical Purity: 97.5% (HPLC, radio detection)
 Chemical Purity: > 99% (HPLC, UV det., 292 nm)

2. Test Soils

Five soils were used (see [Table 7.1.2.1.2- 28](#)). The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. No plant protection products were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm.

B. STUDY DESIGN

1. Experimental Conditions

The biotransformation of [5-¹⁴C]BCS-AA17927 (¹⁴C-PU) was studied in 5 soils for 14 days under aerobic conditions in the dark at 20 °C and 55% WHCmax (max. water holding capacity). The test was performed in static systems consisting of Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds but permeable for oxygen.

2. Sampling

Samples were analyzed at 0, 1, 2, 3, 4, 7, 10 and 14 days after treatment (DAT). Duplicate samples were processed at each sampling date.



Table 7.1.2.1.2- 28: Physico-chemical properties of test soils

Parameter	Results/Units	Results/Units	Results/Units	Results/Units	Results/Units
Soil	AXXa	II	AIIIa		
Soil Taxonomic Classification (USDA)	Sandy floodplain deposits of the lower terrace of the Rhine river, material from the Pleistocene Ice Age	Not available	Finer fluvial sediment above coarse floodplain deposits of the lower terrace of the Rhine river, material from the Pleistocene Ice Age	Loess or loess colluvium (Pleistocene, Holocene)	Not available
Soil Series	Sandy, mixed, mesic Typic Cambudolls	Not available	Loamy, mixed, mesic Typic Argudalfs	Loamy, mixed, mesic Typic Argudalfs	Not available
Texture Class (USDA)	Sandy Loam	Loam	Sandy loam	Loam	Silt Loam
Sand	75%	31%	53%	35%	33%
Silt	19%	42%	28%	50%	55%
Clay	6%	27%	17%	16%	15%
pH in Water	6.0	7.2	7.0	6.9	6.0
pH in saturated paste	6.1	7.7	7.0	6.9	6.0
pH in KCl	5.7	7.1	6.4	6.4	5.3
pH in CaCl ₂	5.9	7.1	6.6	6.8	5.8
Organic Matter ¹⁾	2.9%	8.1%	2.2%	4.8%	4.0%
Organic Carbon	1.7%	4.1%	1.3%	2.8%	2.3%
Soil Biomass ²⁾ (DAT-0 and DAT-21)	Table 8 of report	Table 8 of report	Table 8 of report	Table 8 of report	Table 8 of report
Cation Exchange Capacity (CEC)	9.0 meq/100 g	15.9 meq/100 g	9.4 meq/100 g	13.0 meq/100 g	8.7 meq/100 g
55% of WHC _{max}	25.4 g water ad 100 g soil DM	44.7 g water ad 100 g soil DM	24.8 g water ad 100 g soil DM	37.0 g water ad 100 g soil DM	34.3 g water ad 100 g soil DM

1) % organic matter = % organic carbon x 1.24

2) mg microbial carbon per kg of soil [dry weight]

3. Analytical Procedures

The soil samples were extracted five times by shaking at ambient temperature and once with microwave assistance at 70 °C with methanol/water mixtures. The [¹⁴C]PU residues were analyzed and quantified by HPLC. TLC was used as confirmation method. The identification of the test item was accomplished by LC-MS/MS and LC-¹H-NMR spectroscopy and was confirmed by co-chromatography using a non-labeled reference.



II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.2.1.2- 29: Biotransformation of [¹⁴C]PU in soil [redacted] AXXa under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)							
		0	1	2	3	4	7	10	14
BCS-AA17927 ([¹⁴ C]PU)	Mean	94.8	80.9	69.2	56.9	47.0	25.9	20.9	6.9
	SD	±0.7	±1.0	±1.1	±0.3	±1.3	±2.2	±0.7	±0.1
Unidentified RA	Mean	2.0	2.7	2.2	2.3	2.1	2.6	4.2	5.0
	SD	±0.8	±0.8	±0.2	±0.7	±0.2	±0.6	±0.2	±0.3
Total extractable residues	Mean	96.8	85.6	71.3	59.2	49.0	28.0	12.5	6.6
	SD	±0.1	±0.2	±0.9	±0.5	±1.5	±1.6	±0.3	±0.3
¹⁴ CO ₂	Mean	n.a.	3.5	3.3	2.0	16.6	22.6	38.7	44.9
	SD	n.a.	±0.1	±0.9	±0.2	±0.5	±0.2	±0.3	±0.1
Volatile organics	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	0.0	<0.1
	SD	n.a.						±0.0	
Non-extractable residues	Mean	23	10.7	17.0	24.0	30.4	38.0	43.4	40.6
	SD	±0.3	±0.1	±0.2	±0.4	±0.2	±0.8	±0.3	±0.0
Total Recovery	Mean	99.8	97.8	95.7	95.3	96.0	93.7	94.6	92.2
	SD	±0.1	±0.3	±0.9	±0.0	±0.7	±0.5	±0.3	±0.5

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

Table 7.1.2.1.2- 30: Biotransformation of [¹⁴C]PU in soil [redacted] under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)							
		0	1	2	3	4	7	10	14
BCS-AA17927 ([¹⁴ C]PU)	Mean	92.8	70.1	51.1	37.5	22.0	2.0	0.7	0.4
	SD	±0.6	±0.9	±0.5	±4.7	±3.7	±1.1	±0.1	±0.1
Unidentified RA	Mean	3.2	2.7	2.1	4.0	2.6	3.6	3.9	3.3
	SD	±0.2	±0.3	±0.2	±0.1	±0.1	±1.2	±0.0	±0.1
Total extractable residues	Mean	96.0	83.2	53.2	41.5	24.6	5.6	4.6	3.7
	SD	±0.5	±1	±0.8	±4.7	±3.6	±0.1	±0.1	±0.2
¹⁴ CO ₂	Mean	n.a.	0.1	8.7	14.6	23.2	40.1	44.5	49.4
	SD	n.a.	±0.0	±0.0	±1.3	±1.1	±0.0	±0.5	±0.2
Volatile organics	Mean	n.a.	0.1	<0.1	<0.1	0.1	0.1	<0.1	0.1
	SD	n.a.	±0.0			±0.0	±0.0		±0.0
Non-extractable residues	Mean	3.8	18.5	29.0	34.3	43.0	43.6	41.3	40.4
	SD	±0.1	±0.6	±1.2	±3.0	±1.1	±0.5	±0.3	±0.2
Total Recovery	Mean	99.9	94.9	90.9	90.5	90.8	89.4	90.4	93.5
	SD	±0.5	±0.5	±0.4	±0.4	±1.4	±0.6	±0.3	±0.3

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation



Table 7.1.2.1.2- 31: Biotransformation of [¹⁴C]PU in soil [redacted] AIIIa under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)							
		0	1	2	3	4	7	10	14
BCS-AA17927 ([¹⁴ C]PU)	Mean	94.2	81.4	69.8	54.8	43.8	17.3	13	0.6
	SD	±0.8	±1.2	±0.8	±0.9	±1.3	±0.4	±0.4	±0.1
Unidentified RA	Mean	3.5	2.2	1.9	2.3	2.3	3.4	4	5.6
	SD	±0.3	±1.0	±0.5	±0.1	±0.5	±0.2	±1.0	±0.1
Total extractable res.	Mean	97.6	83.7	71.6	57.1	45.1	20.7	8.5	5.8
	SD	±0.5	±0.2	±1.3	±0.9	±0.8	±0.6	±1.9	±0.2
¹⁴ CO ₂	Mean	n.a.	4	8	31.1	18	20	42.2	48.1
	SD		±0.1	±0.1	±0.6	±0.3	±0.2	±0.4	±0.1
Volatile organics	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	SD								
Non-extractable residues	Mean	2.2	11.0	17.7	25	30.5	40.5	42.9	39.7
	SD	±0.3	±0.2	±0.6	±0.8	±0.5	±0.5	±0.6	±0.2
Total Recovery	Mean	99.9	98.0	97.2	95.9	94.8	93.2	93.7	93.1
	SD	±0.2	±0.1	±0.6	±0.3	±0.0	±0.0	±0.9	±0.1

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

Table 7.1.2.1.2- 32: Biotransformation of [¹⁴C]PU in soil [redacted] under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)							
		0	1	2	3	4	7	10	14
BCS-AA17927 ([¹⁴ C]PU)	Mean	92.7	74.0	58.6	42.6	31.3	8.3	1.1	0.6
	SD	±0.2	±2.5	±3.1	±0.9	±1.6	±0.8	±0.1	±0.1
Unidentified RA	Mean	3.6	3.4	1.9	2.0	2.7	3.1	4.5	3.7
	SD	±0.2	±1.7	±0.6	±0.1	±0.2	±0.0	±0.4	±0.0
Total extractable res.	Mean	96.3	77.4	59.9	44.6	34.1	11.3	5.5	4.3
	SD	±0.7	±0.8	±1.4	±1.0	±18	±0.8	±0.3	±0.1
¹⁴ CO ₂	Mean	n.a.	4.0	9.3	15.2	20.0	34.2	40.9	45.9
	SD		±0.1	±0.5	±0.2	±0.5	±0.7	±0.4	±0.3
Volatile organics	Mean	n.a.	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1
	SD			±0.0		±0.0		±0.0	
Non-extractable residues	Mean	5.4	16.9	26.5	34.8	40.7	47.1	46.8	44.6
	SD	±1.9	±0.0	±1.7	±0.7	±1.1	±0.3	±0.2	±0.0
Total Recovery	Mean	101.7	98.3	95.8	94.7	94.8	92.7	93.3	94.8
	SD	±2.3	±0.7	±0.2	±0.5	±0.3	±0.3	±0.4	±0.4

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

Table 7.1.2.1.2- 33: Biotransformation of [¹⁴C]PU in soil under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Mean SD	DAT (days after treatment)							
		0	1	2	3	4	7	10	14
BCS-AA17927 ([¹⁴ C]PU)	Mean	92.1	72.2	61.5	44.5	32.2	11.8	9.9	1.2
	SD	±1.4	±1.0	±0.4	±2.1	±1.4	±2.3	±0.0	±0.0
Unidentified RA	Mean	3.2	4.2	1.0	1.7	1.3	3.0	2.9	5.9
	SD	±1.1	±0.1	±0.3	±0.1	±0.2	±1.4	±0.3	±0.4
Total extractable res.	Mean	95.3	76.4	62.6	46.2	33.6	14.8	7.6	5.4
	SD	±0.2	±0.8	±0.7	±2.2	±1.2	±0.9	±0.3	±0.4
¹⁴ CO ₂	Mean	n.a.	0.8	0.8	4.1	18.9	37.5	42.2	
	SD		±0.0	±0.1	±0.2	±0.5	±0.4	±0.0	±0.4
Volatile organics	Mean	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	SD		±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0
Non-extractable residues	Mean	3.7	16.9	25.8	35.2	42.1	49.3	49.9	46.5
	SD	±0.2	±0.1	±0.4	±1.3	±0.9	±0.1	±0.0	±0.1
Total Recovery	Mean	99.0	97.8	97.1	95.9	94.3	94.0	94.8	93.8
	SD	±0.5	±0.9	±0.4	±0.7	±0.2	±0.4	±0.1	±0.2

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation

B. METHOD VALIDATION

The DAT-0 extraction efficiency was 95.3 to 97.6% AR (mean 96.4% AR sum of extracts; Table 9 to Table 13). The stability of the test item was verified by a DAT-0 recovery of 92.1 to 94.8% AR for the organic and microwave extracts (mean 93.9% AR). These results indicated that the extraction method was well suited to extract the applied [¹⁴C]-labeled test item from the soil matrix.

The HPLC method (reversed phase RP-18) was used for data evaluation. A good selectivity and reproducibility demonstrated the suitability of the separation and quantitation. Due to the preceding study with a higher application rate no degradation products were expected.

The limit of quantitation values (LOQ) of HPLC for a single peak in the organic soil extracts was approximately 0.3 to 0.4% AR. The HPLC mean recovery determined in the preceding study for this method was approximately 102.0 and 102.5% for the two types of extracts indicating that no significant losses of radioactivity occurred on column, tubings or detectors (data not shown).

Normal phase Si-60 TLC was used to confirm the results (compare Appendix 32 and Appendix 33 of report).

The test conditions outlined in the study protocol were maintained throughout the study. Material balances were 95.6 ± 2.3% (92.2 to 99.1%, soil LX), 92.5 ± 3.7% (89.4 to 99.9%, soil DD), 95.7 ± 2.5% (93.1 to 99.9%, soil LA), 95.8 ± 3.1% (92.7 to 101.7, soil HH) and 95.8 ± 2.0% (93.8 to 99.0%, soil HS) of the applied amount.

C. DEGRADATION OF [¹⁴C]PU

The test item was declining from 94.8, 92.8, 94.2, 92.7% and 92.1% AR at DAT-0 to 0.9, 0.4, 0.6, 0.6 and 1.2% in the soils LX, DD, LA, HH and HS, respectively, at the end of the study. For kinetics evaluation see [Table 7.1.2.1.2- 27](#).

The half-life (SFO, GEOMean) for [¹⁴C]PU in the tested soils kept at 20°C under aerobic conditions was just 2.7 days, and this significantly lower as that determined for the higher test concentrations.



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Non-extractable [¹⁴C]residues increased from 2.3, 3.8, 2.2, 5.4 and 3.7% AR at DAT-0 to 40.6, 40.4, 39.7, 44.6 and 46.5% AR at the end of the study period, respectively. Considerable amounts of ¹⁴CO₂ were formed amounting to 44.9, 49.4, 48.1, 45.9 and 42.2% of AR in the soils LX, DD, LA, HH and HS, respectively, at the end of the study. No volatile organic compounds were measured at values > 0.1% AR at all sampling dates.

III. CONCLUSIONS

The data gathered in the current laboratory investigation demonstrate that the test item is degraded and mineralized more quickly in soil at a lower initial test concentration. For [¹⁴C]PU a DT₅₀ of 2.7 days (GEOmean over the five soils) was calculated, which is by a factor of 2.6 lower than on the comparable study at a higher treatment rate.

As it was indicated a concentration dependence of the degradation rate for PU was shown. In a supplementary non-GLP experiment it was demonstrated that this effect was not caused by scattering activities of different soil batches taken from the same field, but rather is a genuine property of the Propineb metabolite PU.

By the modelling report of [redacted] 2014, the normalized DT₅₀ values for degradation product PU were derived from a number of relevant studies and the geometric mean value after normalization accounts for 5.6 days (see table below).

Table 7.1.2.1.2- 33a: Summary of the DT₅₀ values for PU degradation in soil

Soil	Study	Moisture [% w/w]	Corr. factor [1]	DT ₅₀ [days]	DT _{50ref} [days]
BBA soil 2.2	[redacted] 1993	14.4 %	1.02	7.8	17.8
BBA soil 2.3	[redacted] 1993	14.0 %	0.508	9.6	7.8
[redacted]	[redacted] 2014	opt.	1	5.7	5.7
[redacted]	[redacted] 2012	opt.	1	3.7	3.7
[redacted]	2008a	opt.	1	4.4	4.4
[redacted]	2008b	opt.	1	1.9	1.9
[redacted]	[redacted] 2014	opt.	1	6.5	6.5
[redacted]	[redacted] 2008a	opt.	1	6.9	6.9
[redacted]	2008b	opt.	1	5.4	5.4
[redacted]	[redacted] 1993	24.4 %	0.932	7.7	7.2
[redacted]	[redacted] 2014	opt.	1	8.1	8.1
[redacted]	[redacted] 2012	opt.	1	5.7	5.7
[redacted]	2008a	opt.	1	5.4	5.4
[redacted]	2008b	opt.	1	2.3	2.3
[redacted]	[redacted] 1993	10.3 %	0.509	45.9	23.4
[redacted]	2008a	opt.	1	6.8	6.8
AtIa	[redacted] 2008b	opt.	1	3.0	3.0
[redacted]	[redacted] 2014	opt.	1	5.2	5.2
AXXa	[redacted] 2012	opt.	1	4.6	4.6



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		2008a	opt.	1	5.9	5.9	
			opt.	1	3.4	3.4	
		2008b					
		2012	opt.	1	5.9	5.9	
					Geometric mean	5.9	5.6
					Median	5.7	5.7
					Maximum	45.9	23.4

¹moisture content (grav. %) and if deviating from optimum (i.e. 55% MWHC)

Degradation of 4-Methyl-imidazoline (4-MI)

Justification for inclusion into the Supplemental Dossier for Propineb renewal of approval Annex I:

The metabolite 4-Methyl-imidazoline was identified as a primary metabolite in the new toxic soil metabolism study by [redacted] 2014, and the Propineb-DIDT degradation study [redacted] 2014. It exceeded the trigger for consideration in risk assessments. Therefore, the degradation rate was investigated. This metabolite was as well mentioned in the past, by [redacted] (1996), however, not regarded as relevant for further consideration that time.

The evaluation of the 4-MI degradation data is compiled by the report of [redacted] 2014. Only the data resulting from the Propineb-DIDT degradation study by [redacted] 2014 was to be kinetically evaluated to derive modelling endpoints to be used in exposure assessments, since the data from the parent metabolism studies have limitations to derive valid degradation kinetics data (compare Section 4 of report by [redacted] 2014).

In accordance with FOCUS (2011) the DAT₀ values for Propineb-DIDT were corrected for all detected degradation products and the NER and thus set to the total recovery values from the material balance. Initial values for the metabolites, 4-MI, PTU and PU were set to zero. First values at the limit of detection (LOD) or below LOD were set to 0.5 × LOD. The LOD accounted for 1.0 %AR according to [redacted] and [redacted] (2014). The pre-processed data used is shown in following [Table 7.1.2.1.2- 34](#).

In agreement with the proposed degradation pathway ([Figure 7.1.2.1.2- 1](#)) a compartment model was setup in KinGUI2 to kinetically describe the degradation of Propineb-DIDT and the formation and degradation of its degradation products propylene thiourea, propylene-urea and 4-methyl-imidazoline. The scheme was displayed earlier in [Figure 7.1.2.1.2- 2](#). Two systems of kinetics were evaluated. At first all the degradation kinetics were described by SFO. Secondly the degradation of Propineb-DIDT was described with the bi-phase DFOP model while the degradation of the remaining compounds was still described by SFO kinetics.

Results

The results of the pathway fit are discussed in section 5.1.4 (and details are given in appendix 11.1.4 of modelling report report by [redacted] 2014). For the degradation product 4-MI the SFO model resulted in usually acceptable fits when the precursor Propineb-DIDT was described by DFOP kinetics. The Chi error values for 4-MI were slightly higher for the DFOP approach, however, were still well below 15% (c.f. [Table 7.1.2.1.2- 8](#)) and the visual assessment identified an excellent description of the data. Consequently DT₅₀ values may be derived from these fits to describe the degradation of 4-MI in soils.



Table 7.1.2.1.2- 34: Pre-processed residue data from the study of ██████████ 2014 used in the kinetic optimization. Grey shaded figures were altered to fulfill FOCUS (2011) recommendations; values are given in % of AR

Soil		AXXa				██████████			
Time	Propineb-DIDT	PTU	PU	4-MI	Propineb-DIDT	PTU	PU	4-MI	
0	98.9 ¹	0 ²	0 ²	0 ²	99.9 ¹	0 ²	0 ²	0 ²	
0	99.5 ¹	0 ²	0 ²	0 ²	101.2 ¹	0 ²	0 ²	0 ²	
0.21	30.5	11.0	7.3	7	26.5	11.4	6.3	5	
0.21	32.2	10.7	6.9	6.7	28.2	11.5	6.8	7.6	
1	11.4	5.7	14.2	7.1	8.9	5.6	5.9	14.8	
1	10.0	5.0	14.2	6	10.6	6.5	4.3	14.8	
2	3.6	1.8	18.6	5.7	3.5	2.9	4.7	17.4	
2	4.2	2.0	18.5	5.4	3.3	3.1	5.0	17.9	
5	0.5 ³	0.5 ³	15.2	2.8	0.5 ³	0.5 ³	2.6	17.1	
5	0.5 ³	0.5 ³	14.6	3.3	0.5 ³	0.5 ³	0.5 ³	NA ⁴	
9	NA	NA	7.2	0.5 ³	NA	NA	0.5 ³	0.0	
9	NA	NA	7.3	0.5 ³	NA	NA	NA	11.9	
14	NA	NA	2.2	NA	NA	NA	NA	4.3	
14	NA	NA	1.8	NA	NA	NA	NA	4.2	
SOIL									
Time	Propineb-DIDT	PTU	PU	4-MI	Propineb-DIDT	PTU	PU	4-MI	
0	98.6 ¹	0 ²	0 ²	0 ²	98.1 ¹	0 ²	0 ²	0 ²	
0	99.7 ¹	0 ²	0 ²	0 ²	98.0 ¹	0 ²	0 ²	0 ²	
0.21	17.3	14.4	7.3	6	8.5	6.2	10.5	4.3	
0.21	17.7	14.0	7.3	3	8.0	7	11	6.3	
1	4.9	6.5	14.2	5.3	2.1	2.9	19.9	5.6	
1	5.7	7.1	14.2	5.5	2.8	2.7	20.2	5.5	
2	2.2	1.2	14.5	3.2	0.5 ³	1.2	23.9	4.3	
2	2.2	1.6	15.2	3.7	0.5 ³	1.4	22.8	4.4	
5	0.5 ³	0.5 ³	13.4	2.2	NA	0.5 ³	17.2	1.9	
5	0.5 ³	0.5 ³	14.2	2.4	NA	0.5 ³	17.4	1.7	
9	NA	NA	9.4	0	NA	NA	5.7	0.5 ³	
9	NA	NA	8.8	0.3 ³	NA	NA	5.6	0.5 ³	
14	NA	NA	5.0	NA	NA	NA	1.8	NA	
14	NA	NA	4.6	NA	NA	NA	2.0	NA	

¹ set to the value of the total recovery from the material balance

² set to zero

³ set to 1/2

⁴ not collected as data measurement was not available

In Table 7.1.2.1.2- 35 the DT₅₀ for the degradation of 4-MI in soil are summarized. The DT₅₀ values from ██████████ 2014 data were derived from SFO fits and their corresponding rate constants while the DT₅₀ values derived from the data by ██████████ (1996) were calculated from the DT₉₀ of the FOMC fits by dividing the value for DT₉₀ by 3.32 (c.f. FOCUS, 2011) Whenever two or more DT₅₀ were available from any individual soil their geometric mean value was calculated first before calculating the overall geometric mean value. The summary shows that 4-MI is short living in aerobic soil and degrades with a geometric half-life of 2.2 days (non-normalized). A dependence of the DT₅₀ on soil properties was not detected. In general the new metabolite degradation study resulted in excellent fits that were much better than those derived earlier in ██████████ (1996) for 4-Methylimidazole.



Table 7.1.2.1.2- 35: Summary of DT₅₀ for degradation of 4-Methyl-imidazole in aerobic soil

Soil	Study	Kinetic model	DT ₅₀ [days]
[redacted]	[redacted] 2014	SFO	2.8
		SFO	2.3
		SFO	1.7
		SFO	2.3
		Geometric mean	2.2
	Median	2.3	
	Maximum	2.8	

¹moisture content (grav. %) and temperature if deviating from optimum (i.e. 55% MWHC, 20°C)

4-Methylimidazole is formed from the degradation of Propineb and Propineb-DIDT (c.f. [Figure 7.1.1- 1](#)). The formation fractions (ff) were derived from pathway fits for the formation from Propineb-DIDT and by means of proportional calculation for the formation from Propineb. The values are presented in [Table 7.1.2.1.2- 36](#) for the path from Propineb and in [Table 7.1.2.1.2- 37](#) for the path from Propineb-DIDT.

Table 7.1.2.1.2- 36: Formation fractions (ff) of 4-MI from degradation of Propineb in 4 soils

Soil	Study	Path	ff 4-MI [-]
[redacted]	AXXa	PPB → 4-MI	0.137
[redacted]	[redacted] 2014	PPB → 4-MI	0.107
[redacted]	[redacted]	PPB → 4-MI	0.099
[redacted]	II	PPB → 4-MI	0.082
		Average value	0.106

Table 7.1.2.1.2- 37: Formation fractions (ff) of 4-MI from degradation of Propineb-DIDT in 4 soils

Soil	Study	Path	ff 4-MI [-]
[redacted]	AXXa	DIDT → 4-MI	0.107
[redacted]	[redacted] 2014	DIDT → 4-MI	0.099
[redacted]	[redacted]	DIDT → 4-MI	0.076
[redacted]	II	DIDT → 4-MI	0.068
		Average value	0.088

By the modelling report of [redacted] 2014, the normalized DT₅₀ values for degradation product 4-methylimidazole were derived. It also shows very fast degradation in soil and its geometric mean value after normalization accounts for 2.2 days (see table below).

Table 7.1.2.1.2- 37a: Summary of the DT₅₀ values for 4-methyl-imidazole degradation in soil

Soil	Moisture [% MWHC]	Corr. factor [-]	DT ₅₀ [days]	DT _{50ref} [days]
[redacted]	54.2	1	2.8	2.8
[redacted]	54.2	1	2.3	2.3
[redacted]	54.2	1	1.7	1.7
[redacted]	54.2	1	2.3	2.3
		Geometric mean	2.2	2.2
		Median	2.3	2.3



Maximum 2.8 2.8

CA 7.1.2.1.3 Anaerobic degradation of the active substance

The rate of degradation of Propineb in soil under anaerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7). In conclusion the following was stated:

The degradation of active substance in the saturated zone was not to be studied since Propineb is not expected to reach the saturated zone after its use according to good agricultural practices.

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval. In general, anaerobic conditions are unlikely to occur in soil when Propineb is used.

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

The rate of degradation of Propineb degrades in soil under anaerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and it was not regarded as a relevant process in soil. Therefore, no additional studies on this topic are submitted within this Supplemental Dossier for the Propineb renewal of approval.

Just the following study on the terminal and well water soluble metabolite PU is included in the Baseline Dossier (P-009496-01) which was regarded as relevant during the Annex I inclusion:

Report:	[redacted]; 1999; M-006247-01
Title:	Degradation of propylene urea (PU) in soil under anaerobic conditions
Report No:	FM771
Document No:	M-006247-01-1
Guidelines:	n.a.; deviation not specified
GLP/GEP:	Yes

Summary of study performed by [redacted], 1999

Under the anaerobic experimental conditions used in this study PU disappeared slowly from the system with a DT₅₀ of 334 days from the sediment and with one of 130 days from the aqueous phase.

In general, anaerobic conditions are unlikely to occur in soil when Propineb is used. In the exceptional case that anaerobic conditions occur in soil after Propineb was used, it is expected that, temporarily, the major metabolites, i.e. the PU will be more stable in an anaerobic soil environment, however, will then be rapidly degraded once aerobic conditions are established again (see section CA 7.1.2.1.2 before), subsequently they do not have the potential to reach anaerobic aquifers (see for PECgw calculations in the MCP dossier section 92.4).

CA 7.1.2.2 Field studies

Due to a fast degradation of Propineb and its metabolites under laboratory conditions, no field dissipation studies were performed and required. This was agreed upon during the Annex I inclusion (compare EU Monograph Annex B7), already.

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.



CA 7.1.2.2.1 Soil dissipation studies

Not performed and not required (see chapter before).

CA 7.1.2.2.2 Soil accumulation studies

Field accumulation and soil residue studies have not been performed and are not required for Propineb.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

The adsorption and desorption behaviour of Propineb and its residues in soil was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/7474/VI/97, 2003). However, not any adsorption and desorption data were stated in the LoEP for the metabolites 4-Methyl-imidazole and Propineb-DIDT, since they were not considered for leaching assessment at that time.

The following table summarizes the adsorption constants $K_{OC(ads)}$ in soils to be used for modelling purposes:

Table 7.1.3.1- 1: Overall summary of adsorption constants $K_{OC(ads)}$ in soils of Propineb and its major degradation products

Compound	$K_{OC(ads)}$ ¹ [mL/g]	$K_{OM(ads)}$ [mL/g]	Freundlich exponent 1/n ¹
Propineb	20000	10000 ²	1.0 ²
Propineb-DIDT	162.0	94.0	1.0 ³
PTU	19.0	11.0	1.0 ³
PU ⁴	8.8	5.8	0.992
4-Methyl-imidazole	366.7	202.8	0.883

- ¹ arithmetic mean; ³ default value (due to instability just estimated values for K_{OC}/K_{OM})
- ² due to its polymeric nature the solubility and mobility of Propineb in soil is negligible. This was reflected in the FOCUS calculations by a K_{oc} value of 10000 L/kg (with a default for 1/n of 1.0). Due to its rapid dissipation in soil, the sorption behaviour of propineb will not have a relevant impact on leaching risk assessments. Nevertheless, assuming no sorption would not respect the nature of the compound.
- ⁴ Since the data for PU resulted from 2 different studies, a compilation of data is given by [Table 7.1.3.1- 2](#).

Table 7.1.3.1- 2: Overall summary of adsorption constants $K_{OC(ads)}$ of PU in soils

Soil	Study	Texture class	OC [%]	pH [H ₂ O]	K_{oc} [L/kg]	K_{om} [L/kg]	1/n [-]
██████	██████ 1993	Sand	1.2	6.3	7.4	4.3	1.050
██████	██████ 1993	Silt loam	0.9	8.1	7.3	4.2	1.141
BBA soil 2.2	██████ 1993	Loamy sand	2.6	5.5	6.1	3.5	0.975
██████	██████ 1993	Silt loam	2.4	6.0	10.8	6.3	0.855
AXXa	██████ 2008	Sandy loam	2.0	6.3	7.5	4.4	1.0759
CAY	██████	Clay loam	1.0	8.0	11.6	6.7	0.8095
AKa	██████ 2008	Loam	1.3	6.6	10.8	6.3	1.0596
HaH	██████ 2008	Silt loam	2.5	6.6	7.0	4.1	0.9596
HHF	██████ 2008	Loam	3.3	5.1	11.1	6.4	1.0046



Arithmetic mean 8.8 5.1 0.992

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CA 7.1.3.1.1 Adsorption and desorption of the active substance

The adsorption and desorption behaviour of Propineb in soil was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/7474/VI/97, 2003). However, due to its insolubility in water and rapid decomposition in soil not any adsorption and desorption values were stated in the LoEP for Propineb, since parent compound was not considered relevant for leaching assessment that that time.

However, as it is mentioned in [Table 7.1.3.1- 1](#), assuming no sorption would not respect the nature of the compound. Therefore, a value of 10000 was proposed as a reasonable default for Propineb.

The following statement included in the Baseline Dossier (P-001496-01) was regarded as relevant during the Annex I inclusion:

Report:	[REDACTED] 1989;M-102688-01
Title:	Comment Propineb: Adsorption/desorption measurements
Report No:	RA-355/89
Document No:	M-102688-01-2
Guidelines:	Deviation not specific
GLP/GEP:	No, n.a.

Conclusions

An adsorption and desorption behavior of Propineb as polymer in soil and /or soil/water suspensions cannot be determined due to insolubility and instability in water. Fragments and transformation are formed under these conditions. Therefore it is not possible to determine an adsorption study with a definitive substance.

The following study not yet submitted in the EU (just in Brazil) shows the sorption behavior of the transient polymer fragments and metabolites, which are formed in the aqueous soil suspension and which can form CS₂, representing the relevant moiety of propineb.

Report:	[REDACTED] 1999;M-023175-01
Title:	Soil adsorption / desorption of Antrazol Tecnico
Report No:	M1021
Document No:	M-023175-01-1
Guidelines:	Not mentioned, but study follows OECD Test Guideline No. 106, deviation not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

This study was conducted to determine the adsorption and desorption characteristics of Propineb on three different soils from Brazil (LE: Typic Hapludox; GH: Cumulic Humaquept and LR: Rhodic Hapludox). The following concentrations of active ingredient were used: 0.5, 1.0, 5.0, 10.0 and 20.0 mg propineb/g. Propineb was analyzed with the CS₂ method, which determines the polymer propineb as well as transient fragments and metabolites which are transformed to CS₂. The assay was carried out with two replicates in 200-mL glass flasks containing 10 g of soil and 90 mL of treating solutions, that were agitated for 24 hours at 100 rpm and centrifuged. The supernatant was transferred into a round bottom flask for reaction and the CS₂ was analyzed to quantify the residue remaining in solution. The amount of adsorbed product was then calculated. To quantify the desorbed product, the



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supernatant solution was completely drained, and 90 mL of 0.01M CaCl₂ was added. The flasks were agitated for 24 hours, centrifuged, sampled and analyzed as above mentioned.

According to the results, the Koc for adsorption was in the range of 2314 to 5757 mL/g. This indicates that the fragments and transformation products of propineb, which can form CS₂, are not present in aqueous solution and are considered to be very strongly adsorbed to soil and are not mobile. The desorption Koc was in the range of 4348 – 10472 mL/g.

I. MATERIALS AND METHODS

1. Test Item

Test item: Antracol Technico, applied in acetone
 Sample ID: 231605095
 Specific Activity: none
 Radiochemical Purity: n.a.
 Chemical Purity: 85%

2. Test Soils

Three soils from Brazil were used (see [Table 7.1.3.1.1- 1](#)). The soils represent different soil properties as required by the guidelines. The soils were sampled from the fields (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm and air-dried.

Table 7.1.3.1.1- 1: Physico-chemical properties of test soils

Parameter	Results/Units		
Soil	GH	IL	LR
Geographic Location	Brazil	Brazil	Brazil
Texture Class ^A	Glei Humico, alico, T ₃ textura argilosa	Latosolo, Vermelho Escuro Aliso, a moderate textura media	Latosolo Roxo Distrofico, a moderado, textura muito argilos
Clay (%)	55	20	70
pH (CaCl ₂)	3.7	4.6	4.1
Organic Matter (%)	8.4	2	3.0
Organic Carbon (%)	4.9	1	1.7
Cation Exchange Capacity (cmol/kg)	20.3	8.8	12.1

II. RESULTS AND DISCUSSION

Propineb as polymer is not soluble in aqueous systems. Within the dissolution process, herein in acetone, fragments and transient metabolites are formed artificially (thus not as usual in an aqueous suspension).

According to the results of this study, the amount of formed CS₂ residue adsorbed to soil are > 90%. This indicates that transient polymer fragments and metabolites, which are formed in the dissolution process and which can form CS₂, are immobile.

The calculated adsorption constants Koc of the Freundlich isotherms for the three test soils ranged from 2314 -5757 mL/g (see [Table 7.1.3.1.1- 2](#)). The respective Koc for the desorption were in the range of 4348 - 10472 mL/g.



Table 7.1.3.1.1- 2: Adsorption constants of CS₂ forming residues (i.e. of Propineb, transient fragments, CS₂ forming metabolites) in soil

Soil	Type	pH (CaCl ₂)	Koc [mL/g]
GH	Glei Humico, alico	3.7	2314
LR	Latossolo Roxo Distrofico	4.1	4761
LE	Latossolo, Vermehlo	4.6	5757
Mean			4277

III. CONCLUSIONS

The Koc for adsorption of Propineb applied in acetone into aqueous soil suspensions was calculated in the range of 2314 to 5757 mL/g. However these data are regarded as kind of minimum adsorption values for Propineb, because Propineb itself is not soluble. A mixture of fragments is formed which is determined by the CS₂ method. Anyway the result indicate that CS₂ forming residues (i.e. of Propineb, transient fragments, CS₂ forming metabolites) in soil are very strong adsorbed to soil and are not mobile.

CA 7.1.3.1.2 Adsorption and desorption of metabolites breakdown and reaction products

The adsorption and desorption behaviour of the degradates of Propineb in soil was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/7474/VI/97/2003). However, not any adsorption and desorption data were stated in the LoEP for the metabolites 4-Methyl-imidazoline and Propineb-DIDT, since they were not considered for leaching assessment that that time. The following study for the metabolite PU included in the Baseline Dossier (P-009496-0) was regarded relevant during the Annex I inclusion.

Report No:	CCA 7.1.3.1.2.01; [redacted] 1993; M105212-01
Title:	Adsorption/desorption of propylene urea in soils
Report No:	PF-3885
Document No:	M105212-01-2
Guidelines:	ES EP Pesticide Assessment Guideline No. 163, deviation not specified
GLP/GEP:	Yes

Due to an calculation error this adsorption behavior of PU was re-calculated and reported by an amendment of [redacted] 2004. In addition an new adsorption study of PU with additional soils in order to broaden the data set (i.e. for pH) was performed. The sorption parameter for the soil metabolites Propineb-DIDT, PU 4-Methylimidazoline and were investigated in new studies to close data gaps.

Under consideration of the above mentioned old study report and of all new studies and data the [Table 7.1.3.1- 1](#) summarizes the available adsorption constants K_{OC(ads)} in soil to be used for modelling purposes. In general the sorption behavior of the propineb metabolites did not depend on the pH value of the soils.



Report:	[REDACTED];1993;M-105212-02; Amended: 2004-01-08
Title:	Adsorption/desorption of propylene urea on soils
Report No:	PF-3885
Document No:	M-105212-02-2
Guidelines:	US EPA Pesticide Assessment Guideline No. 163, deviation not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The determination of the adsorption and desorption Koc in study by report PF-3885 Adsorption/desorption of propylene urea (PU) on soils did not consider the initial soil moisture for the calculation. Therefore, the Koc data were re-calculated.

The adsorption of [ring-2-¹⁴C] propylene urea (PU) was investigated on four soils, originating from [REDACTED], [REDACTED], Standard Soil 2.2 and [REDACTED]. When applying the PU at concentrations corresponding to 4.9, 3.6, 2.4 and 0.5 mg PU/L CaCl₂ solution, the percentage of PU adsorbed to the soil phase ranged from 3.4 to 15.3%.

The adsorption constants K_d calculated by means of the Freundlich adsorption isotherm resulted the values shown by [Table 7.1.3.1.2- 1](#). A mean soil carbon based sorption Freundlich adsorption isotherm Koc of 7.9 mL/g resulted for PU.

Table 7.1.3.1.2- 1: Re-calculation of adsorption constants of PU (data from [REDACTED] 1993)

Soil	Type	pH (CaCl ₂ /H ₂ O)	K _d [mL/g]	1/n	R ²	Koc [mL/g]
[REDACTED]	Sand	6.3	0.0893	1.0503	0.9987	7.4
[REDACTED]	Silt loam	7.3 / 8.1	0.0661	1.1451	0.9991	7.3
Standard soil 2.2	Loamy sand	6.2 / 6.5	0.1597	0.9750	0.9945	6.1
[REDACTED]	Silt loam	5.8 / 6.0	0.2599	0.8555	0.9991	10.8
	Mean		0.1438	1.0055		7.9

Report:	[REDACTED];2008;M-310806-01
Title:	5-149 BCS-AA17927 (propineb PU): Adsorption/desorption on five soils
Report No:	MEF-08/356
Document No:	M-310806-01-1
Guidelines:	EU 95/36/EC amending 91/414/EEC; US EPA, Subdivision N, § 163-1; OECD 106; Canadian PMRA DACO No. 8.2.4.2; No deviation with the exception of the extended concentration range.
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The adsorption/desorption behavior of BCS-AA17927 (PU) was studied in five soils (sandy loam, clay loam, loam, silt loam and loam) in batch equilibrium experiments at 20 ± 1°C.

The adsorption phase of the study was carried out using pre-equilibrated air-dried soil with BCS-AA17927 (PU) at 7 different concentrations of about 3.0, 1.0, 0.3, 0.1, 0.03, 0.01 and 0.003 mg/L in 0.01 M aqueous CaCl₂ solution for 120 hours equilibration, in the dark at 20°C ± 1°C and a soil/solution ratio of 20 g soil and 20 mL solution. The adsorption time was chosen due to a steady increase of sorption in the preliminary experiments. Desorption was performed by replacing the adsorption solution with fresh 0.01 M aqueous CaCl₂ solution. The desorption equilibration time was 24 hours. Based on the preliminary tests, BCS-AA17927 was regarded as stable for 144 hours (parental mass balance >90%) under conditions above and the concentration 1 mg/L.

The aqueous supernatant after adsorption and desorption was separated by centrifugation and the



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BCS-AA17927 (PU) residues in the supernatant were analyzed by liquid scintillation counting (LSC). After the desorption step, the soil was dried and combusted. The trapped ¹⁴CO₂ after combustion was measured by LSC. The adsorption parameters were calculated using the Freundlich adsorption isotherm. The overall mass balances were determined by LSC of the supernatants after adsorption and desorption, and combustion and extraction of the remaining soils.

The recovery of the applied radioactivity for the concentrations 3 and 1 mg/L was >90% of AP. The recovery decreased for the lower concentrations to about 59 to 85% indicating losses due to formation of ¹⁴C-carbon dioxide likely formed during the drying process before combustion. This indicates that the degradation rate was higher for low concentrations compared to slow degradation for high concentrations of the test item.

With respect to the mass balance, data for adsorption were calculated for the tests with 3 mg/L and 1 mg/L only. In the definitive adsorption test 12.3 and 13.0%, 13.0 and 14.0%, 14.9 and 14.4%, 10.5 and 8.7% and 26.8 and 26.9% of the applied test material were adsorbed in soils AIIIa, AXXa, respectively.

The calculated adsorption constants $KF_{(ads)}$ of the Freundlich isotherms for the five test soils ranged from 0.12 to 0.36 mL/g. The respective Koc value was in the range of 7.0 to 14.6 mL/g. The Freundlich exponent $1/n$ was in the range of 0.81 to 1.08, based on the two concentrations.

Data for desorption could not be calculated due to the low amount adsorbed. There was no significant correlation indicated between Koc and adsorption for the investigated soils.

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I. MATERIALS AND METHODS

1. Test Item

Test item:	[5- ¹⁴ C]BCS-AA17927
Sample ID:	KATH 6556
Specific Activity:	4.27 MBq/mg
Radiochemical Purity:	> 97.5%
Chemical Purity:	> 99%

2. Test Soils

Five soils were used (see [Table 7.1.3.1.2- 2](#)). The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. No plant protection products were used for the previous 5 years. The soils were sampled from the fields (upper horizon of 0 to 20 cm), sieved to a particle size of $\leq 2\text{ mm}$ and air-dried.

3. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of Teflon[®] centrifuge tubes (volume 42 mL) closed with screw caps. The experiments were performed in duplicate.

In preliminary tests, the adsorption of the test item to the test system surface, the optimal soil-to-solution ratio, the appropriate adsorption and desorption equilibration times and the stability of the test item were determined.

The adsorption phase was carried out using air-dried soils equilibrated in aqueous 0.01 M CaCl₂ solution for 120 hours with soil-to-solution ratios of 1/1. The test item was applied at concentrations of 3.0, 1.0, 0.3, 0.1, 0.03, 0.01 and 0.003 mg/L in aqueous 0.01 M CaCl₂ solution. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ solution. Adsorption and desorption took place for 24 hours equilibration time.

The test systems were shaken by a mechanical overhead shaker in the dark at $20 \pm 1^\circ\text{C}$ in a walk-in climatic chamber.

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Table 7.1.3.1.2- 2: Physico-chemical properties of test soils

Parameter	Results/Units				
Soil / Batch ID	AXXa 200803259	██████████ 20080313	AIIIa 20080325	HaH 20080325	HHF 20080325
Geographic Location (City / State / Country)	██████████ / Northrhine-Westfalia / Germany	██████████ / France	██████████ / Northrhine-Westfalia / Germany	██████████ / Northrhine-Westfalia / Germany	██████████ / Northrhine-Westfalia / Germany
Texture Class ^A	Sandy loam	Clay loam	Loam	Silt loam	Loam
Sand ^A	67%	21%	45%	21%	20%
Silt ^A	19%	45%	33%	39%	53%
Clay ^A	14%	34%	22%	20%	20%
pH (Water)	6.3	8.0	6.6	6.6	5.4
pH (CaCl ₂)	6.1	7.5	6.3	6.6	4.8
pH (KCl)	5.9	7.3	6.7	6.2	4.4
Organic Matter ^B	3.4%	1.7%	2.9%	4.3%	5.7%
Organic Carbon	2.0%	0.0%	1.3%	2.5%	3.0%
Cation Exchange Capacity (CEC)	9.6 meq/100 g	13.3 meq/100 g	9.6 meq/100 g	10.4 meq/100 g	10.5 meq/100 g
Water Holding Capacity 0.33 bar	12.1%	22.2%	14.1%	24.0%	20.0%
Maximum Water Holding Capacity	51.6 g/100g	n.d	49.9 g/100g	66.3 g/100g	75.2 g/100g
Bulk Density	1.23 g/mL	1.21 g/mL	1.23 g/mL	1.10 g/mL	1.05 g/mL

References for test methods: ^A) acc. USDA classification
^B) % organic matter = % organic carbon × 1.74

4. Analytical Procedures

The suspensions were centrifuged and the radioactivity contents in the supernatants were analysed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the soil was additionally extracted three times using methanol/water mixtures. The aqueous supernatant and the combined soil extracts were analysed by reversed phase HPLC/radiodetection to determine the stability of the test item and to establish the parental mass balance.

The partition of the test item in the adsorption and desorption batch equilibrium experiment was determined based on the radioactivity content in the supernatant only due to the stability of the test item demonstrated by the parental mass balance. After desorption, the soil was freeze-dried and the radioactivity content determined by combustion/LSC to establish the material balance (one replicate per soil and concentration).

Adsorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.

II. RESULTS AND DISCUSSION

The overall material balance for all concentrations decreased from higher concentrations to lower concentrations. No degradation products were detected by HPLC.

The recovery of radioactivity was in the range of 91.5 to 96.7% at 3.0 mg/L; 90.1 to 94.6% at 1.0 mg/L; 83.1 to 91.6% at 0.3 mg/L; 76.3 to 92.8% at 0.1 mg/L; 5.5 to 85.6% at 0.03 mg/L; : L: 55.4 to 83.4 at 0.01 mg/L; 59.0 to 85.2% at 0.003 mg/L, each calculated as percentage of the applied radioactivity. The decrease indicates the loss radioactivity in the course of the study (before combustion) especially for low concentrations. As there is no formation of metabolites detected by



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HPLC, this indicates degradation and the formation of carbon dioxide especially for low concentrations without detectable intermediate products.

[5-¹⁴C]BCS-AA17927 (PU) was sufficient stable in pretests. The parental mass balances were lower due to formation of carbon dioxide after desorption and before combustion.

In the definitive adsorption test 12.3 and 13.0%, 13.0 and 14.0%, 14.9 and 14.4%, 10.5 and 8.7% and 26.8 and 26.9% of the applied test material were adsorbed in soils AIIIa, AXXa, respectively.

After the adsorption step one desorption step was performed. The adsorption supernatant was replaced by fresh CaCl₂ solution and the suspensions were shaken for 24 hours. The RA in the supernatant was determined. The adsorption to soil was weak and a high amount of adsorption solution remained in soil after centrifugation. Therefore, the calculated amount desorbed from soil was negative and not valid. It was not possible to determine reliable data for desorption.

With respect to the mass balance, data for adsorption were calculated for the tests with 3.0 mg/L and 1.0 mg/L, only. In the definitive adsorption test 12.3 and 13.0%, 13.0 and 14.0%, 14.9 and 14.4%, 10.5 and 8.7% and 26.8 and 26.9% of the applied test material were adsorbed in soils AIIIa, AXXa, respectively.

The calculated adsorption constants $KF_{(ads)}$ of the Freundlich isotherms for the five test soils and the respective Koc values are shown in [Table 7.1.3.1.2](#). Based on the two highest concentrations the respective mean of Koc was 9.6 (mL/g), and the 1/n was 0.9818.

Table 7.1.3.1.2- 3: Adsorption constants and correlation coefficients of PU in soils

Soil	Type	pH (CaCl ₂ /H ₂ O)	K_f [mL/g]	1/n	R ²	Koc [mL/g]
HHF	Loam	7.8	0.366	1.0046	0.9998	11.1
AXXa	Sandy loam	6.1	0.159	1.0259	1.0000	7.5
AIIIa	Loam	6.3	0.141	1.0396	0.9980	10.8
HaH	Silt loam	6.5	0.175	0.9596	0.9967	7.0
CAY	Clay loam	7.5	0.116	0.8095	0.9950	11.6
Mean			0.189	0.9818	0.9979	9.6

III. CONCLUSIONS

The adsorption constants $KF_{(ads)}$ of [¹⁴C]PU calculated based on the FREUNDLICH isotherms for the five test soils and 2 concentrations (3.0 mg/L and 1.0 mg/L) ranged from 0.1156 mL/g to 0.3661 mL/g. The respective Koc values for adsorption were in the range of 7.0 mL/g and 11.6 mL/g (mean 9.6 mL/g).

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

An overall summary of available adsorption constants of PU is given by [Table 7.1.3.1- 2](#).



Report:	[REDACTED];2012;M-429453-01
Title:	[5-14C] BCS-AA66386: Adsorption/desorption in five different soils
Report No:	AS199
Document No:	M-429453-01-1
Guidelines:	EC, Commission Directive 95/36/EC Amending Council Directive 91/414/EEC (Annexes II + III, Fate and Behavior in the Environment); July 14, 1995. OECD Guideline for Testing of Chemicals, No 106 "Adsorption/Desorption", Jan. 21, 2000. US EPA, Fate, Transport and Transformation Test Guidelines OPPTS 835.1220 Sediment and Soil Adsorption/Desorption Isotherm; deviation not specified.
GLP/GEP:	Yes

EXECUTIVE SUMMARY

Due to the instability of PTU under the required test conditions, the definitive test could not be performed. Even though two different sterilization techniques were used, the degradation half-life of the test item for three of the five soil types ([REDACTED] and [REDACTED]) was < 3 days.

The adsorption/desorption characteristics of [5-¹⁴C]BCS-AA66386 ([¹⁴C]PTU) were studied by batch equilibrium experiments in five different soils, sandy loam [REDACTED], silt loam [REDACTED], loam [REDACTED], loamy sand [REDACTED] AXa, and silt loam [REDACTED] (for soil characteristics see [Table 7.1.3.1.2- 4](#)). The pH values were determined in aqueous CaCl₂ solution for characterization of the soils.

The aqueous supernatant after adsorption was separated by centrifugation and the [¹⁴C]PTU residues in the supernatant were analysed by liquid scintillation counting (LSC) and radio-HPLC. The recovery of radioactivity of the soils was determined by LSC of the supernatants after adsorption and by combustion of the remaining soils and was in a range of 97.2 to 100.2% of applied radioactivity. Samples without soil were used as control and did not show any adsorption to the vessels or degradation. Radioactivity represented >94% of the test item and the radioactivity balance was in a range from 99.1 -100.2%.

Several tests indicated that the test item PTU is not enough stable to derive batch equilibrium adsorption data, even if sterilised soil is taken.

I. MATERIALS AND METHODS

1. Test Item

Test item: [5-¹⁴C] BCS-AA66386
 Sample ID: KATH 6552
 Specific Activity: 362 MBq/mg (9.23 µCi/mg)
 Radiochemical Purity: >98%
 Chemical Purity: >99%

2. Test Soils

Five test soils (see [Table 7.1.3.1.2- 4](#)) were used within this study, chosen to cover a representative range in soil physico-chemical properties. The soils were sampled from the fields (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm and air-dried.



3. Experimental Conditions

In Preliminary Test I the soil to solution ratios were defined to be 1:2 for all soils. 24 hrs after application a purity check of the supernatant was carried out by means of radio-HPLC.

The aqueous supernatant after adsorption was separated by centrifugation. Samples without soil were used as control and did not show any adsorption to the vessels or degradation. The Preliminary Tests II consisted of two parts. First part was carried out with gamma sterilized (25 kgray) soil (sampling 2, 4, 6 and 24 hrs after application) and in the second part NaN_3 as biocide was added to the shaking solution (sampling 2, 4, 6, 24, 48 and 72 hrs after application).

Table 7.1.3.1.2- 4: Physico-chemical properties of test soils

Number	I	II	III	IV	V
Soil Designation		am 4a	U	AXX	T
Abbreviation	WuW	HaH	Dol	AXXa	HH
Textural class [USDA]	Sandy loam	Silt loam	Loam	Loamy sand	Slit loam
Textural analysis [USDA]					
Sand [2000-50 µm]	57	27	37	17	31
Silt [50-2 µm]	30	60	40	16	54
Clay [<2µm]	13	13	23	7	15
pH value:					
Water	5.4	6.5	7.5	6.2	5.5
CaCl ₂	5.1	6.3	7.3	5.9	5.2
Organic carbon (%)	2.0	2.9	4.4	2.0	2.9
Organic matter (%)	3.47*	5.99*	7.57*	3.4*	4.99*
CEC (meq/100 g soil)	10.3	12.9	19.0	9.3	10.0

* Calculated: Organic Matter = Organic Carbon x 1.724

4. Analytical Procedures

The suspensions were centrifuged and the radioactivity contents in the supernatants were analysed by liquid scintillation counting (LSC) and radio-HPLC. The recovery of radioactivity of the soils was determined by LSC of the supernatants after adsorption and by combustion of the remaining soils.

II. RESULTS AND DISCUSSION

In Preliminary Test I, already 24 hrs after application < 8% of the radioactivity in the supernatant represented the unchanged PTU, indicating a very fast degradation under test conditions. The radioactivity balance was in a range from 94.3 - 97.2%.

The instability observed in Preliminary Test I was confirmed by the results of the Preliminary Tests II (determination of Equilibration time for adsorption and parental mass balance). In Preliminary Tests II with gamma sterilized soil (25 Kgray) the samples contained < 19% test item in the supernatant after a shaking period of 24 h. Already after 6 hrs no unchanged [¹⁴C]PTU was detectable in the soil extracts. The corresponding parental mass balances after 24 hrs were < 9%. Due to the insufficient mass balance of the test item it was decided to terminate the test with gamma sterilized soil after 24 hrs.

The degradation of the test item was confirmed in the second part of Preliminary Tests II with NaN_3 as biocide in the shaking solution. 24 hrs after application < 66.1% of the unchanged test item were determined in the supernatants, and < 20.5% in the soil extracts. Depending on the soil type the corresponding parental mass balance was in a range from 68.1 to 88.6% after 4 hrs and from 28.8 to 82.5% after 24 hrs shaking period, respectively. The radioactivity mass balance at all sampling dates were > 97%.



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The compound PTU was not stable under test conditions with gamma sterilized soil and with NaN₃ as biocide. A definitive test was performed to demonstrate the overall recovery of radioactivity but adsorption and desorption constants could not be determined.

III. CONCLUSIONS

Due to the instability of PTU under the test conditions the definitive test could not be performed. Two different sterilization techniques were used but the degradation was too fast to determine the adsorption isotherm.

Since a Koc value could not be calculated for PTU, this was the justification to include an estimation of its Koc by the proposed HPLC-method into the Supplemental Dossier for Propineb renewal of approval Annex I.

The sorption Koc for PTU (as well as for the instable Propineb-DIDT) determined by HPLC is contained as part of the earlier listed study for aerobic degradation of Propineb-DIDT (see [redacted] 2014). This respective part is summarized below.

Report:	[redacted];2014;M-484906-01
Title:	[Propane-1-14C]Propineb-DIDT: Aerobic degradation in four soils
Report No:	EnSa-14-1129
Document No:	M-484906-01-1
Guidelines:	OECD Test Guideline No. 307 Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009 USEPA OCSPF Test Guideline No. 835.4100, deviations not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The estimated Koc for PTU was determined with 19 mL/g.
The estimated Koc for Propineb-DIDT was determined with 162 mL/g

I. MATERIALS AND METHODS

1. Test Items

- Test item: PTU (BCS-AA66386)
- Sample ID: ALB007999-PU-1
- Specific Activity: Not labelled
- Radiochemical Purity: n.a.
- Chemical Purity: 95.6%

- Test item: Propineb-DIDT (BCS-CU99534)
- Sample ID: BCS-CU99534-PU-01
- Specific Activity: Not labelled
- Radiochemical Purity: n.a.
- Chemical Purity: 96.5%

2. Reference Substances

The following reference substances were used according to OECD Guideline No. 121 in order to cover the Koc range: Sodium nitrate, Acetanilid, Methiocarb, Isoproturon, Naphtalene, 1,2,3-Trichlorobenzene, Fenthion, Diclofop-methyl. The reference substances were dissolved in methanol for HPLC

injection on the HPLC.

3. Experimental Conditions

The test system was performed according to OECD Guideline No. 121. The retention times were determined in duplicate.

4. Analytical Method

The isocratic HPLC method was used. The LC-column was Agilent Zorbax CN (5 µm, 6 x 250 mm), the eluent was MeOH/purified -Water/CHCOOH 55/44/1 (v/v/v). The flow rate was 1 mL/min and the injection volume was 100 µL.

The void volume of the test system was determined with sodium nitrate. The retention times of the reference substances were measured and the linear calibration plot (log k' - log Koc reference substances) was calculated. The retention times of the test substances were determined under the same conditions and based on the calibration the log Koc could be calculated.

II. RESULTS AND DISCUSSION

The calibration curve for the reference substances was calculated ($y = 2.0362x + 2.0802$; $R^2 = 0.9743$) from the data presented in [Table 7.1.3.1.2-5](#).

The Koc for PTU was determined with 19 mL/g (see [Table 7.1.3.1.2-6](#)).

In parallel the Koc for Propineb-DiDT was determined with Koc = 162 mL/g (see [Table 7.1.3.1.2-6](#)).

A pH dependence of both the Koc is not expected in the relevant pH range, based on the chemical structures. Both findings were contained in the overall summary on the adsorption behaviour of Propineb and its metabolites shown by [Table 7.1.3.1-1](#).

Table 7.1.3.1.2- 5: Calibration plot with the reference substances used

Reference Item	Retention Time [min]	k'	log k' data	log k' mean	SD	log Koc ¹ [-]	Koc ² [mL/g]
Sodium Nitrate	3.15						
	3.15						
	3.15						
	3.16						
Acetanilid	4.35	0.385	-0.41	-0.41	0.00	1,25	18
	4.37	0.385	-0.41				
Methiocarb	6.68	1.11	0.05	0.05	0.00	3.1	1259
	6.68	1.17	0.05				
Isoproturon	5.93	0.880	-0.06	-0.06	0.00	1.86	72
	5.93	0.880	-0.06				
Naphtalene	8.07	1.558	0.19	0.19	0.00	2.75	562
	8.07	1.558	0.19				
1,2,3-Trichlorbenzene	9.08	1.878	0.27	0.27	0.00	3.16	1445
	9.08	1.878	0.27				
Fenthion	12.00	2.803	0.45	0.45	0.00	3.31	2042
	11.98	2.797	0.45				
Diclofop-methyl	13.85	3.390	0.53	0.53	0.00	4.2	15849
	13.83	3.384	0.53				

¹ Literature values according to OECD test guideline No 121



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² calculated by log-transformation from literature log K_{oc} values

Table 7.1.3.1.2- 6: Results for the test substances

Test Item	Retention Time [min]	k' [-]	log k'			log K _{oc} ³			K _{oc} ⁴ [mL/g]
			data	mean	SD	data	mean	SD	
Propineb-DIDT	5.88	0.9	-0.06	-0.06	0.00	2.21	2.209	0.00	162
	5.88	0.9	-0.06			2.21			
PTU	4.43	0.4	-0.39	-0.39	0.00	1.27	1.272	0.00	19
	4.43	0.4	-0.39			1.27			

³ calculated from calibration function

⁴ calculated by log-transformation from calculated log K_{oc} value

Report:	[REDACTED]; 2014, M-431774-01
Title:	[5-14C] BCS-CT29489: Adsorption/desorption in five different soils
Report No:	AS203
Document No:	M-431774-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No 106 Adsorption/Desorption Using a Batch Equilibrium Method, Jan. 21, 2000 US EPA, Fate, Transport and Transformation Test Guidelines OPPTS 835.1220 Sediment and Soil Adsorption/Desorption Isotherm, January 1998; deviations not specified.
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The adsorption/desorption characteristics of [5-¹⁴C]BCS-CT29489 (4-Methyl-imidazoline) were studied by batch equilibrium experiments in five soils, sandy loam [REDACTED], silt loam [REDACTED], loam [REDACTED], sandy loam [REDACTED], and silt loam [REDACTED], in (for soil characteristics see [Table 7.1.3.1.2- 7](#)).

The adsorption phase of the study (Definitive Test) was carried out using pre-equilibrated air-dried soil with [¹⁴C]4-Methyl-imidazoline at concentrations of nominal 1, 0.3, 0.1, 0.03, and 0.01 mg/L in the dark at 20 °C ± 2 °C for 24 hours. The equilibration solution used was 0.01 M aqueous CaCl₂ solution.

Following soil to solution ratios were defined: for soils [REDACTED], [REDACTED], [REDACTED] and [REDACTED] with 1:8, and for soil [REDACTED] with 1:20.

The aqueous supernatant after adsorption and desorption was separated by centrifugation and the [¹⁴C]4-Methyl-imidazoline residues in the supernatant were analyzed by liquid scintillation counting (LSC).

For all soils the parent mass balance after 48 h showed that >90% of applied [¹⁴C]4-Methyl-imidazoline could be recovered.

The mass balance of the soils was determined by LSC of the supernatants after adsorption and desorption and by combustion of the remaining soils. The overall material balance for all concentrations for individual specimens was in the range of 95.0 to 99.6%, 92.4 to 98.9%, 89.2 to 98.7%, 92.6 to 97.9%, and 81.2 to 95.2% of the applied radioactivity in soils [REDACTED], [REDACTED], [REDACTED], [REDACTED] and [REDACTED], respectively.

In the definitive adsorption test 24.6 to 36.0%, 32.2 to 47.4%, 33.8 to 49.3%, 35.6 to 50.7%, and 41.8



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to 58.7% of the applied test material was adsorbed in soils [redacted], [redacted], [redacted], [redacted], [redacted], respectively.

The calculated adsorption constants K_F of the FREUNDLICH isotherms for the five test soils ranged from 2.7 mL/g to 14.6 mL/g, and the normalized K_{oc} was in the range of 99.3 to 860.8 mL/g. The FREUNDLICH exponents $1/n$ were in the range of 0.8702 to 0.9015, indicating that the concentration of the test item did affect the adsorption behavior.

At the end of one adsorption and one desorption phase, 40.9-57.3%, 25.7-46.8%, 3.1-46.2%, 28.6-44.3% and 26.8-39.8% of the initially adsorbed amount were desorbed in soils [redacted], [redacted], [redacted] 4a, [redacted] II, [redacted] CA, [redacted] NE, respectively.

The mean desorption $KF^{(des)}$ ranged from 3.6 – 32.6 mL/g and the normalized $KF_{oc}^{(des)}$ ranged from 88.7 – 1327.1 mL/g and were 0.98 - 1.54 times higher than those obtained for adsorption phase.

A. MATERIALS

1. Test Item

Test item: [5- ¹⁴C] PCS-C129480
 Sample ID: KML0262
 Specific Activity: 4.31 MBq/mg (116.44 µCi/mg)
 Radiochemical Purity: 97.7%
 Chemical Purity: 96.3%

2. Test Soils

Five test soils (3 from EU, 2 from US) (see [Table 7.1.3J.2-7](#)) were used within this study, chosen to cover a representative range in soil physico-chemical properties. The soils were sampled from the fields (upper horizon of 0 to 20 cm), sieved to a particle size of <2 mm and air-dried. The pH values were determined in aqueous CaCl₂ solution for characterization of the soils.

Table 7.1.3J.2- 7: Physico-chemical properties of test soils

Number	I	II	III	IV	V
Soil Designation	[redacted]	[redacted] 4a	[redacted] II	[redacted] US California	[redacted] US Nebraska
Textural class [USDA]	Sand loam	Silt loam	Loam	Sandy loam	Silt loam
Textural analysis [USDA]					
Sand [2000-50 µm]	5	27	37	56.0	12.7
Silt, [50-2 µm]	30	60	40	32.6	60.8
Clay [<2µm]	13	1	23	11.4	26.5
pH value:					
Water	4	6.5	7.5	6.8	7.2
CaCl ₂	5.1	6.3	7.3	6.7	6.6
Organic carbon (%)	2.0	2.9	4.4	0.7	1.7
Organic matter (%)	3.41*	4.99*	7.57*	1.1	2.9
CEC (meq/100 g soil)	10.3	12.9	19.2	16.1	16.1

* Calculated: Organic Matter = Organic Carbon x 1.724

3. Experimental Conditions

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The test system for adsorption and desorption in batch equilibrium experiments consisted of borosilicate glass centrifuge tubes (volume 42 mL). The experiments were performed in duplicate. In preliminary tests, the adsorption of the test item to the test system surface, the optimal soil-to-solution ratio, the appropriate adsorption and desorption equilibration times and the stability of the test item were determined.

The adsorption phase in the main test was carried out using pre-equilibrated air-dried soil with [^{14}C]BCS-CT29489 at concentrations of nominal 1, 0.3, 0.1, 0.03, and 0.01 mg/L in the dark at $20\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$ for 24 hours. The equilibration solution used was 0.01 M aqueous CaCl_2 solution.

Following soil to solution ratios were defined: for soils [REDACTED], [REDACTED], [REDACTED] and [REDACTED] with 1:8, and for [REDACTED] with 1:20.

Desorption phase of the study was carried out by supplying pre-adsorbed soil specimens with fresh 0.01 M aqueous CaCl_2 solution for one desorption cycle. Samples without soil were used as control in preliminary test and did not show adsorption to the vessels or degradation.

4. Analytical Procedures

The suspensions were centrifuged and the radioactivity contents in the supernatants were analysed by liquid scintillation counting (LSC). The mass balance of the soils was determined by LSC of the supernatants after adsorption and desorption and by combustion of the remaining soils.

In the preliminary parental mass balance test, the soil was additionally extracted three to seven times with 40 mL acetonitrile/0.1 M hydrochloric acid 9:1 (v:v) for 30 min. The aqueous supernatant and the combined soil extracts were analysed by reversed phase HPLC radiodetection to determine the stability of the test item and to establish the parental mass balance.

The partition of the test item in the adsorption and desorption batch equilibrium experiment was determined based on the radioactivity content in the supernatant. After desorption, the soil was freeze-dried and the radioactivity content was determined by combustion/LSC to establish the material balance (one replicate per soil and concentration).

Adsorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.

II. RESULTS AND DISCUSSION

The overall material balance for all concentrations for individual specimens was in the range of 95.0 to 99.6%, 92.4 to 98.9%, 89.2 to 98.7%, 92.6 to 97.9%, and 81.2 to 95.2% of the applied radioactivity in soils [REDACTED], [REDACTED], [REDACTED], [REDACTED], and [REDACTED], respectively.

The test item was stable in aqueous CaCl_2 solution. The parental mass balances were $\geq 90\%$ for all soils after 48 hrs equilibration time. The parental mass balance was calculated as recovery of the test item in supernatants (CaCl_2 solutions) and soil extracts (combined acetonitrile/water extracts).

In the definitive adsorption test 24.6 to 36.0%, 32.2 to 47.4%, 33.8 to 49.3%, 35.6 to 50.7%, and 41.8 to 58.7% of the applied test material was adsorbed in soils [REDACTED], [REDACTED], [REDACTED], [REDACTED], and [REDACTED], respectively.

The calculated adsorption constants $K_F^{(ads)}$ of the FREUNDLICH isotherms for the five test soils ranged from 2.7 mL/g to 14.6 mL/g. The FREUNDLICH exponents $1/n$ were in the range of 0.8702 to 0.9015, indicating that the concentration of the test item did affect the adsorption behavior. The K_{oc} for adsorption was in the range of 90.3 to 860.8 mL/g

At the end of one adsorption and one desorption phase, 40.9 to 57.3%, 25.7 to 46.8%, 13.1 to 46.2%, 28.6 to 44.3% and 26.8 to 39.8% of the initially adsorbed amount were desorbed in soils [REDACTED], [REDACTED], [REDACTED], [REDACTED], respectively. The mean desorption $K_F^{(des)}$ ranged from 3.6 to 22.6 mL/g and and the normalized $K_{F,OC}^{(des)}$ ranged from 88.7 to 1327.1 mL/g and were 0.98 to



1.54 times higher than those obtained for adsorption phase.

The respective constants and correlation coefficients of 4-Methyl-imidazoline in soils are given in [Table 7.1.3.1.2- 8](#) for adsorption, and [Table 7.1.3.1.2- 9](#) for desorption.

Table 7.1.3.1.2- 8: Adsorption constants and correlation coefficients of 4-MI in soils

Soil	Type	pH (CaCl ₂)	K _F [mL/g]	1/n	R ²	Koc [mL/g]
	Sandy loam	5.1	2.6785	0.9015	0.9991	133.9
	Silt loam	6.3	3.7365	0.8818	0.9994	128.8
	Silt loam	6.6	14.643	0.8724	0.9991	860.8
	Sandy loam	6.7	4.9442	0.8866	0.9998	620.6
	Loam	7.3	3.9744	0.8702	0.9998	90.3
Mean			5.8736	0.8925	0.9995	366.9

Table 7.1.3.1.2- 9: Desorption constants and correlation coefficients of 4-MI in soils

Soil	Type	pH (CaCl ₂)	K _D [mL/g]	1/n	R ²	Koc [mL/g]
	Sandy loam	5.1	5.5865	0.8696	0.9983	179.3
	Silt loam	6.3	4.9113	0.8283	0.9989	169.4
	Silt loam	6.6	22.5608	0.8733	0.9993	1327.1
	Sandy loam	6.7	2.9998	0.8720	0.9999	942.8
	Loam	7.3	5.9035	0.7316	0.9975	88.7
Mean			8.3024	0.8350	0.9987	541.5

III. CONCLUSIONS

The adsorption/desorption characteristics of [5-¹⁴C]BCS-CT29489 (¹⁴C)4-Methyl-imidazoline) were studied in five soils.

The K_{oc} for adsorption was in the range of 90.3 to 860.8 mL/g (mean 366.9 mL/g). This finding is contained in the overall summary on the adsorption behaviour of Propineb and its metabolites shown by [Table 7.1.3.1- 1](#).

The desorption K_{oc} (des) ranged from 88.7 – 1327.1 mL/g and were 0.98 - 1.54 times higher than those obtained for adsorption phase.

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

CA 7.1.3.2 Aged sorption

Two studies on aged sorption of Propineb and its residues in soil were evaluated during the Annex I inclusion (compare EU Monograph Annex B7), but they were regarded as not to relevant by the European Commission (SANCO/7474/01/97, 2003).

The leaching behaviour was evaluated by the adsorption/desorption data shown in the section before, in combination with accepted and agreed model calculations of predicted environmental ground water concentration (PEC_{gw}) for parent. Therefore, new studies were not performed and are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009.

CA 7.1.4 Mobility in soil

A plenty of studies on mobility of Propineb and its residues in soil were evaluated during the Annex I inclusion (compare EU Monograph Annex B7), but, as mentioned in the chapter before, they were regarded as not to relevant by the European Commission (SANCO/7474/VI/97/0003).

The leaching behaviour was evaluated by the adsorption/desorption data shown in the section before, in combination with accepted and agreed model calculations of predicted environmental ground water concentration (PEC_{gw}) for parent and its major metabolites. Therefore, new studies were not performed and are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009.

CA 7.1.4.1 Column leaching studies

CA 7.1.4.1.1 Column leaching of the active substance

N/A (see chapter before).

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

N/A (see chapter before).

No new studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

The leaching behaviour can be assessed from the available adsorption/desorption values combined with other relevant input data by accepted modelling estimations, i.e. PEC_{gw} calculations submitted by the respective MCP section 9.2.4.

CA 7.1.4.2 Lysimeter studies

No studies are submitted within this Supplemental Dossier for the Propineb renewal of approval. The leaching behaviour can be assessed from the available adsorption/desorption values combined with other relevant input data by accepted modelling estimations, i.e. PEC_{gw} calculations submitted by the respective MCP section 9.2.4.

CA 7.1.4.3 Field leaching studies

No relevant studies are included in the baseline dossier, since such were not required. No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

CA 7.2 Fate and behaviour in water and sediment

The chemical substance Propineb is different in comparison to most other active ingredients (e.g. fungicides) which are produced as pure chemical with a distinct chemical structure, purity, solubility and stability. Propineb is formed in one reaction step by mixing of propylendiamine, carbon disulfide, zinc sulfate and a small amount of formulation detergents. The resulting product is a polymeric zinc propylene bis(thiocarbamate) with not defined polymer length. The complexes in solid form are practically insoluble in water and after dissolution the polymer reacts immediately with water and other available surrounding substances. The reaction is likely at first a dissolution of the zinc salt forming the highly reactive dithiocarbaminic acid with different chain length. The following decomposition can lead to propylenediamine and carbon disulfide as back-reaction. In the environment, bis(thiocarbamate) is likely to be easily oxidized and forms thiuram disulfides followed by formation of isothiocyanates. The isothiocyanates are highly reactive and can react either with water,

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intramolecularly with other intermediates or with surrounding dissolved or suspended organic matter (e.g. formation of non extractable residues, NER).

The route of degradation of Propineb in the aqueous environment, which was investigated in a set of laboratory studies performed under pure aqueous conditions (hydrolysis; photolysis) as well as under more realistic environmental conditions, i.e. in the presence of natural water and sediment containing oxygen and organic material, can be well explained.

It is concluded that Propineb as a polymer does not dissolve in water. Therefore, the dissolved radioactivity in the aqueous solution of hydrolysis studies must result from spontaneous formed reaction products. Since the total amount of radioactivity found in the hydrolysis test solutions (██████████ 2013) was constant already from the first sampling, the half-life of formation of hydrolysis products was estimated to be less than 0.5 hours at pH 4, pH 7 and pH 9 for all temperatures.

PTU was the main degradation product which was formed in sterile aqueous buffer solutions at pH 4, pH 7 and pH 9. PU was formed as a second terminal transformation product. PTU and PU were stable under the test conditions. The polar zone (in hydrolysis study named M1) was not stable and fragments were identified as precursors of PTU. The transient first unipolar intermediates lead either to Propineb-DIDT, or by elimination of sulfur hydrogen and carbon disulfide to PTU and PU (for pathway of degradation see [Figure 7.2.1.1-1](#)).

The degradation of Propineb under aqueous photolysis conditions is not of relevance due to its rapid degradation in the dark by hydrolysis. Therefore, sunlight is not expected to be a relevant route of degradation for Propineb (and its major residue PTU) after its use according to good agricultural practices.

Propineb TK83 is considered to be "Not Readily Biodegradable". However, it should be considered that the polymer Propineb decomposes immediately in aqueous solution, but the standardized test just measures the complete mineralisation of the transformation products to carbon dioxide at a quite high dose rate.

Due to the before mentioned intrinsic properties of Propineb, studies on aerobic mineralisation in surface water are not to be provided, since contamination of open water (freshwater, estuarine and marine) will not occur.

Brought in contact with natural water, e.g. after its application as suspension into the supernatant water of a water/sediment test system (new water/sediment study using ^{14}C -Propineb by ██████████ 2014) the same degradation products as detected in soil were found. The transient first unipolar intermediates lead either to Propineb-DIDT, or by elimination of sulfur hydrogen and carbon disulfide to PTU and 4-Methyl-imidazoline, possibly via other polar transient degradation products. Propineb-DIDT, 4-Methyl-imidazoline and PTU are also quite short-living transients which are oxidised in several steps, partly via formation of PU or NER to the final degradation product $^{14}\text{CO}_2$. None of other intermediates could be isolated, as it was the case in soil.

From this study it is concluded that Propineb and its degradation products have no potential for accumulation in the aqueous environment. For modelling purposes a worst case DT_{50} of 1.0 and 1.4 days are to be proposed for Propineb and Propineb-DIDT degradation in water, sediment, and total water/ sediment system, respectively. The proposed degradation pathway in natural water is shown in [Figure 7.2.1-1](#).

For the assessment of surface water exposure maximum occurrences in soil were obtained from ██████████ 2014, and accounted for 25.8%, 33.7%, 42.5%, and 12.2%, respectively. For the assessment on surface water exposure a DT_{50} of 0.5 days is used for Propineb, in order to simulate the rapid formation of its metabolites whenever the polymer breaks down rapidly in contact with humid soil.



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Table 7.2- 1 and Table 7.2- 2 summarise the substance related parameters to be used for Propineb and its metabolites in the calculations at FOCUS SW Step 1-2 level and at Step 3/4 Level. The parameters of the aquatic metabolite propineb-DIDT are given by Table 7.2- 3.

No further studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

Table 7.2- 1: Substance parameters for Propineb and its metabolites used in PEC_{sw} calculations at Steps 1-2 level

Parameter	Unit	Propineb	PTT	PU	Propineb-DIDT	4-Methylimidazole
Molar Mass	g/mol	289.8	116.2	100.2	190.3	84.1
Water Solubility	mg/L	0.1	96000	200000	20000	200000
Koc	mL/g	10000	19	8	163	367
Degradation						
Soil	days	0.5	0.2	5.6	0.5	2.2
Total System	days	1	4.9	14	1.7	1000
Water	days	1	1	1	1	1000
Sediment	days	1	1000	1000	1000	1000
Max Occurrence						
Water / Sediment	%	100	26.2	50.4	35	17.5
Soil	%	100	33.7	42.5	25.8	12.2

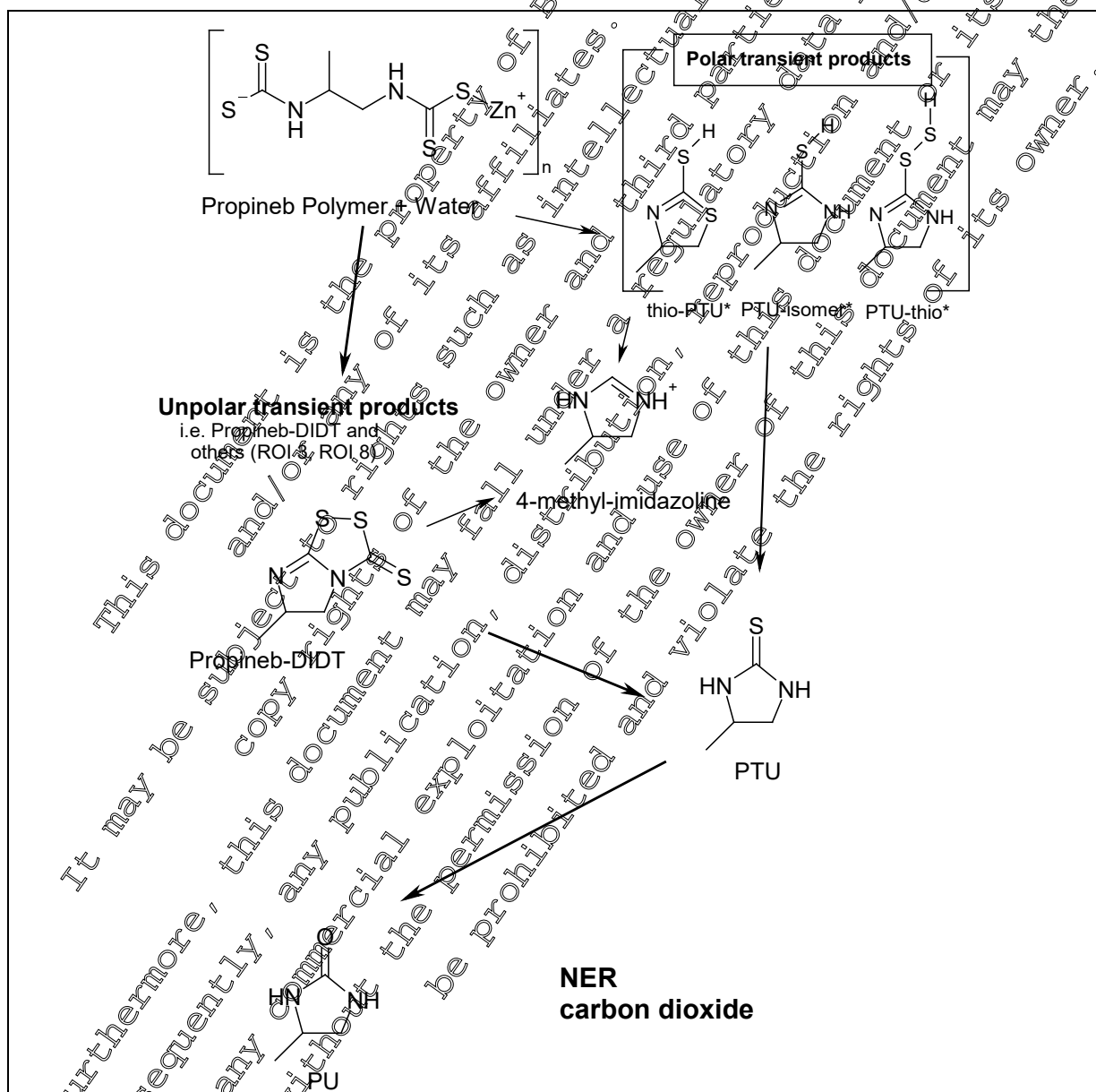
Table 7.2- 2: Substance parameters for Propineb and its metabolite Propineb-DIDT used in PEC_{sw} calculations at Step 3/4 level

Parameter	Unit	Propineb	Propineb-DIDT
Company Code		LH 30Z	BCS-CU99534
SWASH Code		PPB	DIDT
General Parameters			
Molar Mass	g/mol	289.8	190.3
Water Solubility	mg/L	100	200.0
Vapour Pressure	Pa	1.6E-04	6.5E-05
Plant Uptake Factor		0.0	0.0
Wash-Off Factor PRZM	1/cm	0.5	0.5
Wash-Off Factor MACRO	mm	0.05	0.05
Sorption			
Koc	mL/g	10000	162
Freundlich Exponent		1.00	1.00
Degradation			
Soil	days	0.1	0.5
Form. Frac. PRZM	molat basis	-	0.214
Form. Frac. MACRO	mass basis	-	0.141
Water	days	1.0	1.4
Sediment	days	1.0	1000
Walker Exponent		0.7	0.7
Effect of Temperature			
Activation Energy	J/mol	65400	65400
Exponent	1/K	0.095	0.095
Q10		2.58	2.58

Table 7.2- 3: Substance parameters used for the assessment of the aquatic metabolite Propineb-DIDT at Step 3/4 level

Molar Mass Correction Factor	0.65666
Max. Occurrence	35.8%
Tot. Correction Factor	0.23508
Max. Occurrence at Day	0.2

Figure 7.2- 1: Proposed degradation pathway of Propineb in natural water (i.e. water containing oxygen and organic matter like in water/sediment systems).



*: different isomers (position of methyl group) are possible.

Remark: NER and carbon dioxide formation can result from all structures shown (either directly or indirectly).



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

CA 7.2.1.1 Hydrolytic degradation

The hydrolysis of degradation of Propineb was evaluated during the Annex I inclusion (compare EU Monograph Annex B7), and was accepted by the European Commission (SANCO/7474/VI/97/2003). The two following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Report:	[redacted]; 1969; M-102793-01*
Title:	Investigations on the metabolism of propineb
Report No:	M132
Document No:	M-102793-01-2
Guidelines:	n.a., deviation not specified
GLP/GEP:	No

Report:	[redacted]; 1983; M-102733-01
Title:	Properties of pesticides in water - Propineb WP 70
Report No:	M2300
Document No:	M-102733-01-2
Guidelines:	n.a., deviation not specified
GLP/GEP:	No

*: that time this information was filed in the phys.chem section (at MCA 2) also.

Summary of studies performed by [redacted] 1969, and [redacted] 1983

Hydrolysis is the most important factor for the degradation of Propineb in water. The hydrolytical degradation of propineb was investigated in sterile water buffer solutions, under darkness.

Propineb was tested as Antracol WP 70 (around a.i. 14 mg/L); the tests were not conducted according to guidelines and GLP. The study showed that the hydrological degradation of propineb depends on the pH value and the temperature of water solutions. Half-life of propineb in water at 22 °C listed as end points were 24, 36 and 52 hrs at pH 4, 7 and 9 respectively.

The main degradation product of the hydrolytic reaction is propylenethiourea (PTU). The amount of PTU formed ranges from about 20 to 70 to 80% of the applied dose. At pH 9 PTU was formed predominantly, while at pH 4 and 7 other products were formed as CS₂ and propylene diamine. Further products of hydrolysis were propylene-1,2-thiurammonosulfide and propylene thiuramdisulfide. PTU itself was not further degraded during the five days incubation, also at 50 °C.

The degradation of Propineb was determined indirectly using the formation to PTU, which was analysed then. However, since the mass balance was not complete, the data of above mentioned studies did not describe adequately the period shortly after treatment (some max. %-values of major metabolites were missing). Therefore, a new hydrolysis study with ¹⁴C-propineb was regarded necessary for submission within this Supplemental Dossier for the Propineb renewal of approval.



Report:	[REDACTED];2013;M-467875-01
Title:	[Propane-14C]Propineb: Hydrolytic degradation
Report No:	EnSa-12-0750
Document No:	M-467875-01-1
Guidelines:	Commission Directives 94/37/EC and 95/36/EC amending Council Directive 91/414/EEC; OECD Test Guideline No. 111; US EPA OCSPPT Test Guidelines No. 835.2120 and 835.2130; Japanese MAFF New Test Guidelines Annex No. 2-6-1; No deviation
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The hydrolysis of radiolabeled [propane-1-¹⁴C]Propineb was studied in the dark at 50, 25 and 20 °C in sterile aqueous buffer solutions at pH 4 (0.01 M acetate buffer), pH 7 (0.01 M TRIS buffer), and pH 9 (0.01 M borate buffer) for a maximum of 35 days. The buffer solutions were prepared using highly purified and sterilized water and were bubbled with nitrogen to reduce influence of oxygen before application. The nominal concentration of the test item was 1 mg/L. Propineb is a polymer which is regarded as practically insoluble but chemically reactive in water. Therefore, a concentration of propineb dissolved in water cannot be determined. Due to this insolubility, 0.1 mg [propane-1-¹⁴C]propineb was directly applied in solid state to each test system consisting of 100 mL buffer solution. All mixtures were sonicated for 5 minutes and analysed by HPLC/radiodetection within about 0.5 hours (first sampling interval, DAT-0). LSC measurements performed after about 24 hours of incubation demonstrated that about the entire amount of the applied radioactivity (100% of AR) had been dissolved within that time.

Sampling intervals for Test 1 (pre-test, 50 °C) were 0, 0.25, 1, 1.25, 2 and 5 days (pH 4), 0, 0.25, 1, 1.25, 2 and 5 days (pH 7) and 0, 0.25, 1, 1.25, 2, 4 and 7 days (pH 9). In Test 2 (main test, 25 °C) samples were taken after 0, 0.25, 1, 2, 5, 9 and 27 days (pH 4); 0, 0.25, 1, 2, 5, 9 and 27 days (pH 7) and 0, 0.25, 1, 2, 6 and 10 days (pH 9). Sampling intervals for Test 3 (20 °C) were 0, 0.25, 1, 2, 5, 9, 16 and 34 days (pH 4); 0, 0.25, 1, 2, 4, 8, 18 and 35 days (pH 7) and 0, 0.25, 1, 3, 7, 17 and 34 days (pH 9). At each sampling interval, the radioactivity in duplicate samples was determined by LSC. The transformation products were determined by reversed-phase HPLC/radiodetection. Identification of transformation products was performed by HPLC-MS/MS as well as by HPLC co-chromatography or profile comparison.

Material balances (mean values) ranged from 79.4 to 101.3% AR for all tests. The amount of dissolved test item was determined by LSC and the coverage of all transformation products by HPLC was determined using the quotient of the total peak area detected in HPLC divided by the amount of radioactivity measured in the test solutions. This quotient was more or less constant for pH 7 and pH 9 samples throughout the entire incubation period which indicates a complete dissolution of the radioactivity from DAT-0 (0 days after treatment) onwards. In case of the pH 4 test series, the dissolution of the radioactivity was slower (about 80% dissolution at DAT-0). In these samples the radioactivity was completely dissolved from about DAT-1/DAT-5 onwards.

The test item Propineb cannot be detected in the test solutions due to its insolubility and fast degradation. Its degradation under acidic, neutral and alkaline conditions was accompanied by the formation of six fractions in radio-HPLC, 10% AR.

The main transformation product (compare [Table 7.2.1.1-4](#)) in all tests was PTU (propylene-thiourea) which accounted for up to 95.5% AR (DAT-5, pH 7, 50 °C). The second terminal transformation product PU (propylene-urea) was predominantly formed in pH 9 samples and reached up to 17.3% AR (DAT-1, pH 9, 50 °C). Four other peaks > 10% AR were separated in an unpolar group of degradates (late retention times) and a polar group (early retention times) by reversed-phase HPLC/radiodetection. These fractions were regarded as transient in the hydrolysis study as a decrease of these fractions during the course of the study was observed predominantly in pH 7 and pH 9 samples.

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The transient transformation product Propineb-DIDT was identified at a maximum amount of 19.2% AR (DAT-0.25, pH 7, 20 °C). It was the most prominent fraction in the “unpolar group” which included various minor transformation products < 10% AR (M5, M7, M8, M9, M10, M11, M13 and M16).

Three of the transient transformation products (M1, M6, M12) were designated as “polar group”. These products could not be completely separated and accounted for up to 77.5 (M1, DAT-0, pH 9, 50 °C), 11.1 (M6, DAT-3, pH 9, 20 °C) and 19.8% AR (M12, DAT-0.25, pH 4, 20 °C), respectively. An additional polar peak (M18) was detected in the pH 7 / 25 °C samples when a lower sample volume was injected. This peak accounted for up to 8.8% AR (DAT-5). It is probably included in fraction M1 if analyzed using a greater injection volume.

Several attempts were made to identify the transformation products of the polar fraction using HPLC-MS(/MS). The transformation products contained in fraction M1 were isolated from the polar group in pH 7/20 °C samples. They were not stable and decomposed during concentration and/ or HPLC-MS(/MS) analysis, resulting in the formation of the terminal products PTU and PU. Similar results were observed in additional pH 4 samples produced with the 30-fold application. Two separated peaks of the polar fraction (M12 and M1) decomposed to PTU in pH 9 samples also using the 30-fold application, three products contained in fraction M1 were tentatively identified based on their accurate masses: a thio-conjugate of PTU, a PTU-isomer and a thio-PTU-isomer. However, they are considered as precursors of PTU, too. It was not possible to identify unambiguously the compounds by other methods (e.g. NMR) due to the instability of the transition products represented by the polar fraction.

The maximum amount of a minor transformation product was 6.4% AR (M5, DAT-0, pH 4, 25 °C). The diffuse radioactivity which was not assigned to an individual peak but distributed over the baseline accounted for up to 9.8% AR (DAT-0.25, pH 7, 25 °C).

Overall, the degradation of the transient transformation products summarized in the polar and unpolar group was fast at pH 9 and pH 7 while in the pH 4 samples, their amounts as well as the amounts of PTU remained on a low level from DAT-1 or DAT-2 onwards. It was not possible to calculate hydrolysis half-lives DT50 of Propineb under the test conditions (concentration approximately 1 mg/L in sterile aqueous buffer) as Propineb does not dissolve in water. Since the total amount of radioactivity represented transformation products already for the first sampling interval (about 0.5 hours after application), it is concluded that the DT50 is less than 0.5 hours at pH 4, pH 7 and pH 9 for all temperatures.

I. MATERIAL AND METHODS**1. Test Item**

[Propane-1-¹⁴C]Propineb
Batch No.: MXM 6353-1-7
Purity: not determined
Specific RA: 0.75 MBq/mg (20.15 µCi/mg)
CAS No.: 9016-72-3

2. Buffers

The buffer solutions were prepared using highly purified and sterilized water and were bubbled with nitrogen to reduce influence of oxygen before application.
Buffer systems: Acetate, 0.01 M; TRIS, 0.01 M; Borate, 0.01 M

3. Experimental conditions

The hydrolysis of radiolabeled [propane-1-¹⁴C]propineb was studied in the dark at 50 °C, 25 °C and 20 °C in sterile aqueous buffer solutions at pH 4 (0.01 M acetate buffer), pH 7 (0.01 M TRIS buffer), and pH 9 (0.01 M borate buffer) for a maximum of 35 days.

Due to this insolubility, about 0.1 mg [propane-1-¹⁴C]propineb were directly applied in solid state to



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each test system consisting of 100 mL buffer solution. All mixtures were sonicated for 5 minutes and analysed by HPLC/radiodetection within about 0.5 hours (first sampling interval, DAT-0). LSC measurements performed after about 24 hours of incubation at ambient conditions demonstrated that the entire amount of the applied radioactivity (100% of AR) had been dissolved.

II. RESULTS AND DISCUSSION

Specimen examples of results are shown by [Table 7.2.1.1- 1](#) to [Table 7.2.1.1- 3](#), the overall summary is represented by [Table 7.2.1.1- 4](#), and the pathway of degradation in pure buffered water is represented by [Figure 7.2.1.1- 1](#).

Material balances (mean values) ranged from 79.4 to 101.3% AR for all tests. The amount of dissolved test item was determined by LSC and the coverage of all transformation products by HPLC was determined using the quotient of the total peak area detected in HPLC [counts] divided by the amount of radioactivity measured in the test solution [Bq]. This quotient was more or less constant for pH 7 and pH 9 samples throughout the entire incubation period which indicates a complete dissolution of the radioactivity from DAT-0 (0 days after treatment) onwards. In case of the pH 4 test series, the dissolution of the radioactivity was slower (about 80% dissolution at DAT-0). In these samples the radioactivity was completely dissolved from about DAT-1/DAT-5 onwards.

The DT₅₀ is less than 0.5 hours at pH 4, pH 7 and pH 9 for all temperatures. Test item Propineb could not be detected in the test solutions due to its insolubility and fast degradation. Its degradation under acidic, neutral and alkaline conditions was accompanied by the formation of six radio HPLC fractions.

Table 7.2.1.1- 1: Hydrolysis of Propineb, Test 2 (25°C, pH 4) (mean values expressed as % of AR, transformation products or zones shown in case > 10%AR, only)

Compound	DAT (days)						
	0	0.25	1	2	5	9	27
Propineb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M1 (polar zone)	8.8	8.7	7.4	9.4	11.2	10.8	14.6
PTU	45.6	59.3	61.1	67.9	65.7	57.3	66.1
Propineb-DTDT	14.1	5.7	5.6	10.3	9.0	8.5	7.0
M6	10.9	8.5	0.9	n.d.	n.d.	n.d.	n.d.
Total radioactivity in solution	99.0	95.6	87.0	95.7	93.1	90.3	94.5

Table 7.2.1.1- 2: Hydrolysis of Propineb, Test 2 (25°C, pH 7) (mean values expressed as % of AR, transformation products or zones shown in case > 10%AR, only)

Compound	DAT (days)						
	0	0.25	1	2	5	9	27
Propineb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M1 (polar zone)	61.4	56.9	33.3	20.5	10.1	11.8	1.4
PTU	3.6	5.4	31.5	47.1	64.9	74.0	81.4
Propineb-DTDT	9.8	11.2	11.2	7.7	2.3	0.8	n.d.
Total radioactivity in solution	86.7	87.0	89.3	87.4	94.6	91.2	88.1



Table 7.2.1.1- 3: Hydrolysis of Propineb, Test 2 (25°C, pH 9) (mean values expressed as % of AR, transformation products or zones shown in case > 10%AR, only)

Compound	DAT (days)					
	0	0.25	1	2	6	10
Propineb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M1 (polar zone)	67.5	66.9	57.1	39.4	1.8	0.7
PTU	4.9	6.6	14.8	27.7	59.4	70.0
Propineb-DIDT	5.2	7.5	11.2		n.d.	n.d.
PU	n.d.	n.d.	n.d.	9.4	12.4	7.2
Total radioactivity in solution	88.2	90.0	95.0	93.2	89.2	91.5

n.d.: not detected, DAT: days after treatment

The main transformation product in all tests was PTU (propylene-thiourea) which accounted for up to 95.5% AR (DAT-5, pH 7, 50 °C). The second terminal transformation product PU (propylene-urea) was predominantly formed in pH 9 samples and reached up to 17.3% AR (DAT-1, pH 9, 50 °C). PTU and PU did not show further degradation. Four other peaks > 10% AR were separated in an unpolar group of degradates (long retention times in HPLC) and a polar group (short retention times in HPLC). These fractions were regarded as transient in the hydrolysis study as a decrease of these fractions during the course of the study was observed predominantly in pH 7 and pH 9 samples.

The transient transformation product Propineb-DIDT was identified at a maximum amount of 19.2% AR (DAT-0.25, pH 7, 20 °C). It was the most prominent fraction in the “unpolar group” which included various minor transformation products < 10% AR (M5, M7, M8, M9, M10, M11, M14 and M16). Propineb DIDT was fast degraded at pH 7 and pH 9.

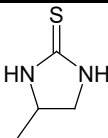
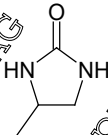
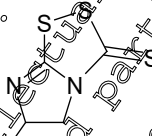
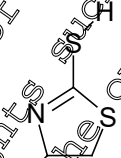
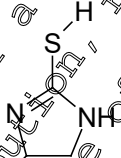
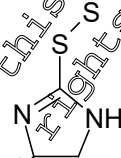
Three of the transient transformation products with retention times in HPLC ranging from approx. 5 to 9 min. (M1, M6, M12) were designated as “polar group”. These products could not be completely separated and accounted for up to 67.5% AR (M1, DAT-0, pH 9, 50 °C), 11.1% (M6, DAT-3, pH 9, 20 °C) and 19.8% AR (M12, DAT-0.25, pH 4, 20 °C), respectively. An additional polar peak (M18) was detected in the pH 7 / 25 °C samples when a lower sample volume was injected. This peak accounted for up to 8.8% AR (DAT-5). It is probably included in fraction M1 if analyzed using a greater injection volume.

Overall, the degradation of the transient transformation products summarized in the polar and unpolar group was fast at pH 7 and pH 9, while in the pH 4 samples, their amounts as well as the amounts of PTU remained on a low level from DAT-1 or DAT-2 onwards. Transient transformation products represented by a polar and non-polar group in HPLC could not be identified or only be tentatively identified. Proposals were made e.g. for M1 like a thio-conjugate, PTU isomer, thio-PTU) due to instability (see [Table 7.2.1.1- 4](#)).

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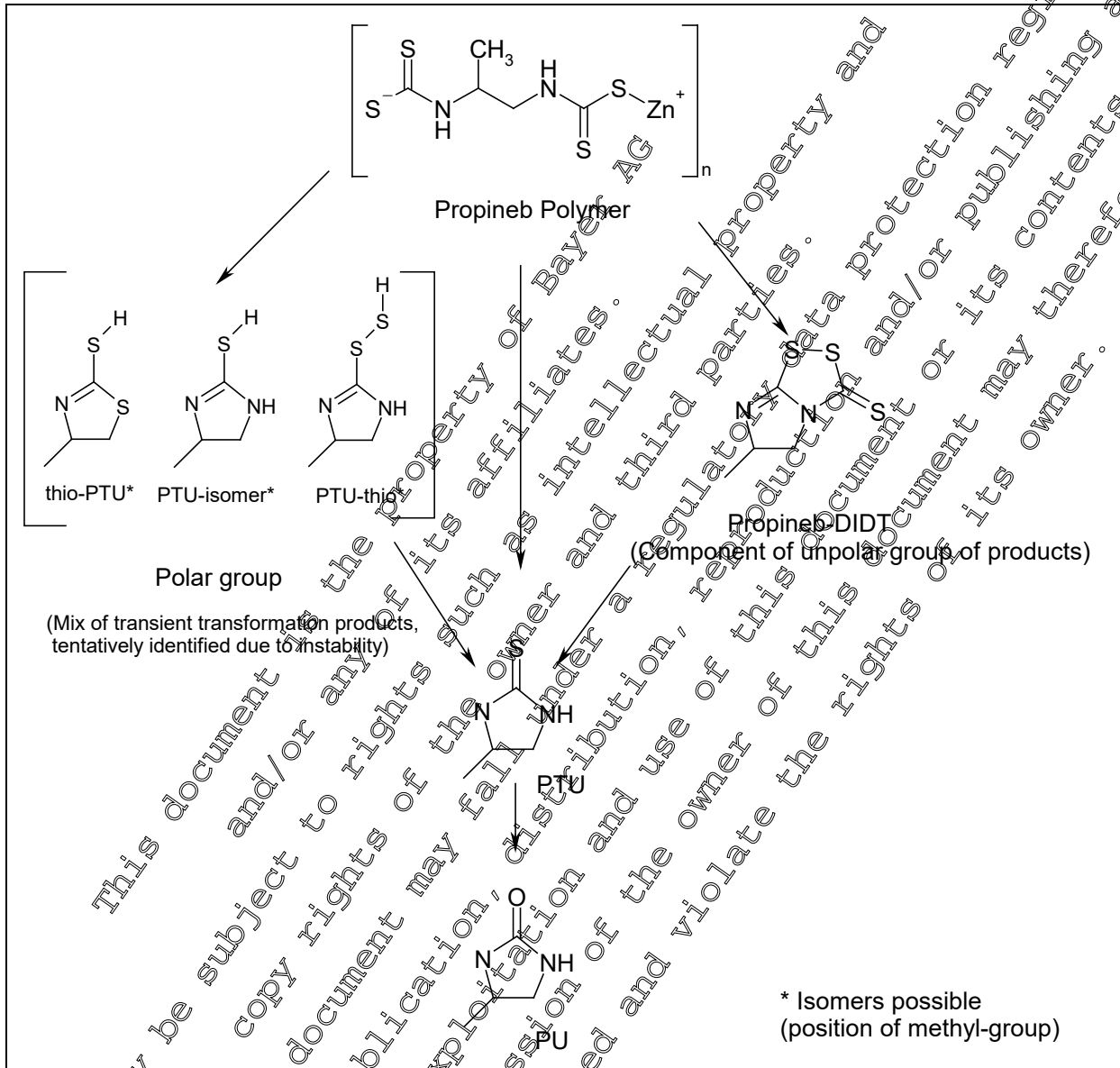


Table 7.2.1.1- 4: Hydrolysis products of Propineb in sterile buffers pH 4, pH 7 and pH 9

<p>Major transformation products</p>	<div style="text-align: center;">  <p>PTU (propylene-thiourea, max. 95.5% AR)</p>  <p>PU (propylene-urea, max. 10.3% AR)</p>  <p>Propineb-DIDT (max. 19.2% AR, most prominent peak in unpolar group)</p> <p>Proposal for transient polar metabolites</p>  <p>*PTU-thio</p>  <p>*PTU isomer</p>  <p>*PTU-thio-conjugate</p> <p>* isomers possible, tentatively identified components of polar group at pH 9), max. of individual component (M.F.: 77.5% AR)</p> </div>
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Figure 7.2.1.1- 1: Proposed degradation pathway of Propineb in pure buffered water (i.e. in water not containing oxygen and organic matter).





III. CONCLUSION

It is concluded that Propineb as a polymer does not dissolve in water. Therefore, the dissolved radioactivity in the aqueous solution must result from spontaneously formed reaction products. Since the total amount of radioactivity found in the test solution was constant already from the first sampling, the half-life of formation of hydrolysis products was estimated to be less than 0.5 hours at pH 4, pH 7 and pH 9 for all temperatures. PTU was the main degradation product which was formed in sterile aqueous buffer solutions at pH 4, pH 7 and pH 9. PU was formed as a second terminal transformation product. PTU and PU were stable under the test conditions. The polar zone M1 was not stable and fragments were identified as precursors of PTU.

The test was performed under sterile conditions, in pure buffer and nitrogen atmosphere. It should be pointed out that especially for the highly reactive substance propineb a different behaviour (e.g. reaction with organic material, faster oxidation) under natural environmental conditions is expected.

A summary of the route and rate of hydrolysis of Propineb in water is given in section CA 7.3 and the outcome on pathway of degradation is incorporated in Figure 7.2.1.

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

CA 7.2.1.2 Direct photochemical degradation

The direct photochemical degradation of Propineb was evaluated during the Annex I inclusion (compare EU Monograph Annex B0, and was accepted by the European Commission (SANCO/7474/VI/97, 2003). The two following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Report:	[redacted];1983;M-102743-01 *
Title:	Orientating light stability - Propineb WP 70
Report No:	M456
Document No:	M-102743-01-2
Guidelines:	n.a.
GLP/GEP:	Yes

Report:	[redacted];1993;M-102893-01 *
Title:	Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation of propylenethiourea (PTU) in water
Report No:	PF3886
Document No:	M-102893-01-1
Guidelines:	n.a.
GLP/GEP:	Yes

*: that time this information was filed in the 1.4.-chem section (at MCA 2.8), also.

Summary of study performed by [redacted] 1983

The photodegradation of Propineb was investigated in a solution of 14.6 mg/L of Antracol WP 70 irradiated for 6 hours. This test showed that Propineb is degradable by light in water with half-life values between 0.6 and 0.8 hours. The main degradation product was PTU.

Conclusion:

The degradation of Propineb under aqueous photolysis conditions is not of relevance due to its rapid degradation in the dark by hydrolysis. Therefore, sunlight is not expected to be a relevant route of degradation for Propineb after its use according to good agricultural practices.



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The following study on the terminal metabolite PTU is included in the Baseline Dossier which was regarded as relevant during the Annex I inclusion:

Summary of study performed by [redacted] 1993

The study on the photodegradation of PTU in water was conducted according to GLP and according to the ECETOC guidelines. Very low degradation rates of PTU were observed in the experiments with light source simulating sunlight (photodegradation in the merry-go-round irradiation apparatus). The estimated half-life concerning direct photodegradation of PTU in water ranges from about 570 days to more than 1 year.

The degradation of PTU under aqueous photolysis conditions indicates that this metabolite is stable under the conditions of irradiation by sunlight.

A summary of the route and rate of degradation of Propineb in water is given in section [CA 7.2](#) and [Figure 7.2-1](#).

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

CA 7.2.1.3 Indirect photochemical degradation

The indirect photochemical degradation of degradation of Propineb was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/7474/VI/97, 2003). The following study included in the Baseline Dossier was regarded as relevant during the Annex I inclusion:

Report:	[redacted] 1984;M-103319-01 *
Title:	The influence of humic substances on the photodegradation of pesticides
Report No:	F2170
Document No.:	M-103319-01-2
Guideline:	n.a.
GLP/GLP:	✓

*: that time this information was found in the phys.-chem section (at MCA 2.8) also.

Summary of study performed by [redacted] 1984

The influence of humic substances on the phototransformation of PTU was investigated. The half-life was reduced depending on the amount of humic substances to 7.5 days indicating that PTU is moderately fast degraded due to irradiation in natural systems. Not any further main degradation products were found in the sensitised test system.

Indirect photochemical reactions are more likely to occur than direct photochemical reactions, since the laboratory DT₅₀ in a sensitised system was 7.5 days, only. However, due to the fast dissipation of PTU observed in the water/sediment test system (see section [CA 7.2.2.3](#)), PTU is only expected to remain available for such reactions for a short period of time.

No additional studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.



CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

With respect to the "ready biodegradability" of Propineb a statement was given as a conclusion the list of end points of Annex I inclusion by the European Commission (SANCO/7474/VI/9, 2005). Thereby, the compound was classified as ready biodegradable (compare page 17). However, this statement was not drawn from an experimental study included in the Baseline Dossier; it was concluded from the fast dissipation of Propineb and its major metabolite PTU observed by the studies mentioned before.

The the following new study is submitted within this Supplemental Dossier for the Propineb renewal of approval.

Report:	[REDACTED] 2011/M-413983-01
Title:	Biodegradation of Propineb TK83
Report No:	2011/0083/01
Document No:	M-413983-01-1
Guidelines:	Council Regulation (EC) No 440/2008, Method C4-D Manometric Respirometry Test (2008). This test method is in all essential parts identical with OECD Guideline 301 F (adopted July 1992).; deviations not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

A suspension of Propineb TK83 in a mineral medium was inoculated and incubated for 28 days under aerobic conditions. During this period the degradation was followed continuously by oxygen consumption (automated BOD determination). Based on this test Propineb TK 83 - or more precise its transformation products in water - is considered to be "Not readily Biodegradable". It should be considered that the polymer Propineb decomposes immediately in aqueous solution. The test measured the biodegradability of the formed transformation products.

I. MATERIAL AND METHODS

1. Test Item

Propineb TK83
Batch No.: EDFU911415
Purity: 84.2% w/w
CAS No.: 9016-72-2

2. Test System

A mixed population of aquatic microorganisms (activated sludge) from an aeration tank of a wastewater plant treating predominantly domestic sewage ([REDACTED] area water authority, WWTP [REDACTED], Germany). Concentration of inoculum : 30 mg/L suspended solids.

3. Study Design

A suspension of 100 mg/L test item in a mineral medium, equalling to 50-100 mg ThOD or COD/L as the nominal sole source of organic carbon, was stirred in a closed flask and inoculated at a constant temperature (22 ± 1 °C) for up to 28 days under aerobic conditions in the dark. The consumption of oxygen (BOD) was determined by measuring the drop in pressure in the automated respirometer flasks. Evolved carbon dioxide was absorbed in sodium hydroxide. The



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amount of oxygen taken up by the test item (corrected for uptake by blank inoculum, run in parallel) was expressed as a percentage of chemical oxygen demand (COD).

The endogenous activity of the inoculum was checked running parallel blanks with inoculum but without test item. A reference compound (sodium benzoate) was run in parallel to check the operation of the procedures.

A toxicity control (test item and reference compound mixed) was run in parallel, to ensure that the chosen concentration of the test item was not inhibitory to microorganisms.

Degradation was followed by the determination of oxygen uptake and measurements were taken at frequent intervals to allow the identification of the beginning and end of biodegradation and the slope of the biodegradation curve.

The test lasted for 28 days.

Because of the nature of biodegradation and of the mixed bacterial populations used as inoculum, determinations of reference compound were carried out in duplicate and of test item and inoculum blank in triplicate.

The oxygen uptake was calculated from the readings taken at regular and frequent intervals using the method given by the manufacturer of the equipment. At the end of incubation, the pH was measured in the flasks.

II. RESULTS AND DISCUSSION

Propineb TK83 showed

1% degradation after 7 days

0% degradation after 14 days

0% degradation after 21 days

0% degradation after 28 days

The reference compound sodium benzoate showed 89% degradation after 14 days. Within 28 days, a degradation rate of 0% was determined for Propineb TK83.

III. CONCLUSION

Propineb TK83 is considered to be "Not Readily Biodegradable"

However, it should be considered that the polymer Propineb decomposes immediately in aqueous solution. This standardized test measures the complete mineralisation of the transformation products to carbon dioxide at a high dose rate.

CA 7.2.2.2 Aerobic mineralisation in surface water

Since this topic was not yet part and thus not evaluated by the European Commission during the last Annex I inclusion of Propineb, no respective study is included in the Baseline Dossier. However, the applicant believes that the circumstances in which the study is required are not fulfilled for Propineb, considering its intrinsic properties (i.e. available information on the fate and behaviour in the environment) and realistic exposure conditions.

“Studies on aerobic mineralisation in surface water shall be provided unless the applicant shows that contamination of open water (freshwater, estuarine and marine) will not occur” (Commission Regulation (EU) No 283/2013, L 93, Section 7.2.2.2, page 52).

Propineb is used as spray application in various crops, and the main exposure of surface water is spray-drift. However, in order to reach an acceptable risk for aquatic organisms, it is necessary to implement mitigation measures such as drift reduction nozzles or buffer zones to limit the amount of Propineb that will reach the water bodies at the edge of the field. Moreover, Propineb is immobile and



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rather short living in soil (see below and section CA 7.1.3.1); accordingly, drainage entires to water bodies are very unlikely. Last but not least Propineb is insoluble and rather short living in water. It is thus very unlikely that contamination of open water (i.e. surface water far away from the edge of the field) will occur.

The most important situations of exposure and degradation of Propineb and its residues at the edge of a treated field are described by all the laboratory studies summarized in the following section. The applicant therefore believes that no further testing is required to meet the current section 7.2.2 of Commission Regulation (EU) No 283/2013.

CA 7.2.2.3 Water/sediment study

In principle, route and rate of degradation of Propineb in water/sediment systems under aerobic conditions were evaluated during the Annex I inclusion. However, due to the before-mentioned special intrinsic properties of Propineb, it was accepted to evaluate a study performed with the [¹⁴C] labelled PTU as a surrogate, since PTU was regarded as the major part of residues formed from in Propineb in a water/sediment system.

The following studies included in the Baseline Dossier (U-009496-01) were regarded relevant during the Annex I inclusion:

Report:	[REDACTED], 1993, M-022332-02
Title:	Degradation and metabolism of propylene thiourea in the system water/sediment
Report No:	DF388
Document No:	M-022332-02-1
Guidelines:	-/-
GLP/GEP:	Yes

Report:	[REDACTED], 1997, M-022369-01
Title:	Calculation of the T-50 values of metabolite of propineb based on data from a water/sediment study
Report No:	MR-328/97
Document No:	M-022369-01-1
Guidelines:	-/-
GLP/GEP:	No

Summary of study performed by [REDACTED] 1993

The degradation of [¹⁴C]PTU was investigated using two water/sediment systems (" [REDACTED] and " [REDACTED] ") according to the BBA Guidelines and GLP standards. The samples were incubated in the dark at 20 °C for in all 100 days.

The major proportion of the radioactivity applied was translocated into the sediment with the higher percentage of organic substance. Thus, a maximum amount of 57% was localised in the sediment of the system [REDACTED], and 33% in the sediment of the system [REDACTED] after 60 days. The unextracted portion of radioactivity increased to 44% in the [REDACTED] and to 24% in the system [REDACTED]. The extracted portion of radioactivity reached a maximum of 15 to 17 days after an incubation of 14 to 30 days and then decreased until the end of the test. The radioactivity of the surface water declined to 28% in the system [REDACTED], and to 10% in the system [REDACTED].



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Total mineralisation by formation of carbon dioxide proceeded faster in the system [redacted] than in the system [redacted]. The rate of carbon dioxide amounted to 53.6% (including carbon dioxide released by acidification of sediment) in the case of system [redacted], and to 14.8% in the case of the system [redacted].

Summary of kinetics study performed [redacted] 1997

The DT₅₀ and DT₉₀ values for the degradation of PTU in both types of water/sediment systems can be considered low (DT₅₀ = 2.5 and 4 days; DT₉₀ = 8.4 and 13.2 days).

One value was to be calculated for the degradation of PU, i.e. a DT₅₀ of 19.6 days in the the system [redacted] resulted.

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The following presented new aerobic water/sediment metabolism study performed with ¹⁴C-Propineb was regarded necessary since the current data did not adequately describe the period shortly after dosing Propineb into such a test system (earlier [¹⁴C]PTU was taken as test item). Therefore, information about the formation fraction or maximum occurrence of primary degradates was missing. However, such information on the behaviour of the transformation products is required for predicting the environmental concentrations in water.

Report:	[REDACTED];2014;M-487541-01
Title:	[Propane-1- ¹⁴ C]propineb: Aerobic aquatic metabolism
Report No:	EnSa-13-0416
Document No:	M-487541-01-1
Guidelines:	OECD Test Guideline No. 308, Aerobic and Anaerobic Transformation in Aquatic Sediment Systems, 2002 US EPA OCSPP Test Guideline No. 835.4300 / 835.4400, Aerobic and Anaerobic Aquatic Metabolism, 2008, deviation not specified
GLP/GEP:	Yes

EXECUTIVE SUMMARY

The aerobic transformation of [propane-1-¹⁴C]Propineb was studied in two types of water/sediment (see [Table 7.2.2.3- 1](#)) for up to 100 days at 20 ± 0.1 °C in the dark.

Table 7.2.2.3- 1: Test systems used

Water/Sediment System	ID	Source	Sediment			Water	
			Type	pH	TOC [%]	pH	TOC [mg/L]
[REDACTED]	[REDACTED]	[REDACTED] Germany	Sand	7.0 (6.6)	0.33	7.8	4.4
[REDACTED]	[REDACTED]	Close to [REDACTED] Germany	Silt loam	6.1 (5.2)	8.20	6.1	6.3

Prior to study pH of sediment (values in brackets) were derived from suspensions in aqueous 0.01 M CaCl₂ (sed./water 1:2); all other values given are the mean values measured in DAT-0 test systems.

The anticipated amount of test item for the treatment of the test systems was based on the intended single maximum field use rate of Propineb (i.e. 2250 g Antracol®/ha for a technical material having 70% a.i. content), implying a possible maximum surface water contamination to be in the same order of magnitude. In order to overcome analytical hurdles, a treatment of approx. 188 µg of ¹⁴C-Propineb/test system, suspended in water (initial concentration 312 µg Propineb/L water), was scheduled for the study, i.e. an overdosing factor of 2.3 was taken into account.

Laboratory microcosm flasks each filled with a volume ratio of water to sediment of 3:1 were treated with 900 µL aqueous suspension containing the ¹⁴C-Propineb. The flasks were equipped with traps for the collection of carbon dioxide and volatile organic compounds. During incubation the supernatant water was in smooth motion, but the sediment remained undisturbed.

The value of 100% applied radioactivity (100% of AR) for this study was set by the mean value of the total recovery of radioactivity from the processing of the respective DAT-0 samples. The 100% of AR was determined with 156.099 kBq (corresponding to 208.1 µg/batch) for system [REDACTED] (A) and with 148.792 kBq (corresponding to 198.4 µg/batch) for system [REDACTED] (W).



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Duplicate samples were processed and analyzed 0, 0.167, 1, 3, 8, 15, 30, 58, 78, 100 days after application. The DAT-0 samples were processed approximately 1 hour after application.

At each sampling interval the water was separated from the sediment by decantation into a centrifuge beaker. The water was centrifuged, decanted, and the volume was determined; aliquots were taken for analysis by LSC and HPLC/radiodetection analysis.

The solid remainder after centrifugation was combined with the sediment phase. The entire sediment of a test vessel was transferred into the same centrifuge beaker as used before for the work-up of the water using some extraction solvent. The sediment was extracted two times with acetonitrile/water 4/1 (v/v) at ambient conditions using a mechanical shaker. Furthermore, a microwave-accelerated extraction step was performed using acetonitrile/water 1/1 (v/v) at 70 °C. The sediment extracts were combined for HPLC/radiodetection analyses. The extraction procedure was found to be adequate to decompose all polymeric residues of [¹⁴C]Propineb contained in a sediment sample.

The exhaustively extracted sediment was air-dried, homogenized by a mortar grinder and non-extractable radioactivity (NER) was determined by combustion/LSC. The evolved ¹⁴CO₂ was determined by investigation of the soda lime trap. Determination of carbonates in exhaustive extracted sediment was performed for the last sampling interval (DAT-100).

The amounts of Propineb and its degradation products in water and sediment extracts were determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. Degradation products were identified by HPLC-MS(/MS) including accurate mass determination and/or by co-chromatography with reference items.

The test conditions throughout the study were as follows: pH in the water ranged from 7.6 to 8.9 in [redacted], and from 5.1 to 8.4 in [redacted] test systems. The corresponding pH in sediment was neutral to alkaline in [redacted], and acidic in the [redacted] systems. In both test systems the measured oxygen content and the positive values for the redox potential indicated aerobic conditions throughout the entire incubation period.

The overview on material balance and distribution of radioactivity in the two test series is summarized by [Table 7.2.2.3- 2](#).

Table 7.2.2.3- 2: Results synopsis on material balance and distribution of applied ¹⁴C

Water/Sediment System	[redacted]	[redacted]
Material Balance [% AR] *	94.9 – 104.8 (mean: 100.1)	100.0 – 104.9 (mean: 102.3)
Water Phase [% AR]	15.8 (DAT-78) – 69.1 (DAT-0.167)	14.2 (DAT-100) – 73.7 (DAT-0.167)
Sediment Extract [% AR]	5.2 (DAT-78) – 14.8 (DAT-0)	9.1 (DAT-0.167) – 13.9 (DAT-15)
Mean Max. ¹⁴ CO ₂ [% AR]	37.2	13.6
Mean NER [% AR]	19.2 (DAT-0) – 49.5 (DAT-3) 35.2 at DAT-100	21.5 (DAT-0.167) – 67.5 (DAT-15) 61.1 at DAT-100

*: minimum values noted at the last samplings; NER = non extractable sediment residues

The mean material balance was 100.1% of AR for system [redacted], and 102.3% of AR for system [redacted]. The complete material balance found at all sampling intervals for both water/sediment systems demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

The maximum mean amount of carbon dioxide was 37.2 and 13.6% of AR at study end (DAT-100) for [redacted] and [redacted] systems, respectively. Formation of volatile organic compounds (VOC) was insignificant for both water/sediment systems.



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In both test systems the mean radioactivity dosed to the water phase decreased during the study, i.e. to 19.6% of AR in [redacted] systems, and to 14.2% of AR in [redacted] systems at DAT-100. Propineb residues dissipated from the water rapidly due to degradation as well as by translocation of residues into the sediment (mainly forming NER therein).

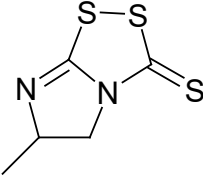
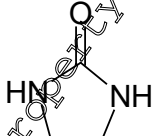
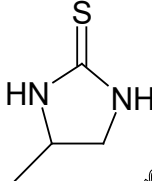

Degradation of Propineb was accompanied by the formation of four degradation products in water. The following maximum amounts were observed: Propineb-DIDT with a maximum of 31.7% of AR at DAT-0.167 (system [redacted]), PU with a maximum of 42.3% of AR at DAT-3 (system [redacted]), PTU with a maximum of 24.0% of AR at DAT-0.167 (system [redacted]) and 4-MI with a maximum of 17.1% of AR at DAT-0 (system [redacted]). Further, in water the unpolar intermediate ROI3 amounted to a maximum of 25.7% of AR at DAT-0 (system [redacted]). For the short living ROI3 a kind of dimeric form of Propineb-DIDT could be made as structural proposal. The unpolar intermediate ROI8 was detected with a maximum of 2.5% of AR at DAT-0.167 (system [redacted]).

In general, extractable residues in sediment were on a comparable low level during the study, from 14.8 to 5.9% of AR in system [redacted], and between 9.1 and 13.9% of AR in system [redacted]. Therein, three degradation products with following maximum amounts were observed: Propineb-DIDT with a maximum of 4.1% of AR at DAT-0 and DAT-0.17 (system [redacted]), PU with a maximum of 11.4% of AR at DAT-75 (system [redacted]) and PTU with a maximum of 3.5% AR at DAT-0 (system [redacted]). In sediments, the unpolar intermediate ROI3 amounted to a maximum of 11.1% of AR at DAT-3 (system [redacted]) and the unpolar intermediate ROI8 was detected with a maximum of 1.1% of AR at DAT-0 (system [redacted]). NER in sediment increased from 19.2% of AR at DAT-0 to 49.5% of AR at DAT-3, and then declined to 35.2% of AR at DAT-100 in [redacted] systems. In [redacted] systems, NER increased from 27.3% of AR at DAT-0 to 67.5% of AR at DAT-15, and then slowly declined to 61.1% of AR at DAT-100.

The overview on metabolism of propineb in the water/sediment systems under dark aerobic conditions is summarized by the following table. For proposed pathway of degradation see [Figure 7.2- 1](#).

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Table 7.2.2.3- 3: Results synopsis on metabolism of Propineb in water/sediment systems

Identified major degradation products (mean maximum occurrence)	
CO ₂ (37.2% AR)	
Propineb-DIDT (35.8% AR) 	PU (50.4% AR) 
PTU (26.6% AR) 	4-MI (17.1% AR) 

Degradation of Propineb in the total system showed four identified degradation products, and the following maximum amounts were observed:

Propineb-DIDT with a maximum occurrence of 35.8% AR at DAT-0.17 (system [redacted]), PU with a maximum occurrence of 50.4% AR at DAT-3 (system [redacted]), PTU with a maximum occurrence of 26.6% AR at DAT-0.17 (system [redacted]) and 4-MI with a maximum occurrence of 17.1% AR at DAT-0 (system [redacted]).

In the total system, the unpolar intermediate ROI3, a kind of dimeric form of Propineb-DIDT, amounted max 36.4% of AR at DAT-0 (system [redacted]). The unpolar intermediate ROI8 was detected with a maximum of 2.9% of AR at DAT-0.17 (system [redacted]). The non-identified structures ROI3 and ROI8 are regarded as unpolar fragments of propineb. Procedures to isolate and identify such unpolar intermediates of Propineb failed and resulted in PTU and PU as ¹⁴C-degradates, finally.

Since the current study was designed as a route of degradation study in water and sediment, and since the starting point of propineb degradation cannot be analysed for such a polymeric compound, the resulting data are not adequate to derive degradation kinetics for propineb, nor of its primary degradation products.

Altogether, available propineb DT₅₀ data indicate that it is degrading quite fast, dependent on temperature, pH and concentration of suspension (for the latter, the lower the faster). Supportive LSC measurements within this study indicated that it lasts some time (max. approx. 1 day) until the maximum amount of the water soluble metabolites are to be observed in a water phase. Therefore, a worst case DT₅₀ of 1 day for propineb degradation in natural surface water could be taken for modelling purposes. During such period the finding of short living primary degradates could have been caused by fresh formation via destruction of polymeric propineb still present in the test systems.

Therefore, the dissipation of the primarily formed major metabolite was investigated in an additional test using [propane-¹⁴C]Propineb-DIDT as test item dosed to the supernatant water of some further water/sediment test flasks. Each 212 µL test item dissolved in methanol were dosed in each one flask of [redacted] and [redacted] test system. Then, each twelve 1-mL aliquots distributed over the entire incubation period of 48 hours were taken, i.e. 0.25, 1, 2, 3, 4, 5, 6, 7, 8, 9, 24 and 48 hours after treatment of the supernatant. This water samples were analyzed by LSC and radio-TLC without further processing.

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The experimental data could be well described by single first order (SFO) and double first order in parallel (DFOP) kinetic models. The calculated half-life for the dissipation of the major metabolite (Propineb-DIDT) from the water was 1.4 and 0.004 days for system [redacted] and [redacted] respectively (see table below). Obviously, the more acidic conditions in the supernatant water of [redacted] accelerate the dissipation of Propineb-DIDT to a great extent. On the other hand, most of the observed degradates seem to be a little more stable in the alkaline [redacted] test system.

Table 7.2.2.3- 4: Results synopsis on “best fit” dissipation kinetics for Propineb-DIDT in the supernatant water layer (persistence endpoints)

System / Radiolabel (Sediment Type)	Best Fit Kinetic Model	DT ₅₀ [d]	DT ₉₀ [d]	Chi ² Error [%]	Visual Assessment
[redacted] (sand)	SFO	1.4	4.6	3.6	+
[redacted] (silt loam)	DFOP	0.004	0.2	3.6	+

¹ SFO: Single first order, DFOP: Double first order in parallel

² Visual assessment: + good

From this study it is concluded that Propineb and its degradation products have no potential for accumulation in the aqueous environment. For modelling purposes a worst case DT₅₀ of 1.0 and 1.4 days are to be proposed for propineb and Propineb-DIDT degradation in water, sediment and total water plus sediment system, respectively.

I. MATERIALS AND METHODS

1. Test Item

[Propane-1- ¹⁴ C]Propineb:	MXM 953-1 i.e. TK 83 (approx. 86.3% of propineb)
Specific Radioactivity:	0.75 MBq (20.15 µCi) / mg
Radiochemical Purity:	Not to be determined
Chemical purity:	Not to be determined

For additional test

[Propane-1- ¹⁴ C]Propineb-DIDT	KML 9670
Specific Radioactivity:	3.46 MBq (91.80 µCi) / mg
Radiochemical Purity:	> 98% (DPLC with radioactivity detector) > 99% (GLC, scan)
Chemical purity:	> 99% (HPLC with UV-detector, 280 nm)

2. Test Systems

The study was carried out with two different natural water/sediment systems sampled in each a 30-L-hobcock on 2014-11-02 (batch ID 20111102):

- [redacted], [redacted], Germany: This small lake is a reclaimed gravel-pit, which is used for fishing only. The lake is entirely enclosed by a fence.
- [redacted], close to [redacted] near [redacted], Germany: This is a fresh water dam that is used for the preparation of drinking water. Water and sediment were collected from the forebay

Fresh water and sediment samples were taken separately and poured into plastic containers prior to the start of the study. A description of water and sediment collection and storage is given in the report. The results of the on-site measurements as well as the other system characteristics are given in



[Table 7.2.2.3- 5](#). Samples of the same origin of water/sediment systems were used for the additional test.

B. STUDY DESIGN

1. Experimental Conditions

One day after sampling, the collected sediments were sieved to ≤ 2 mm, the waters were passed through a 0.063 mm mesh. Static test flasks, laboratory microcosm flasks, for degradation in aquatic systems under aerobic conditions were used. These are special cylindrical glass containers (volume approx. 1000 mL, inner diameter approx. 10.5 cm, surface area approx. 86.6 cm²), and each container is fitted with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

For preparation of the test systems, wet sediment with a weight equivalent to a volume of 175 mL was weighed into each vessel and 520 mL of the corresponding water were added. The water-to-sediment volume ratio used was approximately 3/1 with a water layer of approximately 6 cm and a sediment layer of approximately 2 cm.

The untreated test systems were equilibrated to study conditions by placement in a temperature-controlled walk-in climatic chamber at 20 °C in the dark for 11 days prior to application. The equilibration was proven by repeated measurement of the oxygen saturation of the water, the pH of the water and the sediment as well as the redox potential of the water and the sediment in representative test systems.

For the purpose of isolation and identification of formed metabolites some further flasks (ID MID) were prepared.

Later, for the purpose of isolation and identification of formed metabolites each new test flasks (ID MID) were prepared on 2012-03-14. They were filled with 343.4 and 210.2 g of wet sediment from systems [REDACTED] and [REDACTED], respectively, and 520 mL of the corresponding water (batch ID 20120313).

The test item was suspended in water and the gently stirred suspension was directly used as application solution. On 2011-11-14, the day of application an amount of 12.12 mg [¹⁴C]Propineb was freshly suspended in 10 mL pure water, resulting in an application solution with a nominal concentration of 1.2 mg/mL (0.9 MBq/mL), labeled as WU55Appl. The resulting suspension was continuously mixed/stirred on the Vortex Genie 2 equipment until the end of application.

An aliquot of 156 μ L application solution WU55Appl was applied dropwise onto the water surface of the respective equilibrated test systems in order to obtain a nominal concentration of 188 μ g/test system. The application was performed under continuous stirring of the application solution.

After application, each test vessel (except the DAT-0 samples) was sealed with the special trap attachment and placed into a temperature-controlled walk-in climatic chamber for incubation at 20 °C in the dark.

The amount of applied test item and the homogeneity of the application were determined by transferring each 156 μ L of the application solution WU55Appl into graduated cylinders before, during and after the application. Since some variation of measured values was obvious (as it is not surprising in case that such suspension of a polymer is applied) the conclusion was drawn to better set the value of 100% applied radioactivity (100% of AR) for the current study by taking the mean value of the total recovery of radioactivity from the processing of the respective DAT-0 samples:

In case of test system [REDACTED] (A) the 100% AR was determined with 156.099 kBq, corresponding to 208.2 μ g/batch. In case of test system [REDACTED] (W) the 100% AR was determined with 148.792 kBq corresponding to 198.4 μ g/batch.

Thus, for both test systems the nominal dose of 188 μ g/batch was slightly exceeded. During incubation for up to 100 days at 20 \pm 0.1 °C in the dark the supernatant water was in smooth motion, but the sediment remained undisturbed.



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For the additional test [propane-1-¹⁴C]Propineb-DIDT was dissolved in 10 mL methanol, resulting in a stock solution with a nominal concentration of 0.5 mg/mL (1.7 MBq/mL) labeled as JR64-SS1. The radioactivity content was determined by liquid scintillation counting (LSC) as 1.6 MBq/mL (equal to 0.47 mg/mL). The stock solution stored at < -18 °C in the dark. This solution was used as application solution for the additional test.

212 µL of application solution JR64-SS1 were pipetted to the water surface of the test systems. Afterwards, the samples were incubated under continuous shaking (70 U/min) in a climatic chamber at 20 °C. One sample was prepared for each water/sediment system. No attempts were made to trap volatiles, and to analyse the sediments.

2. Sampling

For the main test ten sampling intervals were distributed over the entire incubation period of 100 days, respectively. Duplicate samples were processed and analyzed at 0, 0.167, 1, 3, 8, 15, 30, 58, 78, 100 days after application. The DAT-0 samples were processed approximately 1 hour after application. Prior to opening an incubated test system for processing of water and sediment, volatiles possibly still present in the head space of the test system were sucked through the trap attachment by placing the test flask for 10 minutes in an exsiccator (except for DAT-0 samples). Afterwards, the trap attachment was removed. Aliquots of the water were taken to determine the radioactivity content and the amount of dissolved carbon dioxide. Then the redox potential, pH and the oxygen content were determined and the water was separated from the sediment by decantation. The sediment was extracted completely.

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Table 7.2.2.3- 5: Physico-chemical properties of water and sediment

Parameter	Results/Units	
	(A), Batch no 20111102	(B), Batch no 20111102
Sediment Designation		
Properties of Water		
Temperature [°C]	1,2	13.2
pH	1,2	6.7
Redox Potential E _H [mV]	1,2	123
Oxygen Saturation [mg/L]	1,2	10.1
pH	1	7.8 (DAT-0)
Redox Potential E _H [mV]	1	190 (DAT-0)
Oxygen Saturation [mg/L]	1	8.6 (DAT-0)
Total Organic Carbon (TOC) [mg/L]	3,4	20 / 4.4
Properties of Sediment		
Temperature [°C]	1,2	13.0
pH	1,2	6.9
Redox Potential E _H [mV]	2	230
pH	1	7.0 (DAT-0)
Redox Potential E _H [mV]	1	167 (DAT-0)
Texture Class		Sand ⁶
Sand [%] [50 µm – 2 mm]	6	9
Silt [%] [2 µm – 50 µm]		36
Clay [%] [< 2 µm]		54
		10
pH (sediment / 0.01 M CaCl ₂ 1/2)		6.6
pH (sediment / water 1/1)		5.4
Organic Matter [%]	4,5,8	0.67 / 0.57 / 0.78
Total Organic Carbon (TOC) [weight-%]	3,4,5	0.30 / 0.33 / 0.45
Total Nitrogen [weight-%]	3	0.1
Total Phosphorus [mg/kg]	3,4	130
Cation Exchange Capacity [meq/100 g]	4,6	2.9
Moisture [g H ₂ O ad 100g dry weight]		20.25
		234.03

¹ BCS-D-EnSA Testing

³ [redacted] GmbH & Co. OHG, [redacted] Germany

⁵ DAT-0 / DAT-100

⁷ according to USDA classification

² day of sampling

⁴ start of equilibration

⁶ [redacted] Laboratories, [redacted] USA

⁸ % organic matter = % organic carbon x 1.724

At each sampling interval the water was separated from the sediment by decantation into a centrifuge beaker. The water was centrifuged, decanted, and the volume was determined; aliquots were taken for analysis by LSC and HPLC/radiodetection analysis.

The solid remainder after centrifugation was combined with the sediment phase. The entire sediment of a test vessel was transferred into the same centrifuge beaker as used before for the work-up of the water using some extraction solvent. The sediment was extracted two times with acetonitrile/water 4/1 (v/v) at ambient conditions using a mechanical shaker. Furthermore, a microwave-accelerated extraction step was performed using acetonitrile/water 1/1 (v/v) at 70 °C. After each extraction step, extract and sediment were separated by centrifugation (approximately 10 minutes at 5000 x g) and decantation. The sediment extracts were combined for HPLC/radiodetection analyses. The combined

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extract was stored at approx. 20 °C in the freezer prior and post analyses. The extraction procedure was found to be adequate to decompose all polymeric residues of [propane-1-¹⁴C]Propineb contained in a sediment sample.

The exhaustively extracted sediment was air-dried, homogenized by a mortar grinder and non-extractable radioactivity (NER) was determined by combustion/LSC. The evolved ¹⁴CO₂ was determined by investigation of the soda lime trap. Determination of carbonates in exhaustive extracted sediment was performed for the last sampling interval (DAT-100).

For the additional test twelve sampling intervals were distributed over the entire incubation period of 48 hours. Aliquots of 1 mL of the water phase were analyzed 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 24 and 48 hours after application.

3. Analytical Procedures

The amounts of Propineb and its degradation products in water and sediment extracts were determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. All LSC measurements were carried out without concentration steps.

For radio-TLC analyses of water and of combined sediment extract no further concentration step was needed. For the primary analyses of combined sediment extracts performed by radio-HPLC an aliquot of 2 mL was concentrated to approx. 1 mL (in order to get off the acetonitrile prior to analyses), then re-dissolved in 2 mL by adding purified water again. The recovery of this processing step was on average 92.7% and 75.5% for combined sediment extract samples of [redacted] and [redacted], respectively.

Degradation products were identified by HPLC-MS/MS including accurate mass determination and/or by co-chromatography with reference items.

The 1-mL water samples taken at the additional test were analyzed by LSC and TLC/radiodetection without further processing.

II. RESULTS AND DISCUSSION

The test parameter measurements indicated that the anticipated standardized aerobic laboratory conditions were maintained throughout the water/sediment study.

A constant temperature for up to 100 days at 20 ± 0.1 °C in the dark was maintained.

The pH in the water ranged from 7.6 to 8.9 in [redacted] test systems, and from 5.1 to 8.4 in [redacted] test systems. The corresponding pH in the sediment ranged from 6.6 to 8.2 in [redacted] test systems and from 5.7 to 6.9 in [redacted] test systems.

The oxygen content in the water ranged from 8.5 to 9.2 mg/L in [redacted], and from 7.8 to 8.7 mg/L in the [redacted] test systems. The redox potential determined in the water and the sediment was in a high positive E_H range during the incubation. However, variations between different test systems were observed. In [redacted] test systems, the E_H values in water ranged from +256 to +393 mV. The corresponding E_H values in sediment were between +121 and +391 mV. In [redacted] test systems, the E_H values in water ranged from +298 to +490 mV. The corresponding E_H values in sediment were between +18 and +308 mV. The clearly positive values for the redox potential and the magnitude of oxygen content indicate aerobic conditions throughout the entire incubation period.

The measured microbial activity in the sediments indicated that the systems were biologically active at the start of the study.



A. DATA

All calculations for radioactivity (as % of applied radioactivity) in water and sediment extract, in the solid materials and in the trap attachments are listed in [Table 7.2.2.3- 6](#) and [Table 7.2.2.3- 7](#), the overview was presented by [Table 7.2.2.3- 2](#) and [Table 7.2.2.3- 3](#), already.

The mean material balance was 100.1% of AR for system [REDACTED], and 102.3% of AR for system [REDACTED]. The complete material balance found at all sampling intervals for both water/sediment systems demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

Significant formation of $^{14}\text{CO}_2$ was observed in both water/sediment systems. At termination of the study (DAT-100), the $^{14}\text{CO}_2$ recovery (mean values of duplicates) was 37.2% and 14.6% of AR for [REDACTED] and [REDACTED] systems, respectively. Formation of volatile organic compounds (VOC) was insignificant for both water/sediment systems.

NER increased from 19.2% of AR at DAT-0 to 49.5% of AR at DAT-3, and then declined to 35.2% of AR at DAT-100 in [REDACTED] systems. In [REDACTED] systems, NER increased from 27.3% of AR at DAT-0 to 67.5% of AR at DAT-15, and then slowly declined to 61.1% of AR at DAT-100. NER was further characterized for the samples taken at the end of the study. Thereby, the fulvic acid fraction represented the largest proportion (20 - 27% of AR).

The mean radioactivity dosed to the water phase decreased from DAT-0 to DAT-100 from 66.0 to 19.6% of AR in [REDACTED] systems and from 62.0 to 14.2% of AR in [REDACTED] systems. Propineb residues dissipated from the water rapidly, due to degradation as well as by translocation of residues into the sediment (mainly forming NER therein).

In general, extractable residues in sediment were on a comparable low level during the study, from 14.8 to 5.9% of AR in system [REDACTED], and between 9.0 and 13.9% of AR in system [REDACTED].

Extractable residues in the total system (water and sediment extracts) decreased in system [REDACTED] from 80.8 at DAT-0 to 21.2% of AR at DAT-78, and then slightly increased to 25.5% of AR at DAT-100. In system [REDACTED], extractable residues in the total system decreased from DAT-0 to DAT-100 from 72.7 to 26.7% of AR.

B. METHOD VALIDATION

Due to its polymeric nature Propineb is practically insoluble in water and in organic solvents. Since the polymeric propineb shows decomposition, i.e. if water is present, any observed solubility is caused by degradation but not by dilution. In consequence, the parent compound propineb cannot be analyzed itself. In case valid values of its content are to be determined it must be guaranteed that the entire propineb polymer still present in a sample is degraded to products which are soluble and can be measured. These facts had to be considered for the processing of samples.

For the test item investigated in the current study a recovery even shortly after the treatment of water/sediment systems cannot be given. Therefore, the overall mass balance and the distribution pattern of products received during the study (based on LSC and HPLC/radiodetection analysis data) are regarded as the important quality parameter for this study. Those results demonstrated that the sample processing methods were gentle enough to recover quite short living degradates for a distinct period of time.

For the early water samples a waiting duration of approx. 1 day was found to be adequate. Then, the maximum of water soluble metabolites were to be observed in the water phase, indicating that all polymeric Propineb was degraded.

Further the method was adequate to destroy the total amount of polymeric Propineb still present in a sediment sample at the respective sampling interval. However, since the primary degradates of



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polymeric propineb are highly reactive species the formation of comparatively high portions of NER cannot be avoided in sediments (compare Table 7.2.2.3- 6 and Table 7.2.2.3- 7).

The primary HPLC/radiodetection method was well suited for the quantitative analysis of the samples of this study as demonstrated by overall mean HPLC recoveries for water and combined sediment extracts of 96.6% for [redacted] systems (results filed in the raw data).

The LOD of the primary HPLC/radiodetection method was determined as 1.2% of AR.

Table 7.2.2.3- 6: Material balance of radioactivity in [redacted] test systems applied with [propane-1-¹⁴C]Propineb, expressed as % of AR

	Repl. No.	Days after treatment (DAT, daf)									
		0	0.167	1	3	8	15	30	58	78	100
Volatile Radioactivity											
¹⁴ CO ₂	1	n.a.	0.1	1.0	3.5	8.0	17.5	23.2	41.5	41.4	
	2	n.a.	0.1	1.1	2.6	6.5	9.7	14.3	20.5	32.9	
	Mean	n.a.	0.1	1.0	2.8	5.9	9.3	15.9	21.9	34.6	37.2
Volatiles Organic Compounds (VOC)	1	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
	2	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
	Mean	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
Total Volatiles	1	n.a.	0.1	1.0	3.0	5.5	9.5	13.2	41.5	41.4	
	2	n.a.	0.1	1.1	2.7	5.5	9.7	14.3	20.5	32.9	
	Mean	n.a.	0.1	1.0	2.8	5.9	9.3	15.9	21.9	34.6	37.2
Water Layer and Sediment Extractable Radioactivity											
Water Layer	1	66.6	68.9	57.1	40.9	23.3	34.2	29.4	25.3	9.9	20.1
	2	67.4	69.3	48.9	43.7	39.1	35.9	32.4	29.4	21.8	19.1
	Mean	66.0	69.1	53.0	42.3	40.7	35.0	30.9	27.4	15.8	19.6
Sediment Extractable Radioactivity											
Ambient Extract	1	7.2	7.4	7.3	7.1	8.2	7.4	6.3	6.1	2.7	4.8
	2	8.9	6.1	7.4	6.6	7.4	8.9	7.2	5.9	4.7	4.6
	Mean	8.0	7.1	7.4	6.8	7.8	8.1	6.7	6.0	3.7	4.7
Microwave Extract	1	6.6	4.3	4.5	5.5	2.7	8.0	2.0	1.9	1.3	1.3
	2	6.8	3.7	4.3	3.2	2.7	2.8	2.4	1.7	1.9	1.2
	Mean	6.8	4.3	4.4	3.3	2.7	2.9	2.2	1.8	1.6	1.2
Total Sediment Extractables	1	14.8	13.9	14.8	10.6	7.0	10.4	8.3	7.9	4.0	6.1
	2	15.5	9.7	11.7	9.8	10.0	11.7	9.5	7.5	6.7	5.7
	Mean	14.8	11.4	11.7	10.2	10.5	11.0	8.9	7.7	5.3	5.9
Total Water Layer and Sediment Extractables	1	80.6	81.3	68.9	51.4	53.3	44.5	37.8	33.3	13.9	26.2
	2	80.0	79.0	60.6	53.5	49.1	47.6	42.0	36.9	28.5	24.8
	Mean	80.8	80.4	64.7	52.5	51.2	46.1	39.9	35.1	21.2	25.5
Non-Extractable Sediment Residues (NER)	1	19.7	19.1	35.7	51.0	45.1	41.7	44.9	40.4	42.1	37.4
	2	18.7	20.1	39.7	48.0	47.1	38.8	44.1	45.6	36.2	33.1
	Mean	19.2	20.1	37.8	49.5	46.1	40.2	44.5	43.0	39.1	35.2
Material Balance	1	100.3	101.6	105.7	105.4	103.7	95.2	100.2	96.9	97.4	105.0
	2	99.9	100.2	101.3	104.1	102.7	96.0	100.4	103.0	92.3	90.8
	Mean	100.0	100.6	103.5	104.8	103.2	95.6	100.3	100.0	94.9	97.9

n.d.: not detected, n.a.: not analyzed

Material balance values calculated from the Means: MIN = 94.9%; MAX = 104.8%; Mean = 100.1% (RSD = 3.1%)



Table 7.2.2.3- 7: Material balance of radioactivity in [REDACTED] test systems applied with [propane-1-¹⁴C]Propineb, expressed as % of AR

	Repl. No.	Days after treatment (DAT, days)									
		0	0.167	1	3	8	15	30	58	78	106
Volatile Radioactivity											
¹⁴ CO ₂	1	n.a.	0.1	0.3	0.6 ¹	1.6	2.5	4.7	8.9	9.6	13.4
	2	n.a.	0.1	0.3	0.8	1.6	2.4	4.1	7.4	9.9	13.2
	Mean	n.a.	0.1	0.3	0.8	1.6	2.4	4.4	8.1	9.8	13.6
Volatiles Organic Compounds (VOC)	1	n.a.	< 0.1	< 0.1	0.1 ¹	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	2	n.a.	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Volatiles	1	n.a.	0.1	0.3	0.6 ¹	1.6	2.5	4.7	8.9	9.6	13.4
	2	n.a.	0.1	0.3	0.8	1.6	2.4	4.1	7.4	9.9	13.7
	Mean	n.a.	0.1	0.3	0.8	1.6	2.4	4.4	8.1	9.8	13.6
Water Layer and Sediment Extractable Radioactivity											
Water Layer	1	62.2	72.3	52.2	35.7 ¹	27.4	21.3	24.8	20.3	19.1	15.2
	2	61.8	75.1	41.8	42.5	25.8	20.7	19.5	15	14.6	13.3
	Mean	62.0	73.7	47.0	42.5	26.6	21.0	22.2	15.8	16.9	14.2
Sediment Extractable Radioactivity											
Ambient Extract	1	7.0	6.8	7.3	13.2 ¹	9.2	12.0	11.7	11.6	11.3	10.9
	2	7.3	7.3	10.5	7.8	8.6	9.1	10	10.0	8.4	9.6
	Mean	7.2	7.0	9.0	7.8	8.9	10.5	11.0	10.8	9.9	10.2
Microwave Extract	1	3.8	2.3	3.0	4.6 ¹	3.5	3.7	2.6	2.1	3.9	2.3
	2	3.3	1.8	3.4	3.2	3.7	3.1	2.8	2.3	3.6	2.2
	Mean	3.5	2.1	3.2	3.2	3.6	3.4	2.7	2.2	3.8	2.2
Total Sediment Extractables	1	10.8	9.1	10.3	17.8 ¹	12.7	15.7	14.3	13.7	15.2	13.1
	2	10.5	9.1	14.1	11.1	12.3	12.2	13.0	12.3	12.0	11.8
	Mean	10.7	9.1	12.2	11.1	12.5	13.9	13.7	13.0	13.6	12.5
Total Water Layer and Sediment Extractables	1	73.0	81.4	63.6	43.5 ¹	40.1	36.9	39.2	34.0	34.3	28.3
	2	72.4	84.2	55.9	53.6	38.1	32.9	32.5	27.6	26.7	25.1
	Mean	72.7	82.8	59.2	53.6	39.1	34.9	35.9	30.8	30.5	26.7
Non-Extractable Sediment Residues (NER)	1	26.8	26.8	37.4	7.9 ¹	59.7	73.0	57.5	61.6	66.4	60.0
	2	38.1	22.3	46.3	48.5	59.8	62.0	63.4	66.4	61.5	62.2
	Mean	27.3	21.5	41.9	48.5	59.8	67.5	60.5	64.0	64.0	61.1
Material Balance	1	99.5	102.3	100.2	102.0 ¹	101.5	112.4	101.4	104.5	110.4	101.7
	2	100.5	106.6	102.5	102.8	99.5	97.3	100.1	101.3	98.0	100.9
	Mean	100.0	104.4	101.4	102.8	100.5	104.9	100.8	102.9	104.2	101.3

n.d.: not detected, n.a.: not analyzed

¹ outlier, not considered for evaluation

Material balance values calculated from the Means: MIN = 100.0%; MAX = 104.9%; Mean = 102.3% (RSD = 1.6%)

C. DEGRADATION OF PARENT COMPOUND

A synopsis on biotransformation of Propineb in aerobic water/sediment test systems is shown by by [Table 7.2.2.3- 2](#) and [Table 7.2.2.3- 3](#), already. The findings were included in the proposed pathway of degradation in water and sediment (see [Figure 7.2- 1](#)). More detailed data (expressed as percent of applied radioactivity, mean ± SD) are summarized for the [REDACTED] test system in [Table 7.2.2.3- 8](#) and for the [REDACTED] test system [Table 7.2.2.3- 9](#), respectively



Table 7.2.2.3- 8: Degradation of [propane-1-¹⁴C]Propineb in [redacted] test system under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Source	Mean SD	Days after treatment (DAT, days)									
			0	0.167	1	3	8	15	30	58	78	100
Propineb	Water Layer		Not measurable									
	Sediment		Not measurable									
	Entire System		Not measurable									
4-MI	Water Layer	Mean SD	17.1 ± 4.1	n.d.	n.d.	n.d.	6.0 ± 0.4	6.3 ± 0.6	5.2 ± 0.5	4.7 ± 0.6	4.7 ± 0.0	5.1 ± 0.4
	Sediment	Mean SD	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	17.1 ± 4.1	n.d.	n.d.	n.d.	6.0 ± 0.4	6.3 ± 0.6	5.2 ± 0.5	4.7 ± 0.6	4.7 ± 0.0	5.1 ± 0.4
PU	Water Layer	Mean SD	n.d.	n.d.	17.2 ± 0.4	42.3 ± 0.4	34.7 ± 2.0	28.8 ± 0.9	25.7 ± 1.1	22.6 ± 0.5	11.1 ± 6.0	14.5 ± 1.0
	Sediment	Mean SD	4.0 ± 0.3	2.7 ± 0.4	4.3 ± 0.4	8.1 ± 0.5	8.3 ± 2.6	15.0 ± 0.7	8.9 ± 0.6	10.7 ± 0.2	n.d.	5.9 ± 0.2
	Entire System	Mean SD	4.0 ± 0.3	2.7 ± 0.4	21.5 ± 0.8	50.4 ± 2.0	43.7 ± 4.6	39.8 ± 1.5	34.7 ± 1.5	30.4 ± 1.3	11.1 ± 6.0	20.4 ± 1.1
PTU	Water Layer	Mean SD	12.4 ± 1.1	24.0 ± 1.2	18.8 ± 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	2.5 ± 0.2	2.5 ± 0.5	2.2 ± 0.9	n.d.	2.2 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	16.0 ± 1.4	26.0 ± 0.6	21.0 ± 0.6	n.d.	2.2 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.
ROI 3	Water Layer	Mean SD	6.4 ± 0.2	10.9 ± 1.4	7.3 ± 0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	1.8 ± 0.3	LOD	2.1 ± 0.2	1.5 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	8.0 ± 0.4	12.0 ± 0.3	9.9 ± 0.5	1.5 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propineb-DIB ¹	Water Layer	Mean SD	30.1 ± 3.7	31.7 ± 1.8	9.7 ± 2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	4.1 ± 0.5	4.1 ± 0.4	3.1 ± 0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	34.2 ± 3.2	35.8 ± 2.2	12.8 ± 2.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ROI 4	Water Layer	Mean SD	n.d.	2.5 ± 0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	1.2 ± 0.0	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	1.2 ± 0.0	2.5 ± 0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected, n.a.: not analyzed, SD: standard deviation



Table 7.2.2.3- 9: Degradation of [propane-1-¹⁴C]Propineb in [redacted] test system under aerobic conditions, expressed as % of AR (mean ± SD)

Compound	Source	Mean SD	Days after treatment (DAT, days)									
			0	0.167	1	3	8	15	30	58	78	100
Propineb	Water Layer		Not measurable									
	Sediment		Not measurable									
	Entire System		Not measurable									
4-MI	Water Layer	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PU	Water Layer	Mean SD	n.d.	n.d.	n.d.	13.6 ± 1.0	20.0 ± 2.0	28.1 ± 2.0	22.2 ± 2.0	17.8 ± 0.5	16.9 ± 2.2	14.2 ± 1.0
	Sediment	Mean SD	n.d.	n.d.	n.d.	n.d.	7.3 ± 0.7	6.0 ± 0.8	5.0 ± 0.9	10.8 ± 0.9	11.4 ± 1.5	10.7 ± 0.6
	Entire System	Mean SD	n.d.	n.d.	n.d.	13.6 ± 0.4	27.0 ± 1.8	24.7 ± 3.6	31.2 ± 3.6	28.3 ± 3.4	28.3 ± 3.8	24.9 ± 1.5
PTU	Water Layer	Mean SD	18.3 ± 0.1	23.3 ± 0.5	21.5 ± 0.5	6.3 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	18.3 ± 0.1	23.3 ± 0.5	21.5 ± 0.5	12.6 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ROI 3	Water Layer	Mean SD	25.7 ± 1.0	22.3 ± 0.5	3.6 ± 0.0	n.d.	6.6 ± 0.0	2.8 ± 0.0	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	10.7 ± 0.1	n.d.	n.d.	11.1 ± 1.0	5.2 ± 1.0	7.4 ± 1.0	4.7 ± 0.2	2.3 ± 0.2	2.2 ± 0.0	1.8 ± 0.1
	Entire System	Mean SD	36.4 ± 1.0	22.3 ± 0.5	3.6 ± 0.0	11.1 ± 0.0	11.8 ± 0.6	10.3 ± 3.8	4.7 ± 0.2	2.3 ± 0.2	2.2 ± 0.0	1.8 ± 0.1
Propineb-DIB	Water Layer	Mean SD	18.0 ± 1.2	28.0 ± 1.0	19.8 ± 1.1	16.3 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	18.0 ± 1.2	28.0 ± 1.4	19.8 ± 0.1	16.3 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ROI 4	Water Layer	Mean SD	n.d.	n.d.	2.1 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Sediment	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Entire System	Mean SD	n.d.	n.d.	2.1 ± 0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected, n.a.: not analyzed, SD: standard deviation

**Document MCA: Section 7 Fate and behaviour in the environment
Propineb****Water phase**

Degradation of Propineb was accompanied by the formation of four degradation products in water, and following maximum amounts were observed: Propineb-DIDT with a maximum of 31.7% of AR at DAT-0.167 (system [REDACTED]), PU with a maximum of 42.3% of AR at DAT-3 (system [REDACTED]), PTU with a maximum of 24.0% of AR at DAT-0.167 (system [REDACTED]) and 4-MI with a maximum of 17.1% of AR at DAT-0 (system [REDACTED]). Further, in water, the unpolar intermediate ROI3 amounted to a maximum of 25.7% of AR at DAT-0 (system [REDACTED]). For the short living ROI3 a kind of dimeric form of Propineb-DIDT could be made as structural proposal. The unpolar intermediate ROI8 was detected with a maximum of 2.5% of AR at DAT-0.167 (system [REDACTED]).

Sediment phase

In general, extractable residues in sediment were on a comparable low level during the study. Therein, three degradation products with following maximum amounts were observed: Propineb-DIDT with a maximum of 4.1% of AR at DAT-0 and DAT-0.167 (system [REDACTED]), PU with a maximum of 11.4% of AR at DAT-78 (system [REDACTED]) and PTU with a maximum of 3.5% of AR at DAT-0 (system [REDACTED]). In sediment extracts the unpolar intermediate ROI3 amounted to a maximum of 11.1% of AR at DAT-3 (system [REDACTED]) and the unpolar intermediate ROI8 was detected with a maximum of 1.2% of AR at DAT-0 (system [REDACTED]).

Total test system

Degradation of Propineb in the total system was accompanied by the formation of four degradation products following maximum amounts observed: Propineb-DIDT with 35.8% of AR at DAT-0.167 (system [REDACTED]), PU with 50.4% of AR at DAT-3 (system [REDACTED]), PTU with 26.6% of AR at DAT-0.167 (system [REDACTED]) and 4-MI with 17.1% of AR at DAT-0 (system [REDACTED]). In the total system, the unpolar intermediate ROI3 amounted to a maximum of 36.4% of AR at DAT-0 (system [REDACTED]), and the unpolar intermediate ROI8 was detected with a maximum of 2.9% of AR at DAT-0.167 (system [REDACTED]). ROI3 and ROI8 are regarded as short living unpolar fragments of propineb. Finally, all the procedures to isolate the unpolar intermediates of Propineb resulted in PTU and PU as degradates.

Kinetic analysis of data

Since the current study was designed as a route of degradation study in water and sediment, and since the starting point of Propineb degradation cannot be analysed for such a polymeric compound, the resulting data are not adequate to derive degradation kinetics for Propineb, nor of its primary degradation products. Altogether, available Propineb DT₅₀ data indicated that it is degrading quite fast, dependent on temperature, pH and concentration of suspension (for the latter, the lower the faster). Supportive ESC measurements within this study indicated that it lasts some time (max. approx. 1 day) until the maximum amount of the water soluble metabolites are to be observed in a water phase, i.e. after centrifugation in order to separate particles still present in a water sample. Therefore, a worst case DT₅₀ of 1 day for Propineb degradation in natural surface water could be taken for modelling purposes. During such period, the finding of short living primary degradates could have been caused by fresh formation via destruction of polymeric Propineb.

Therefore, the dissipation of the primarily formed major metabolite was investigated in an additional test using [¹⁴C]Propineb-DIDT as test item dosed to the supernatant water of water/sediment test flasks. The radioactivity determined in the water phase of the additional test is presented in [Table 7.2.2.3- 10](#), and the residual amounts of Propineb-DIDT found in each replicate test system at each sampling interval are shown in [Table 7.2.2.3- 11](#).

The experimental data could be well described by single first order (SFO) and double first order in parallel (DFOP) kinetic models. The calculated half-live for the dissipation of Propineb-DIDT from the water was 1.4 and 0.004 days for system [REDACTED] and [REDACTED], respectively (see [Table 7.2.2.3- 4](#)). Obviously, the more acidic conditions in the supernatant water of [REDACTED] accelerate the dissipation of Propineb-DIDT.



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Propineb

Table 7.2.2.3- 10: Radioactivity in water of additional test systems applied with [propane-1-¹⁴C]Propineb-DIDT (expressed as % of AR)

System:

	Time after treatment (hours)											
	0.25	1	2	3	4	5	6	7	8	9	24	48
Water phase	100.0	99.5	98.2	98.4	96.6	94.9	92.0	91.6	91.2	90.6	76.7	62.4

System:

	Time after treatment (hours)											
	0.25	1	2	3	4	5	6	7	8	9	24	48
Water phase	99.9	92.2	89.9	85.4	79.0	75.5	68.8	68.1	67.0	64.3	36.2	22.8

Table 7.2.2.3- 11: Dissipation of [propane-1-¹⁴C]Propineb-DIDT (additional test, expressed as % of AR)

System:

Compound	Source	Time after treatment (hours)											
		0.25	1	2	3	4	5	6	7	8	9	24	48
Propineb-DIDT	Water	94.6	90.5	92.2	90.0	90.7	86.6	84.2	87.4	87.7	87.7	66.8	29.9
4-MI	Water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PTU	Water	1.4	1.4	1.4	n.d.	2.1	2.8	2.0	1.7	n.d.	n.d.	n.d.	n.d.
Unkown 1	Water	2.5	4.9	2.7	3.0	2.9	5.0	2.0	2.6	2.3	2.6	2.3	
Diffuse Residues	Water	1.0	< LOD	< LOD	LOD	LOD	LOD	LOD	LOD	1.0	< LOD	1.0	< LOD

n.d.: not detected

System:

Compound	Source	Time after treatment (hours)											
		0.25	1	2	3	4	5	6	7	8	9	24	48
Propineb-DIDT	Water	83.3	83.8	80.8	81.6	73.8	64.2	61.8	65.0	61.9	59.7	28.2	9.0
4-MI	Water	1.5	1.4	1.2	n.d.	n.d.	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	1.5
PTU	Water	1.4	1.4	< LOD	n.d.	n.d.	1.8	n.d.	n.d.	n.d.	n.d.	2.5	n.d.
Unkown 1	Water	3.2	4.8	5.8	3.0	5.0	6.8	6.7	2.2	3.4	2.6	3.4	4.6
PU	Water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0
Unkown 2	Water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.6
Diffuse Residues	Water	0.2	0.2	0.8	0.8	0.2	0.1	0.4	0.2	0.6	0.1	0.2	0.1

n.d.: not detected



III. CONCLUSIONS

Based on the results of the study, a pathway for the degradation of Propineb in water/sediment systems under aerobic conditions is proposed (compare [Figure 7.2- 1](#)), with the following possible processes involved:

- Formation of Propineb-DIDT directly from [propane-1-¹⁴C]Propineb
- Formation of 4-MI directly from [propane-1-¹⁴C]Propineb via polar transient products or from Propineb-DIDT.
- Formation of PTU from [propane-1-¹⁴C]Propineb via unpolar transient products like Propineb-DIDT, ROI3 and ROI8. Obviously, the more acidic conditions in the supernatant water of ██████████ accelerate their degradation to PTU
- Formation of PU from PTU
- Mineralization (carbon dioxide formation)
- Formation of non-extractable residues (NER).

From this study it is concluded that Propineb and its degradation products have no potential for accumulation in the aqueous environment.

For modelling purposes a worst case DT₅₀ of 1.0 and 1.4 days are to be proposed for Propineb and Propineb-DIDT degradation in water, sediment, and total water plus sediment system, respectively. The outcome is included in the summary on the behaviour of Propineb and its major degradation products in water given under section [CA 7.2](#).

Report:	██████████ ; 2014; M 487719-01
Title:	Kinetic evaluation of the degradation of propylene-thiourea and its degradation product in water-sediment according to FOCUS kinetics
Report No:	EnSa-14-0685
Document No:	M 487719-01-1
Guidelines:	FOCUS (2011): Generic guidance for estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 1.0, 23 November 2011.
GLP/GEP:	No

EXECUTIVE SUMMARY

The degradation of propylene-thiourea (PTU) in water sediment systems from the study by ██████████ 1993, was kinetically evaluated to derive trigger and modelling endpoints. The degradation product propylene-urea (PU) was also considered. Evaluations followed FOCUS kinetics (2011) recommendations and were conducted up to level P-II for the parent and up to level M-I for the degradation product.

At level P-I for both the trigger and the modelling endpoint the SFO fit was identified and delivered DT₅₀ values of 4.9 and 2.1 days for the two investigated systems ([Table 7.2.2.3- 12](#)).



Table 7.2.2.3- 12: Summary of the kinetic evaluation for degradation of PTU in water sediment at level P-I

System	Kinetic model ¹	Chi ² error-%	Visual assessment	DT ₅₀ [days]
[redacted]	SFO	5.93	+	4.9
	FOMC	6.32	o	4.9
[redacted]	SFO	5.41	+	2.4
	FOMC	5.31	+	2.4

¹ SFO: Single first order, FOMC: First order multi compartment

² Visual assessment: + = good, o = moderate, - = poor
bold letters indicate the model of choice

In order to obtain separate DT₅₀ values for the water and sediment compartment a level P-II evaluation was conducted. The evaluation resulted only in one reasonable fit, i.e. for the [redacted] system where for both the water and the sediment compartment acceptable fits were achieved. The corresponding DT₅₀ values are 4.5 and 1.3 days for PTU degradation in water and sediment, respectively ([Table 7.2.2.3- 13](#)).

Table 7.2.2.3- 13: Summary of the kinetic evaluation for degradation of PTU in water sediment at level P-II

System	Chi ² error-%	Visual assessment ²	DT ₅₀ [days]
[redacted] PTU _{wat} :	3.92	+	4.5
[redacted] PTU _{sed} :	17.0	+	1.3
[redacted] All:	16.62	+	

¹ values for PTU, PU and the whole model respectively

² Visual assessment: + = good, o = moderate, - = poor.

A level M-I evaluation was performed with the residues of PTU and its degradation product PU in the total system. For both investigated system reasonable fits were obtained that described the degradation and formation of parent and degradation product quite well. The results are summarized in [Table 7.2.2.3- 14](#).

Table 7.2.2.3- 14: Summary of the kinetic analysis for PTU degradation and the formation and degradation of PU in water-sediment systems at level M-I

System	Chi ² error-% ¹	Visual assessment ²	DT ₅₀ [days]	
[redacted]	PTU _{tot} :		6.61	
	PU _{tot} :	14.6	+	5.6
	All:	9.9	+	27.6
[redacted]	PTU _{tot} :	13.0	o	3.7
	PU _{tot} :	2.77	+	147
	All:	12.9		

¹ values of PTU, PU and the whole model respectively

² Visual assessment: + = good, o = moderate, - = poor.



I. METHODS

The objective of the present study was the kinetic evaluation of residue data from [redacted] 1993, on the degradation and metabolism of propylene-thiourea in water/sediment systems to derive endpoints for trigger evaluation and for modelling purposes.

The kinetic evaluation of the residue data was conducted in accordance with recommendations of FOCUS (FOCUS, 2011) to derive degradation half-lives (DT₅₀) to be used in environmental exposure assessments. The software KinGUI2.1 was employed.

Details on kinetic models, statistical evaluation, identification of the appropriate kinetic model and specifics for water sediment systems were described in sections 3.1 to 3.4 of report.

[redacted] 1993, investigated the degradation of PTU in natural water sediment systems. PTU is a degradation product of propineb in soil and in water (c.f. [redacted] 2014; [redacted] 2010). It forms the degradation product PU which was also detected by ([redacted] 1993, in the water sediment study. Thereby, incubation was performed in the dark at a temperature of 20°C

In accordance with FOCUS (2011) the DAT₀ values for total system were set to 100% of A.R. First values at the limit of detection (LOD) or below LOD were set to 0.5 * LOD. The LOD accounted for 0.1% of AR. [Table 7.2.2.3- 15](#) summarizes the pre-processed data.

Table 7.2.2.3- 15: Pre-processed residue data from the study of [redacted] 1993, used in the kinetic optimization; grey shaded figures were altered to fulfil FOCUS (2011) recommendations; values are given in percent of applied radioactivity

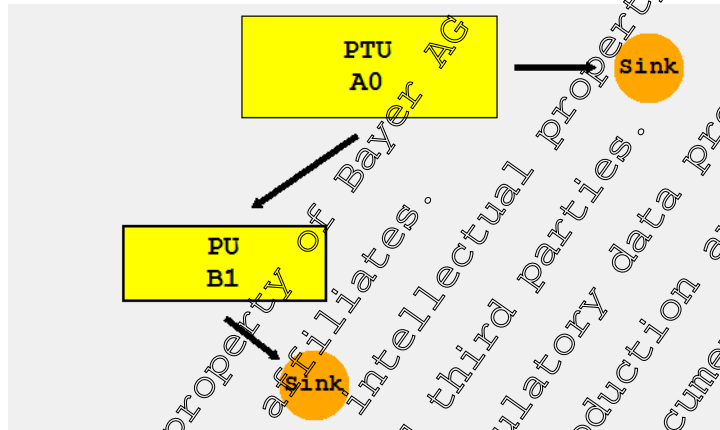
System	Time	PTU _{tot}	PTU _{wat}	PTU _{sed}	PU _{tot}	PU _{wat}	PU _{sed}
[redacted]	0	100	NA	NA	NA	NA	NA
	0.042	90.7	90.7	NA	1.4	1.4	NA
	0.25	91.1	88.1	3.0	1.3	0.9	0.4
	1	74.4	79.9	5.3	5.3	4.9	0.8
	2	52.3	66.5	5.8	15.7	14.1	1.6
	7	40.5	44.6	5.9	41.4	36.6	4.8
	14	7.8	5.5	2.3	63.9	55.2	8.7
	30	0.1	0.05	0.05	54.2	47.5	8.7
	60	NA	NA	NA	26.0	19.8	6.2
	100	NA	NA	NA	1.5	0.4	1.1
[redacted]	0	100	NA	NA	NA	NA	NA
	0.042	86.6	86.6	NA	2.8	2.8	NA
	0.25	83.9	83.9	0.9	3.0	2.4	0.6
	1	64.5	62.3	1.2	9.9	8.5	1.4
	2	48.0	46.4	1.6	16.0	12.0	4.0
	7	11.9	10.9	0.8	39.9	30.0	9.9
	14	1.9	0.9	0.9	48.7	36.8	11.9
	30	0.1	0.05	0.05	49.9	34.9	15.0
	60	NA	NA	NA	42.9	31.2	11.7
	100	NA	NA	NA	35.4	25.7	9.7

NA: not available

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Propineb

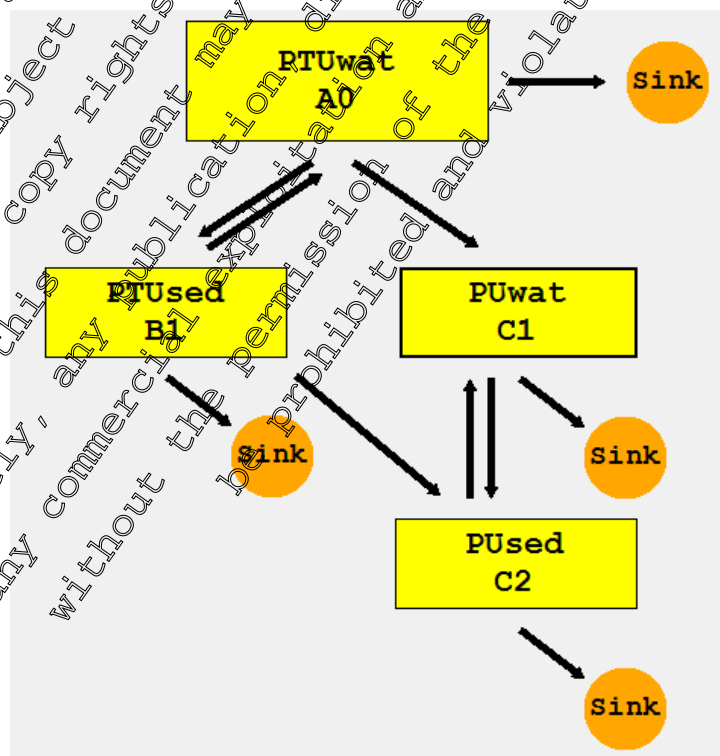
For level P-I and M-I evaluations a simple compartment model was setup in KinGUI2.1 to represent dissipation of the two compounds (level M-I) respectively of the parent (level P-I) in the total system (see figure below).

Figure 7.2.2.3 -1: Two compartment model to describe the total system degradation of PTU and the formation and degradation of PU in water sediment systems, in KinGUI2



For level P-II and level M-II evaluations a more complex compartment system was established to be able to describe the water and sediment phase separately (c.f. figure below). Level M-II evaluations were not performed.

Figure 7.2.2.3 -2: Multi-compartment model to describe the degradation of PTU and the formation and degradation of PU in separate phases, i.e. water and sediment, KinGUI2





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II. RESULTS

The level P-I evaluation for both systems revealed SFO as the model of choice to describe the residue data in the of PTU total system the best (c.f. Table 7.2.2.3- 16). For the system [redacted] the SFO fit clearly shows the best representation of the data and resulted in the lowest Chi² error percentage value. The corresponding rate constant is statistically well determined and yields a DT₅₀ value of 4.9 days. For the [redacted] system the visual assessment indicated a slightly better data representation by the FOMC than by the SFO fit. However, the differences were only marginal and, therefore, the SFO was selected also as the best fit.

Table 7.2.2.3- 16: Summary of the kinetic evaluation for degradation of propylene-thiourea in water sediment systems ([redacted] 1993)

System	Kinetic model ¹	Chi ² error-%	Model parameters ²	Visual assessment	DT ₅₀ [days]	Details, report section
[redacted]	SFO	5.93	k: 0.1414***	+	4.9	8.2.1.1
	FOMC	6.32	alpha: 1.0974# beta: 7.595#	o	4.9	8.2.1.2
[redacted]	SFO	5.41	k: 0.3807***	+	2.1	8.2.2.1
	FOMC	5.31	alpha: 4.74 beta: 1.067	o	2.0	8.2.2.2

¹ SFO: Single first order, FOMC: First order multi compartment
² k = degradation rate constant, alpha = FOMC parameter, beta = FOMC parameter
³ Visual assessment: + = good, o = moderate, - = poor
t-prop: ***<0.001, **<0.01, *0.05, #>0.05
bold letters indicate the model of choice

The level P-II evaluation for the system [redacted] resulted in visually acceptable fits of the two compartments. The transfer rates between water and sediment clearly point towards degradation in water being the dominant process as the back transfer rate from sediment to water is much higher than from water to sediment. Consequently the DT₅₀ value derived for the sediment compartment was >1000 days. Therefore, no further evaluation at level P-II was performed. The results at this stage would not differ from the default option derived from level P-I, i.e. use the total system DT₅₀ value for the water and a default of 1000 days in sediment. For the system [redacted] the visual assessment also revealed a very good representation of the data by the level P-II approach. In contrast to the [redacted] system, however, degradation in both compartments was derived. The results are presented in Table 7.2.2.3- 17, and the obtained rate constants correspond to DT₅₀ in water of 4.5 days and 1.3 days in sediment, respectively. This result was achieved because the fit yielded a zero back transfer rate from water to sediment. Compared to the level P-I results these results match very well and may therefore be used when separate DT₅₀ values are needed in exposure calculations.

Table 7.2.2.3- 17: Summary of the kinetic analysis for PTU degradation and the formation and degradation of PU from the data of ([redacted] 1993)

System	Chi ² error-% ¹	Model parameters ²	Visual assessment ³	Details, report section
[redacted]	PTU(wat):	0.1546***	+	8.3.1
	PTU(sed):	0.5188***	+	
	All:	5.62		

¹ values for PTU, PU and the whole model respectively
² k = degradation rate constant
³ Visual assessment: + = good, o = moderate, - = poor.
t-prop: ***<0.001, **<0.01, *<0.05, #>0.05



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At level M-I were total system residues of the parent degrade into total system residues of the metabolite the kinetic evaluation resulted in visually excellent to acceptable fits for both systems (c.f. 8.4.1 and 8.4.2 of report). Both fits indicate again the fast degradation of propylene-thiourea with DT₅₀ values of 5.6 and 3.7 days, respectively. The formation and degradation of the degradation product propylene-urea was well described which is also reflected in the excellent values for the Chi² error percentage considering it is a metabolite (Table 7.2.2.3- 18). The DT₅₀ values for the metabolite account for 27.6 and 147 days in the [redacted] and [redacted] system, respectively.

Table 7.2.2.3- 18: Summary of the kinetic analysis for PTU degradation and the formation and degradation of PU in water sediment systems

System	Chi ² error-% ²	Model parameters ³	Visual assessment ⁴	DT ₅₀ [days]	Details report section
[redacted]	PTUtot: 6.61	k (PTU): 0.1235*	+	5.6	
	PUtot: 14.6	k (PU): 0.0252**		27.6	8.4.1
	All: 9.9				
[redacted]	PTUtot: 13.0	k (PTU): 0.1868***	o	3.7	
	PUtot: 2.77	k (PU): 0.0047**		147	8.4.2
	All: 12.9				

¹ SFO: Single first order

² values for PTU, PU and the whole model respectively

³ k = degradation rate constant

⁴ Visual assessment: + = good, o = moderate, - = poor.

t-prop: ***<0.001, **<0.01, *0.05, >0.05

CA 7.2.2.4 Irradiated water sediment study

The degradation of Propineb under dark conditions is very fast (see section CA 7.2.2.3 before). Therefore, a comparatively low influence of sunlight is expected. No studies on that topic were part of the baseline dossier and no new studies are submitted within this Supplemental Dossier for the Propineb renewal of approval.

CA 7.2.3 Degradation in the saturated zone

The degradation in the saturated zone was not studied since Propineb is not expected to reach the saturated zone after its use according to good agricultural practices. No additional studies are submitted within Supplemental Dossier for the Propineb renewal of approval.

CA 7.3 Fate and behaviour in air

A possible entry into the air (i.e. the vapour pressure) of Propineb was evaluated during the Annex I inclusion (compare EU Monograph Annex B7), and was accepted by the European Commission (SANCO/7473/VI/97/2003). It was concluded that Propineb has a low vapour pressure, extrapolated with 1.6×10^{-4} Pa (at 20°C), indicating a low volatility of the active substance. Anyway, a vapour pressure cannot be specified for Propineb due to its polymer structure. The transition of Propineb into the gaseous state can occur only under decomposition. Therefore, it is highly probable that the before mentioned vapour pressure measured by the mean of the vapour pressure balance is that of the decomposition product PTU.

Henry's law constant of propineb was not to be calculated, because an exact determination of the water solubility is not possible. The vapour pressure for PTU is 6.46×10^{-5} Pa. The vapour pressure for PU is 5.41×10^{-4} Pa. These values indicate that the air affinity of propineb, PTU and PU is negligible.



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The chemical half life for PTU in air is 0.87 hours, and the chemical half life for PU is 11.2 hours, only.

According to these results, an accumulation or long-range transport of Propineb residues in the air and a subsequent contamination by wet or dry deposition are not to be expected.

CA 7.3.1 Route and rate of degradation in air

Route and rate of degradation of degradation of Propineb was evaluated during the Annex I inclusion (compare EU Monograph Annex B7), and was accepted by the European Commission (SANCO/7474/VI/97, 2003). The following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Report:	[redacted];1988;M-024586-01 *
Title:	Vapour pressure curve of Propineb
Report No:	PC 234
Document No:	M-024586-01-1
Guidelines:	US EPA OPPTS 830.2950; no deviation
GLP/GEP:	No

Report:	[redacted];2002;M-196620-01 *
Title:	Results from Vapour Pressure Measurements of Propineb Newly Interpreted
Report No:	REG02-0052
Document No:	M-196620-01-1
Guidelines:	US EPA OPPTS Guideline No. 830.2950; deviation not specified
GLP/GEP:	No, no

Report:	[redacted];1994;M-024996-01 *
Title:	Calculation of the Henry Law Constant of PTU
Report No:	PC 30
Document No:	M-024996-01-1, filed under KCM 2.2
Guidelines:	US EPA OPPTS N/A; deviation not specified
GLP/GEP:	No

Report:	[redacted];1994;M-102917-01 *
Title:	Calculation of the chemical lifetime of propyleneurea and 1,2-diaminopropane in the troposphere (degradates of propineb)
Report No:	PF 014
Document No:	M-102917-01-1
Guidelines:	/-, deviation not specified
GLP/GEP:	No

Report:	[redacted];2000;M-027851-01 *
Title:	Calculation of the chemical lifetime of propyleneurea in the troposphere
Report No:	M-010
Document No:	M-027851-01-1
Guidelines:	/-, deviation not specified
GLP/GEP:	No

*: that times all this information was filed in the pys.-chem section (at MCA 2.8), also. Today, the same is true for the 1st three studies on vapour pressure and Henry's Law Constant, but the last two studies (chemical lifetime of PTU and PU in air) not any longer belong to section MCA 2.8.



Summary of before mentioned studies

It was concluded that Propineb has a low vapour pressure, extrapolated with 1.6×10^{-4} Pa (at 20°C), indicating a low volatility of the active substance. Anyway, a vapour pressure cannot be specified for Propineb due to its polymer structure. The transition of Propineb into the gaseous state can occur only under decomposition. Therefore, it is highly probable that the before mentioned vapour pressure measured by the mean of the vapour pressure balance is that of the decomposition product PTU.

Henry's law constant of propineb was not to be calculated because an exact determination of the water solubility of Propineb is not possible. The vapour pressure for PTU is 6.46×10^{-4} Pa. The vapour pressure for PU is 5.41×10^{-4} Pa. These values indicate that the air affinity of propineb, PTU and PU is negligible.

The chemical half life for PTU in air is 0.87 hours, and the chemical half life for PU is 0.2 hours, only.

CA 7.3.2 Transport via air

According to the before mentioned properties of Propineb and its major degradates (see section [CA 7.3.1](#)), an accumulation or long-range transport of Propineb residues in the air and a subsequent contamination by wet or dry deposition are not to be expected. No new studies are submitted within Supplemental Dossier for the Propineb renewal of approval.

CA 7.3.3 Local and global effects

Local and global effects of Propineb are not to be considered since the half-life of its residues in air are ≤ 2 days (see section [CA 7.3.1](#)). No new studies are submitted within Supplemental Dossier for the Propineb renewal of approval.

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The proposed residue definitions relevant for exposure assessments, which can be used as basis for risk assessments in each compartment, are the following:

Compartment	Residue Definition
Soil	Propineb (LH 30 Z) 4-Methyl-imidazoline (BCS-AB78877) Propineb-DIDT (BCS-CU99534) PTU (BCS-AA66386) PU (BCS-AA17927)
Groundwater	Propineb (LH 30 Z) 4-Methyl-imidazoline (BCS-AB78877) Propineb-DIDT (BCS-CU99534) PTU (BCS-AA66386) PU (BCS-AA17927)
Surface water	Propineb (LH 30 Z) 4-Methyl-imidazoline (BCS-AB78877) Propineb-DIDT (BCS-CU99534) PTU (BCS-AA66386) PU (BCS-AA17927)



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Sediment	Propineb (LH 30 Z)
Air	Propineb (LH 30 Z)

CA 7.4.2 Definition of the residue for monitoring

For the compartments soil, groundwater, surface water, sediment and air the proposed residue definition for monitoring is Propineb (LH 30 Z).

CA 7.5 Monitoring data

According to the before mentioned properties of Propineb and its major degradates in soil, water and air (see sections [CA 7.1](#), [CA 7.2](#) and [CA 7.3](#)) monitoring data of Propineb were not regarded relevant for inclusion and evaluation in the Baseline Dossier.

No new studies were performed or were found in published literature with respect to monitoring of soil, surface water, ground/drinking water, sediment and air.

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