Document Title

Summary of the fate and behaviour in the environment for Methiocarb

Data Requirements

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

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

Date

2015-11-27, revised 2017-07-28

Author(s)

[redacted]

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Version history

Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2015-11-27	Original document	M-541464-01-1
2017-07-28	Added under CA 7.5 Information on effect of water treatment processes on nature of residues when surface water is abstracted for drinking water, response on RMS request to assess the effect of water treatment on the residue.	M-541464-02-1

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

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INTRODUCTION

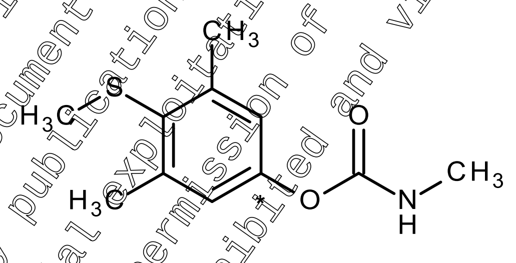
Methiocarb is an insecticide and repellent active substance and was included into Annex I of Directive 91/414 on 1st October 2007 (Directive 2007/5/EC).

This Supplementary Dossier contains only data which were not submitted at the time of the Annex I inclusion of methiocarb under Directive 91/414/EEC and which were therefore not evaluated during the first EU review. All data which were already submitted by Bayer for the Annex I inclusion under Directive 91/414/EEC are contained in the DAR, its Addenda and are included in the Baseline Dossier provided by Bayer. These data are only mentioned in the Supplementary Dossier for the sake of completeness and only general information (e.g. author, reference etc.) is available for these data. In order to facilitate discrimination between new data and data submitted during the Annex I inclusion process under Directive 91/414/EEC, the old data are written in grey typeface. For all new studies, detailed summaries are provided within this Supplementary Dossier.

CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

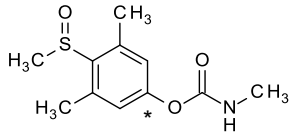
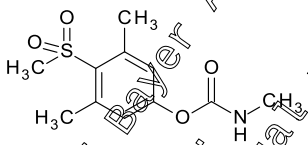
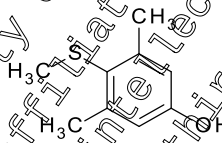
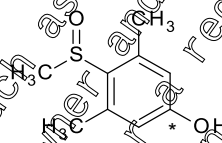
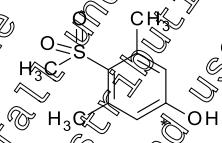
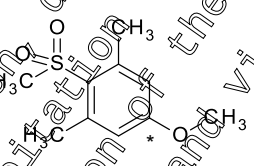
Data on the fate and behaviour of methiocarb in soil, water, sediment and air were submitted within the EU Dossier (Baseline Dossier). [redacted]ver, for a better understanding of the behaviour of methiocarb in soil, water and sediment and air, short summaries including the results of all environmental fate studies are given additionally in this summary in sections CA 7.1, CA 7.2 and CA 7.3.

The studies concerning the fate and behaviour of methiocarb in the environment were conducted using the [phenyl-1-^{14}C]-labelled methiocarb, as well as unlabelled methiocarb as test item. This radiolabel position is considered sufficient to define the route of degradation of methiocarb. The structure of methiocarb and the positions of the different radiolabels are depicted below.

Report Name (Codes and Synonyms)	**Chemical Structure**	**Radiolabel Positions**
methiocarb (H 321, BCS-AA44548, AE F082618, MTC mercaptodimethur, Mesurol)		*[phenyl-1-^{14}C]

The results of the studies are summarised in the sections 7.1 to 7.5. The proposed degradation pathways in soil, water and sediment are given in Figure 7.1.1-1 and Figure 7.2.2.4-1, respectively.

In addition, studies have been performed with the radiolabelled and unlabelled major degradation products. An overview is given in the table below.

Report Name[1] (Codes and Synonyms)	Chemical Structure	Radiolabel Positions
Methiocarb sulfoxide (M01) AE 1371422 MSO		*[phenyl-1-^{14}C]
Methiocarb sulfone (M02) AE C417187 MON		No radiolabel used
Methiocarb phenol (M03) AE C416779 MP		No radiolabel used[2]
Methiocarb sulfoxide phenol (M04) AE 1371423 MSOP		*[phenyl-1-^{14}C]
Methiocarb sulfone phenol (M05) AE 1371425 MSOOP		*[phenyl-1-^{14}C]
Methiocarb methoxy sulfone (M10) AE 1371424 MMS		*[phenyl-4-^{14}C]

1 for complete list of synonyms please see Doc N3: substances and metabolites
2 no further studies conducted

In original reports study authors may have used different names or codes for degradation products of methiocarb. 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 in Document N3 submitted with this dossier.

CA 7.1 Fate and behaviour in soil

CA 7.1.1 Route of degradation in soil

The route of degradation of methiocarb under aerobic conditions was studied in a number of soils at different temperatures and soil moistures, using [phenyl-1-^{14}C]-labelled methiocarb as test item. Methiocarb was stable to photolysis, while degradation was observed in microbial active soil.

CA 7.1.1.1 Aerobic degradation

The route of degradation of methiocarb in soil under aerobic conditions in the dark in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (Commission Directive 2007/5/EC). The following studies are included in the baseline dossier. No new studies have been conducted:

Report: KCA 7.1.1.1/01; [redacted]; 1989; M-004134-02-1
Title: Fate of methiocarb under aerobic and anaerobic soil conditions
Report No.: MR99206
Document No.: M-004134-02-1
Guideline(s): EPA Rep. 162-1 Aerobic Soil Metabolism; 162-2 Anaerobic Soil Metabolism
Guideline deviation(s): not specified
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Report: KCA 7.1.1.1/02; [redacted]; 2003; M-067648-01-2
Title: Analysis report - Accurate mass measurement of the major component in KTS 9424
Report No.: WEA03-031
Document No.: M-067648-01-2
Guideline(s): not applicable
Guideline deviation(s): not applicable
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Report: KCA 7.1.1.1/03; [redacted]; 2003; M-067503-01-1
Title: Answer to request for assessment of minor soil metabolite methiocarb sulfone quinone (M06) dated 18th August 2003
Report No.: MC04-004081
Document No.: M-067503-01-1
Guideline(s): not applicable
Guideline deviation(s): not applicable
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Analysis report [redacted].; 2003; M-067648-01-2 and Answer to request for assessment [redacted]; 2003; M-067503-01-1 reassign metabolite methiocarb sulfone quinone (M09) from [redacted].; 1989; M-004134-02-1 as as methiocarb methoxy sulfone (M10) based on the known metabolite methiocarb methoxy sulfone (M10) from the aerobic soil metabolism study [redacted]; 2002; M-053610-01-1 and analysis of the mass spectrum. In the below table summary Table 7.1.1.1/01-2 the metabolite is listed as methiocarb methoxy sulfone (M10) as already done the by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR, July 2005 (public version).

The aerobic soil degradation study [redacted].; 1989; M-004134-02-1 was evaluated and summarized by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR, July 2005 (public version). A copy of this summary is given below.

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb
Description:	Not stated
Lot/Batch:	Not stated
Specific Activity:	5.53 MBq/mg (33.5 mCi/mmol)
Radiochemical Purity:	98 %
Chemical Purity:	Not stated

2. Soil

The soil characteristics are summarized in Table 7.1.1.1/01-1

Table 7.1.1.1/01-1: Physico-chemical properties of test soil

Parameter		Soil
Geographic location - city - state - country		[redacted] Indiana USA
GPS Coordinates		no information available
Site description		no history of pesticide usage, after sampling the soil was planted with soybeans and maintained outdoors prior to use.
Soil taxonomic classification (USDA)		no information available
Soil series		no information available
Texture class (USDA)		sandy loam
Sand [%]	[50 µm – 2 mm]	65
Silt [%]	[2 µm – 50 µm]	25
Clay [%]	[< 2 µm]	10

pH (0.01 M $CaCl_2$)	6.7
Organic carbon [%] [1]	1.0
Organic matter [%][1]	1.9
Microbial biomass [mg microbial carbon/kg soil]	no information available
Cation Exchange Capacity [meq/100 g]	14
Moisture at 1/3 bar (pF 2.5) [%]	10.2
75 % at 1/3 bar Moisture [%]	7.6
Bulk density (disturbed) [g/cm³]	2.6

n.a. = not analyzed, n.d. = not detected
GPS: global positioning system
USDA: United States Department of Agriculture
[1] calculated as: OM [%] = OC [%] x 1.9

A study was conducted on one USA soil at 24°C in the dark for up to 217 days. Except for the study duration, it was carried out according to SETAC (1995), the USAEPA assessment guidelines (162-1, 1982), and in accordance with the principles of GLP. The study was carried out under aerobic and anaerobic conditions. The anaerobic phase of the study is reported under KCA 7.1.1.2/01.
The test was conducted in a sandy loam soil [redacted] (Indiana, USA) with [phenyl-1-^{14}C]methiocarb at an average concentration of 1.5 mg as/kg soil (dry weight). This was equivalent to a field application rate of 1.125 kg as/ha. The conversion was based on a soil depth of 5 cm. The soil moisture was maintained at 75 % of the water holding capacity at 1/3 bar.
The sandy loam used in this study was obtained from [redacted], Indiana and had no history of pesticide usage. In order to assure that the soil was biologically active, the soil was planted with soybeans and maintained outdoors prior to use. Immediately prior to use the soil was sieved through a 2 mm screen to remove rocks and debris.

The soil properties are given in Table 7.1.1.1/01-1.

^{14}C methiocarb (33.7 mCi/mmole; 6.78 mg; 1.02 mCi; radiochemical purity 98%) was diluted with ethanol. This solution was applied to 100 g (dry wt) of sandy loam. The methiocarb solution was applied dropwise to the surface of the soil in each flask. The actual concentration of methiocarb found in the soil at 0-time was 1.447 mg/kg (1.447 mg/kg dry soil).
The soil moisture was determined and aliquots of soil equivalent to 100g DM were weighed into flasks. Four Erlenmeyer flasks were attached to a glass and Teflon flow through apparatus. The flasks attached to the flow-through system were used to monitor volatile radioactive methiocarb metabolites and $^{14}CO_2$ evolved during the course of the study. The air was humidified with distilled water prior to passing the air over the soil samples. The air was then sequentially passed through ethylene glycol to trap volatile organic compounds and a solution of 1N potassium hydroxide to trap $^{14}CO_2$. . All soil samples were maintained at a constant temperature of 24 ± 2°C for 217 days. Samples were taken for analysis at nine intervals between day 0 and 217 post-treatment (at days 0, 1, 3, 7, 14, 29, 64, 91 and 217).
At each sampling interval, soil samples were extracted in a Soxhlet apparatus for 18 hours using 700 ml of chloroform/methanol (7:3) containing 0.1% acetic acid. The chloroform/methanol extracts were evaporated using acetonitrile to form an azeotrope with water. The dry residue was dissolved in methanol containing 0.1% acetic acid. The methanol solution was concentrated to a small volume using a stream of nitrogen. The methanol extract was centrifuged for 10 min prior to radioassay. Aliquots of this extract were subjected to reverse-phase HPLC and to TLC. At the completion of the aerobic metabolism study, soils from the flow-through system were extracted and radioassayed in order to obtain a mass balance.
The soil extracts were also subjected to HPLC analysis to show that the metabolic products were similar in both the soil samples attached to the flow-through system and the soil samples not attached to the flow-through system. The extracted soils were air dried at room temperature, weighed, and

radioassayed. An aliquot of the extracted soil from the 91-day interval was subjected to a 2-hour reflux with methanol. The soil/methanol mixture was centrifuged and the supernatant was radioassayed. The soil solids were subjected to a 2N hydrochloric acid (HCl) reflux for 2 hours. The hydrolyzate was allowed to cool to room temperature prior to being partitioned with acetone/chloroform (3:2). The acetone/chloroform solution was radioassayed and concentrated using a rotary vacuum evaporator (25°C); the concentrate was subjected to TLC analysis.
Metabolites were identified by TLC in comparison with authentic reference standards.
The results from the aerobic vessels are presented in Table 7.1.1.1/01-2.

Table 7.1.1.1/01-2: Recovery of radioactivity and distribution of the active substance and metabolites after application of [phenyl-1-^{14}C]methiocarb to sandy loam soil and aerobic incubation (values are given in % of the applied radioactivity, mean of two values)

Days after appl	Methio-carb	M01	M02	M03	M04	M05	M10 a)	Other	$^{14}CO_2$	Extrac-ted	Unex-tracted	Total
0	96	2	0	2	0	0	0	0	0	100	<1	100
1	91	7	0	0	<1	0	0	0	0	98	3	101
3	83	13	0	0	<1	0	0	0	1	96	3	100
7	70	21	0	0	3	0	0	0	0	94	6	100
14	48	28	0	0	8	0	0	0	4	84	12	100
29	24	30	1	0	10	3	0	1	5	75	20	100
64	8	13	1	0	18	7	2	1	16	50	34	100
91	6	8	1	0	15	9	3	1	17	44	39	100
217	3	2	0	0	7	7	8	1	30	27	43	100

a) M09 = methiocarb sulfone quinone reassigned [redacted], W.; 2003; M-067503-01-1) as M10 = methiocarb methoxy sulfone
M01 = methiocarb sulfoxide, M02 = methiocarb sulfone, M03 = methiocarb phenol, M04 = methiocarb sulfoxide phenol, M05 = methiocarb sulfone phenol

Report: KCA 7.1.1.1/04; [redacted].; 2002; M-053610-01-1
Title: Aerobic degradation and metabolism of methiocarb in soil
Report No.: MR-059/02
Document No.: M-053610-01-1
Guideline(s): EC: Commission Directive 95/36/EC amending Council Directive 91/414/EEC concerning the placing of plant protection products on the market, July 14, 1995; SETAC-Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995
Guideline deviation(s): none
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

The aerobic soil degradation study [redacted].; 2002; M-053610-01-1was evaluated and summarized by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR, July 2005 (public version). A copy of this summary is given below.

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb
Description:	Not stated
Lot/Batch:	11246/1
Specific Activity:	5.54 MBq/mg (149.6 µCi/mg)
Radiochemical Purity:	> 98 %
Chemical Purity:	> 98 %

2. Soil

The soil characteristics are summarised in Table 7.1.1.1/04-1

Table 7.1.1.1/04-1: Physico-chemical properties of test soil

Parameter	Results / Units			
Soil Designation	[redacted] AXXX	[redacted]	[redacted] a	Standard soil BBA 2.2
Geographic Location				
City	[redacted]	[redacted]	[redacted]	[redacted]
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	Rhineland Palatinate
Country	Germany	Germany	Germany	Germany
Soil Taxonomic Classification (USDA)	Sandy, mixed, mesic Typic Camhudolls	Not available	loamy, mixed, mesic Typic Argudalfs	Sandy, mixed, mesic Typic Psammaquoll
Soil Series	no information available			
Textural Class (USDA)	Sandy loam	Silt loam	Silt	Loamy sand
Sand [%] [50 µm – 2 mm]	72.4	22.9	8.5	80.5
Silt [%] [2 µm – 50 µm]	22.4	63.3	81.3	12.3
Clay [%] [< 2 µm]	5.0	13.8	10.2	7.2
pH				
- in $CaCl_2$	6.4	7.6	7.2	6.3
- in water	7.0	8.4	7.8	6.0
- in water (saturated paste)	n/a	n/a	n/a	n/a
- in KCl	n/a	n/a	n/a	n/a
Organic Carbon [%]	1.8	0.72	2.62	2.48
Organic Matter [%]	3.1	1.24	4.51	4.27
Cation Exchange Capacity [meq/100 g]	8	15	15	10
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil DW]	36.4	41.6	63.1	44.9
40 % of max. water holding capacity [g H_2O *ad* 100 g soil DW]	14.6	16.6	25.2	18.0
Bulk Density (disturbed) [g/cm^3]	2.5	2.66	2.09	2.45

Microbial Biomass [mg microbial carbon / kg soil DW] [2]				
DAT-0 (BIO-)	215	399	1123	333
DAT-120 (BIO- / BIO+)	156 / 144	311 / 335	733 / 771	223/ [illegible]

[1] calculated as: OM [%] = OC [%] · 1.724

[2] BIO- samples were left untreated, BIO+ samples were applied with application solution

DAT: days after treatment

DW: dry weight USDA: United States Department of Agriculture

An aerobic soil degradation study was conducted on four German soils according to SETAC guidelines (1995) and in accordance with the principles of GLP.

The route and rate of [phenyl-1-14C]-labelled methiocarb was investigated under aerobic conditions in the dark at 20°C. The soils used were a sandy loam ([redacted] AXXa), a silt loam soil ([redacted]), a silt soil ([redacted] am [redacted]) and a loamy sand (BBA 2.2). The soil characteristics are given in Table 7.1.1.1/04-1.

The soils were freshly sampled prior to commencement of the degradation study. Stones and plant parts were removed before the soils were gently air-dried and sieved to < 2 mm. The soil moisture, i.e. the percentage of water per 100 g dry matter (DM), measured at 105 °C was determined ([redacted] AXXa: approx. 8%, [redacted]: approx. 10%, [redacted] approx. 15%, Standard soil BBA 2.2: approx. 14%). After application (see Section 8.2.2) the soil moisture was adjusted to 40% of WHCmax (maximum water holding capacity) and closed with a trap attachment for absorption of volatile radioactivity (see Section 8.3.1). Determination of the microbial biomass of soils was performed at the beginning and end of the experiment.

Test soils were treated with [phenyl-14C] methiocarb at an average concentration of 0.13 mg a.s./ kg soil (dry weight). This was equivalent to a field application rate of 100 g a.s./ha. The conversion was based on a soil depth of 5 cm, and a soil density of 1.5 g/cm³. The soil moisture was maintained at 40 % of the soil's maximum water holding capacity. The Erlenmeyer flasks were closed with a trap attachment for the absorption of volatile compounds using soda lime and polyurethane foam. The soils were incubated in the dark under aerobic conditions at 20°C for 120 days. Samples were taken for analysis at day 0, 0.5, 1, 2, 7, 14, 45, 85 and 120 post-treatment.

Soil samples were extracted using methanol/water (8:2, v/v). Extraction was performed four times at room temperature and once under reflux conditions for one hour. The radioactivity was determined in all samples and the extracts were analysed by TLC methods. Radioactive zones on the TLC plates were measured using a Bio-Imaging Analyser. Metabolites were identified by NMR- and mass-spectroscopy (LC/MS/MS) and by comparison with authentic reference compounds. Volatile radioactivity was trapped using soda lime. $^{14}CO_2$ was identified by the reaction of carbon dioxide with phenylmagnesium bromide to form benzoic acid.

The results concerning the distribution of the active substance and the degradation products and recovery are summarised in Table 7.1.1.1/04-2:

Table 7.1.1.1/04-2: Recovery of radioactivity and distribution of the active substance and metabolites after application of [phenyl-1-^{14}C]methiocarb to four soils after aerobic incubation at 20 °C and TLC analysis (in % of the applied radioactivity).

Soil	DAT (d)	Methiocarb	M01	M02	M04	M05	M10	Others[1)]	$^{14}CO_2$	Extract-ed	Non extracted	Total
[redacted]	0	80.0	15.4	n.d.	<0.1	n.d.	n.d.	0.1	0.0	96.0	4.0	100.0
AXXa	0.25	72.8	20.6	n.d.	1.4	n.d.	n.d.	<0.1	0.1	95.0	4.9	99.9
	1	48.6	35.8	n.d.	6.6	n.d.	n.d.	<0.1	0.3	91.9	7.6	100.1
	3	17.7	48.2	n.d.	18.2	n.d.	n.d.	n.d.	1.0	86.5	13.3	101.1
	7	2.9	34.9	n.d.	30.5	1.5	n.d.	0.3	4.8	71.1	22.8	97.7
	17	1.6	14.1	0.3	25.1	8.0	n.d.	1.3	11.3	53.0	37.6	99.9
	45	n.d.	9.5	0.2	2.7	1.[illegible]	8.6	6.6	23.8	11.1	42.9	96.8
	60	n.d.	1.6	n.d.	3.2	[illegible]4	9.4	[illegible]	29.9	22.8	45.5	98.2
	120	n.d.	0.6	n.d.	0.9	1.5	2.7	0.1	35.3	6.1	40.4	76.8
[redacted]	0	77.4	17.1	n.d.	0.9	n.d.	n.d.	0.2	0.0	96.3	3.7	100.0
	0.25	68.8	17.7	n.d.	4.8	n.d.	n.d.	n.d.	0.0	91.5	5.5	97.0
	1	45.9	33.7	n.d.	13.1	n.d.	n.d.	n.d.	0.2	93.2	8.6	101.0
	3	14.5	32.2	n.d.	32.[illegible]	1.5	n.d.	n.d.	1.2	81.[illegible]	16.7	97.5
	7	0.8	13.8	n.d.	3[illegible]	4.[illegible]	n.d.	0.2	5.3	57.7	35.4	97.4
	17	n.d.	0.9	n.d.	4.0	2.[illegible]	5.[illegible]	n.d.	14.9	24.8	57.1	96.8
	45	n.d.	0.5	n.d.	0.7	0.4	1.5	1.4	30.5	7.7	53.[illegible]	95.8
	60	n.d.	0.3	n.d.	0.2	0.2	0.6	2.4	37.[illegible]	4.[illegible]	57.8	99.5
	120	n.d.	n.d.	n.d.	0.5	0.2	0.3	n.d.	38.6	4.0	49.9	92.6
[redacted]	0	80.0	15.2	n.d.	0.9	n.d.	n.d.	0.3	0.0	97.4	2.6	100.0
[redacted] 4a	0.25	59.[illegible]	28.3	n.d.	4.7	n.d.	n.d.	<0.1	0.1	92.[illegible]	4.3	97.0
	1	30.[illegible]	46.4	n.d.	11.[illegible]	n.d.	n.d.	0.4	0.[illegible]	92.2	7.3	95.9
	3	9.2	40.4	n.d.	20.5	1.[illegible]	n.d.	0.[illegible]	1.7	83.0	12.4	97.0
	7	4.3	27.2	1.9	21.9	10.8	n.d.	0.2	6.1	66.9	25.0	97.9
	17	n.d.	3.[illegible]	n.d.	7.5	11.[illegible]	9.8	1.1	19.[illegible]	33.8	41.8	95.4
	45	n.d.	1.3	n.d.	0.[illegible]	0.[illegible]	7.7	0.1	34.6	10.3	42.6	92.6
	60	n.d.	0.7	n.d.	0.8	1.[illegible]	4.4	0.[illegible]	50.2	7.7	42.4	100.2
	120	n.d.	0.3	n.d.	0.4	0.5	2.6	n.d.	23.5*	5.6	37.2	66.3*
BBA 2.2	0	8[illegible]9	1[illegible]	n.d.	<0.[illegible]	n.d.	n.d.	0.2	0.0	97.0	3.0	100.0
	0.25	[illegible].8	[illegible].3	n.d.	0.8	n.d.	n.d.	n.d.	0.1	95.2	3.6	98.9
	1	51.6	40.0	n.d.	[illegible].7	n.d.	n.d.	n.d.	0.3	97.2	4.5	102.0
	3	20.4	58.8	n.d.	12.3	n.d.	n.d.	n.d.	1.0	92.4	5.9	99.3
	7	[illegible].7	5[illegible]	1.[illegible]	2.[illegible]	0.2	n.d.	0.3	2.3	87.5	10.5	100.3
	17	n.d.	[illegible].8	[illegible]	[illegible].8	[illegible].8	7.[illegible]	2.0	14.8	62.8	21.1	98.6
	45	n.d.	1.6	<0.1	3.3	7.0	13.2	<0.1	39.0	28.5	31.5	99.1
	60	n.d.	0.[illegible]	n.d.	1.3	2.3	9.4	n.d.	49.1	16.5	30.3	96.0
	120	n.d.	0[illegible]	n.d.	0.[illegible]	0.[illegible]	5.3	n.d.	58.0	9.8	31.2	99.0

DAT = days after treatment, n.d. = not detected
1) all results of volatile organic compounds (other than CO_2) were < 0.1 %
* value not reliable due to loss during CO_2 liberation
M01 = methiocarb sulfoxide, M02 = methiocarb sulfone, M04 = methiocarb sulfoxide phenol, M05 = methiocarb sulfone phenol, M10 = methiocarb methoxysulfone

CA 7.1.1.2 Anaerobic degradation

The route of degradation of methiocarb in soil under anaerobic conditions in the dark in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (Commission Directive 2007/5/EC). The following study is included in the Baseline Dossier, no new studies have been conducted:

Report:	KCA 7.1.1.2/01; [redacted].; 1989; M-004134-02-1
Title:	Fate of methiocarb under aerobic and anaerobic soil conditions
Report No.:	MR99206
Document No.:	M-004134-02-1
Guideline(s):	EPA Ref.: 162-1 Aerobic Soil Metabolism; 162-2 Anaerobic Soil Metabolism
Guideline deviation(s):	not specified
GLP/GEP:	**no**

Previous evaluation: In DAR for original Annex I inclusion (2005)

The anaerobic soil degradation study [redacted]; 1989; M-004134-02-1 was evaluated and summarized by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR, July 2005 (public version). A copy of this summary is given below.

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb
Description:	Not stated
Lot/Batch:	Not stated
Specific Activity:	1.53 MBq/mg (53.7 mCi/mmol)
Radiochemical Purity:	98 %
Chemical Purity:	Not stated

2. Soil

The soil characteristics are summarized in Table 7.1.1.1/01-1.

A study was conducted on one USA soil at 24°C in the dark for up to 217 days. Except for the study duration, it was carried out according to SETAC (1995), the USA EPA assessment guidelines (152-1, 1982), and in accordance with the principles of GLP. The study was carried out under aerobic and anaerobic conditions. The aerobic phase of the study is reported under KCA 7.1.1.1/03. Except where stated below, the methodology was identical to the aerobic methodologies described earlier.
At approximately one half-life under aerobic soil conditions (14 days post-treatment), two of the four [^{14}C] methiocarb-treated soil samples attached to the flow-through apparatus were flooded with 100 ml of pH 5 high purity water and reattached to the flow-through system. These two samples were used to monitor volatile radioactive losses during anaerobic incubation. At the time of flooding, the flow-through apparatus was adapted to allow inert gas (nitrogen) to pass over the two soil samples. The exiting nitrogen was passed through ethylene glycol to trap volatile organic compounds and through a solution of 1 N KOH to trap $^{14}CO_2$. In addition, eight [^{14}C] methiocarb-treated soil samples were also flooded with 100 ml of high purity water (pH5), purged with nitrogen and fitted with ground glass stoppers. All soil samples were placed in a laboratory hood and maintained at a constant temperature of 24±2°C.

The extraction methods used were essentially the same as for the aerobic phase of the study reported under KCA 7.1.1.1/03. The results for the anaerobic vessels are presented in Table 7.1.1.2/01-1.

Table 7.1.1.2/01-1: Distribution of the active substance and degradation products after application of [phenyl-1-^{14}C]methiocarb to sand loam soil [redacted] and incubation at 24°C under anaerobic conditions
(values are given in % of the applied radioactivity, mean of two values)

Days after flooding	Methiocarb	M01	M02	M03	M04	M05	$^{14}CO_2$	Extracted	Unextracted	Total
0	55	24	0	0	8	0	0	87	6	93
15	43	3	0	31	5	<1	<1	82	10	92
29	37	2	0	37	3	<1	2	80	10	90
64	27	1	<1	47	1	<1	4	76	12	92

M01 = methiocarb sulfoxide, M02 = methiocarb sulfone, M03 = methiocarb phenol, M04 = methiocarb sulfoxide phenol, M05 = methiocarb sulfone phenol

CA 7.1.1.3 Soil photolysis

The route of degradation of methiocarb in soil under photolytic conditions was evaluated during the Annex I Inclusion and was accepted by the European Commission (Commission Directive 2007/5/EC). The following studies are included in the Baseline Dossier:

Report: KCA 7.1.1.3/01 [redacted] 1988; M-004122-01-1
Title: Soil surface photolysis of [14C]Mesurol in natural sunlight
Report No.: M5991
Document No.: M-004122-01-1
Guideline(s): 162-3 Photodegradation on Soil; U.S. Environmental Protection Agency Guidelines (Subdivision N; 161-3)
Guideline deviation(s): --
GLP/GEP: no

Previous evaluation: In DAR for original Annex I inclusion (2005).

The photolysis on soil study [redacted]; 1988; M-004122-01-1 was evaluated and summarized by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR July 2005 (public version). A copy of this summary is given below.

MATERIALS

1. Test Item

Test Item: [phenyl-1-^{14}C]methiocarb
Description: Not stated
Lot/Batch: Not stated
Specific Activity: 33 µCi/mmole
Radiochemical Purity: >99.4 %
Chemical Purity: Not stated

2. Soil

Table 7.1.1.3/01-1: Physico-chemical properties of test soil

Parameter	Soil
Geographic location - city - state - country	[redacted] USA
Soil taxonomic classification (USDA)	-
Soil series	-
Texture class (USDA) Sand [%] [50 µm – 2 mm] Silt [%] [2 µm – 50 µm] Clay [%] [< 2 µm]	sandy loam 48.02 49.65 2.33
pH	6
Organic carbon [%] [1]	0.76
Organic matter [%]	1.45
Cation Exchange Capacity [meq/100g]	10
Moisture at 1/3 bar (pF 2.0) [%]	10.8
75 % at 1/3 bar Moisture [%]	
Bulk density (disturbed) [g/cm³]	2.53

USDA: United States Department of Agriculture
[1] calculated as: OM [%] = OC [%] x 1.9

The photodegradation of [phenyl-1- ^{14}C]methiocarb (radiochemical purity 99.4%) under natural sunlight was investigated on a sandy loam soil ([redacted]) according to EPA (161-3, 1982) and SETAC (1995) guidelines, and in accordance with the principles of GLP. The soil properties are summarised in Table 7.1.1.3/01-1.

Soil was initially air-dried, passed through a 2 mm sieve, then autoclaved. Individual slurries were prepared for each test plate and soil plates were air-dried leaving a uniform layer of soil approximately 0.5 mm in thickness. Test material was prepared in ethyl acetate such that each plate was dosed with 9.32 x 10^6 dpm (28.2 µg) at 19.1 ppm. The soil thin layers were exposed to natural sunlight in a controlled chamber in Kentucky, USA (latitude 38.0°N). Dark controls were incubated in parallel. Air was drawn through the chamber to collect volatiles. Duplicate samples as well as dark controls were taken for analysis at 0, 5, 10, 15, 20 and 30 days post-treatment.
Soils were extracted with chloroform/methanol (1:1 v/v). The radioactivity was determined in all samples and the extracts analysed by HPLC and TLC-methods. Metabolites were identified or characterised by comparison with authentic reference compounds.

The results are presented in Table 7.1.1.3/01-2.

Table 7.1.1.3/01-2: Recovery of radioactivity and distribution of the active substance and metabolites after application of [phenyl-1-^{14}C]methiocarb to thin soil layers of a sandy loam soil under natural sunlight conditions and in the dark (in % of the applied radioactivity, mean of n = 2).

Sampling	Methiocarb	M01	M04	Unknown	Unextracted	Total
Day 0	87.9	n.d.	n.d.	n.d.	0.9	88.9
dark control	96.8	n.d.	n.d.	1.3	1.2	99.3
Day 5	79.5	13.7	n.d.	0.4	4.2	97.7
dark control	91.2	0.9	n.d.	3.2	1.5	96.8
Day 10	74.2	15.2	1.6	0.8	9.9	101.7
dark control	89.7	3.4	0.5	0.7	4.1	98.4
Day 15	64.3	42.8	n.d.	1.5	10.9	0.6
dark control	88.0	4.5	n.d.	0.9	7.4	100.8
Day 20	61.3	23.8	0.5	0.8	16.4	102.8
dark control	92.1	3.4	n.d.	n.d.	8.0	103.8
Day 30	47.3	23.1	3.1	0.0	19.4	93.5
dark control	75.2	3.1	n.d.	1.0	8.0	87.2

Sandy loam soil: 48.02 % sand, 49.65 % silt, 2.33 % clay, organic carbon 0.76, pH: 6.6
n.d. = not detected
M01 = methiocarb sulfoxide; M04 = methiocarb sulfoxide phenol

Report: KCA 7.1.1.3/02; S[redacted]; 2002; M-041883-01-1
Title: [Methiocarb]: Photolysis of methiocarb on soil surface
Report No.: MR-693/01
Document No.: M-041883-01-1
Guideline(s): EC: Official Journal of the European Communities, No L 175 (EN), July 22, 95. Commission Directive 95/36/EC, amending Council Directive 91/414/EEC concerning the placing of plant protection products on the market: Annex II, Fate and Behaviour in the Environment, 7.1.1/VI/94-EN, 7.1.1.1.2 Soil Photolysis; SETAC-Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995, Section 1.2 (Soil Photolysis); (U.S.) Environmental Protection Agency Pesticide Assessment Guidelines Subdivision N, Chemistry: Environmental Fate § 161-3 Photodegradation Studies on Soil
Guideline deviation(s): none
GLP/GEP: yes

Previous evaluation: In DAR for original Annex I inclusion (2005).

The photolysis on soil S[redacted] 2002; M-041883-01-1was evaluated and summarized by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR, July 2005 (public version). A copy of this summary is given below.

MATERIALS

1. Test Item

Test Item [phenyl-1-^{14}C]methiocarb
Description: Not stated
Lot/Batch: 13824/1
Specific Activity: 3.73 MBq/mg (100.9 µCi/mg)
Radiochemical Purity: > 99 %
Chemical Purity: Not stated

2. Soil

Table 7.1.1.3/02-1: Physico-chemical properties of test soil

Parameter	Soil
Geographic location - city - state - country	[redacted] Indiana USA
Soil taxonomic classification (USDA)	Typic Argiudolls
Soil series	Shinshe sandy loam
Texture class (USDA) Sand [%] [50 µm – 2 mm] Silt [%] [2 µm – 50 µm] Clay [%] [< 2 µm]	sandy loam 25.7 26.4 7
pH	
- in $CaCl_2$	6.7
- in water	6.7
- in KCl	7
Organic carbon [%] [1]	1.12
Organic matter [%][1]	1.93
Microbial biomass (0 day) [mg microbial carbon/kg soil]	266/287 [2)]
Cation Exchange Capacity [meq/100 g]	10
Moisture at 1/3 bar (pF 2.5) [%]	14.4
75 % at 1/3 bar Moisture [%]	
Bulk density (disturbed) [g/cm³]	1.53

n.a. = not analyzed, n.d. = not detected
GPS: global positioning system
USDA: United States Department of Agriculture
[1] calculated as: OM [%] = OC [%] x 1.72
[2] BIO-A/B

The photodegradation of [phenyl-^{14}C]-methiocarb (radiochemical purity > 99%) was investigated on a sandy loam soil [redacted] at 20°C according to EPA (161-3, 1982) and SETAC (1995) guidelines, and in accordance with the principles of GLP. The soil properties are summarised in Table 7.1.1.3/02-1.

The soil was collected from the field, shipped to Germany and stored under vegetation in a greenhouse in a large container (about 1 m²). An aliquot of about 500 g was sampled and stones and plant parts were removed before the soil was gently air-dried and screened to < 2mm. The soil moisture was determined and aliquots of soil equivalent to 30 g DM were weighed into the test vessels and adjusted to a moisture level corresponding to 75% of the 1/3 bar MWHC with demineralised water. The dose rate was 2.59 µg/g soil (dry substance) corresponding to approximately 120 g as/ha (calculated for a soil density of 1.53 g/cm³ and 1 cm depth).
^{14}C-methiocarb was applied to the surface of the soil by dosing aliquots of 200 µl of application solution as small droplets using a pipette. All the vessels (except the day 0 samples) were then closed and fitted with trap attachments for volatiles.
The soil thin layers were continuously irradiated with a Xenon lamp simulating the natural sunlight (Suntest). The spectrum was cut off at wavelengths below 290 nm and the light intensity was 1839 mW/m². The temperature of the test system was maintained at 20°C ± 2°C. Duplicate samples were taken for analysis 0, 0.25, 1, 2, 5, 7 and 9 days post-treatment. Dark control samples (single samples)

were taken at same sampling dates. Irradiation corresponded to 46.1 environmental solar days at an intensity similar to the conditions in [redacted], AZ, USA (latitude 33.3°N).

The soil was extracted with acetonitrile:water immediately after sampling.
Any volatile organic compounds in the polyurethane plugs were extracted with ethylacetate and radioassayed by LSC. The $^{14}CO_2$ absorbed by the soda lime was quantified by LSC. The portion of non-extracted radioactivity was determined by combustion LSC.

The extracts were analysed by Reverse and Normal Phase TLC to determine the concentration of the test substance and the degradation products.
The total recovered radioactivity ranged from 97.2 to 103.8 % of the amount applied in the irradiated samples, and from 98.0 to 106.0 % in the dark controls. The results are presented in Table 7.1.1.3/02-2.

Table 7.1.1.3/02-2: Recovery of radioactivity and distribution of the active substance and metabolites after application of [phenyl-1-^{14}C]methiocarb to thin soil layers of sandy loam under artificial light conditions and in the dark (in % of the applied radioactivity)

Conditions	Exposure time [days]	methiocarb	M01	M02	M03	M04	M10	Others	CO_2	Extracted	Non-extracted	Total
Irradiated	0	98.5	3.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	102.1	0	102.2
	0.25	a)	a)	a)	a)	a)	a)	a)	2.8	89.4	8.9	101.2
	1	34.2	4.2	1.4	0.6	6.6	n.d.	n.d.	0.4	100.2	3.3	103.8
	2	18.3	51.4	2.6	1.2	17.5	n.d.	2.4	1.3	95.1	5.5	102.5
	5	15.8	31.0	3.1	1.5	26.1	0.5	3.3	4.8	83.8	8.8	97.6
	7	16.9	27.9	2.2	1.4	28.8	0.9	2.6	8.0	88.8	11.0	100.8
	9	12.0	28.9	2.4	1.3	20.4	n.d.	2.8	7.6	84.0	12.6	97.2
Dark control	0.25	97.8	5.5	n.d.	n.d.	0.6	n.d.	n.d.	<0.1	105.4	0.5	106.0
	1	93.2	9.4	n.d.	n.d.	0.6	n.d.	n.d.	<0.1	103.8	1.0	104.8
	2	84.1	13.9	n.d.	n.d.	1.2	n.d.	n.d.	<0.1	101.0	1.9	102.9
	5	76.6	18.3	n.d.	n.d.	1.7	n.d.	n.d.	<0.1	99.2	2.3	101.5
	7	74.2	21.3	n.d.	n.d.	2.8	n.d.	n.d.	<0.1	99.1	2.4	101.7
	9	68.6	20.4	n.d.	n.d.	3.8	n.d.	n.d.	<0.1	94.8	3.2	98.0

a) values for that sampling date are not reported due to the extracts being allowed to stand overnight at 8°C
n.d. = not detected
M01 = methiocarb sulfoxide, M02 = methiocarb sulfone, M03 = methiocarb phenol
M04 = methiocarb sulfoxide phenol, M10 = methiocarb methoxy sulfone

Summary of CA 7.1.1 Rout of degradation

Based on the results of the laboratory degradation studies investigating methiocarb it was clearly demonstrated that methiocarb is rapidly degraded in soil and thoroughly metabolised to the final degradation product carbon dioxide. Major metabolites involved in the degradation are methiocarb sulfoxide (M01), methiocarb sulfoxide phenol (M04), methiocarb sulfone phenol (M05) and methiocarb methoxy sulfone (M10).

The degradation pathway of methiocarb in the soil is shown in Figure 7.1.1-1. A summary of maximum occurrences in soil of major degradation products derived from laboratory studies is shown in Table 7.1.1- 1.

Figure 7.1.1-1 Proposed degradation pathway of methiocarb in soil

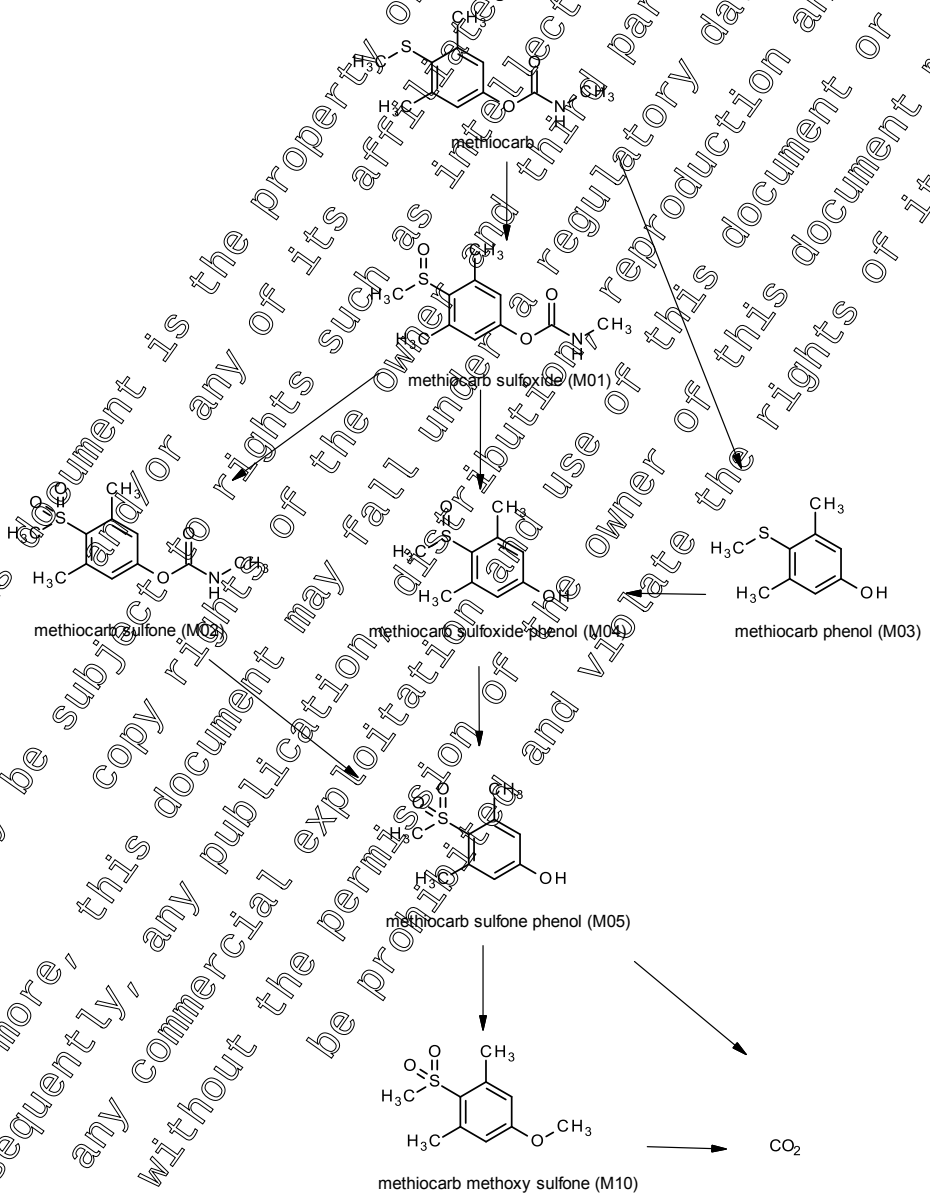


Table 7.1.1- 1: Summary of maximum occurrences in soil of major methiocarb degradation products derived from laboratory studies (in percentage of applied radioactivity [% AR])

Degradation Product	Aerobic Soil [% AR]	Anaerobic Soil [% AR]	Soil photolysis [% AR]
methiocarb sulfoxide (M01)	58.8	24[1)]	57.2
methiocarb phenol (M03)	-	47.0	-
methiocarb sulfoxide phenol (M04)	35.8	-	28.8
methiocarb sulfone phenol (M05)	19.8	-	-
methiocarb methoxy sulfone (M10)	13.2	-	-

[1)]Considered to be residual from aerobic phase of study

CA 7.1.2 Rate of degradation in soil

Methiocarb was rapidly degraded in soil under aerobic and anaerobic conditions. The kinetic models and DT_{50} values in soil of methiocarb and its major degradation products used for modelling purpose and trigger evaluation (best-fit) as well as the formation fractions in soil for major degradation products are summarized in sections CA 7.1.2.1.1 and CA 7.1.2.1.2.

CA 7.1.2.1 Laboratory studies

CA 7.1.2.1.1 Aerobic degradation of the active substance

Report: KCA 7.1.2.1.1/01; [redacted], P. L., 1989; M-004134-02-1
Title: Fate of methiocarb under aerobic and anaerobic soil conditions
Report No.: MR99206
Document No.: M-004134-02-1
Guideline(s): EPA Ref.: 162-1 Aerobic Soil Metabolism; 162-2 Anaerobic Soil Metabolism
Guideline deviation(s): not specified
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Executive Summary: Report also under KCA 7.1.1.1 /01; DT_{50} and DT_{90} values were subsequently determined according to FOCUS kinetic and are provided in KCA 7.1.2.1.1 /03.

Report: KCA 7.1.2.1.1/02; B[redacted].; 2002; M-053610-01-1
Title: Aerobic degradation and metabolism of methiocarb in soil
Report No.: MR-05/02
Document No.: M-053610-01-1
Guideline(s): EC Commission Directive 95/36/EC amending Council Directive 91/414/EEC concerning the placing of plant protection products on the market, July 14, 1995; SETAC Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995
Guideline deviation(s): none
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Report also under KCA 7.1.1.1 /04. DT_{50} and DT_{90} values were subsequently determined according to FOCUS kinetic and are provided in [redacted].; 2015; M-535501-01-1.

Report:	KCA 7.1.2.1.1/03; [redacted].; 2015; M-535501-01-1
Title:	Methiocarb (MTC) and its metabolites - Kinetic Evaluation of Aerobic Metabolism in Soil According to FOCUS Kinetics
Report No.:	EnSa-14-1290
Document No.:	M-535501-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

Previous evaluation: No previous evaluation, submitted for the purpose of active substance renewal.

Executive Summary

The modelling and trigger endpoint DT50 values and formation fractions for methiocarb and its metabolites are summarized in Table 7.1.2.1.1/03-1 and Table 7.1.2.1.1/03-2.
Methods are described in this section as well as results for methiocarb, for the results on metabolites see CA 7.1.2.1.2.

Table 7.1.2.1.1/03-1: Degradation parameters of methiocarb and its metabolites (modelling endpoints) including normalisation. The abbreviation ff denotes formation fraction, and FC is field capacity

Compound	n	$DT50_{SFO}$ [1] [days]	$DT50_{SFO}$ (100% FC, 20°C) [1] [days]	ff [2] [-]
Methiocarb (MTC)	5	2.1	1.8	
Methiocarb sulfoxide (MSO, M01)	5	6.0	5.1	1.000 $_{MTC \rightarrow MSO}$
Methiocarb sulfoxide phenol (MSOP, M04)	4	6.8	5.9	1.000 $_{MSO \rightarrow MSOP}$
Methiocarb sulfone phenol (MSOOP, M05)	3	11.2	9.9	0.491 $_{MSOP \rightarrow MSOOP}$
Methiocarb methoxy sulfone (MMS, M10)	3	31.1	27.6	1.000 $_{MSOOP \rightarrow MMS}$

[1] geometric mean of n values
[2] arithmetic mean of n values

Table 7.1.2.1.1/03-2: Degradation parameters of methiocarb and its metabolites (trigger endpoints)

Compound	n	DT50 [1] [days]	DT90 [1] [days]
Methiocarb (MTC)	5	13.7	55.8
Methiocarb sulfoxide (MSO, M01)	5	15.3	56.2
Methiocarb sulfoxide phenol (MSOP, M04)	4	16.7	55.6
Methiocarb sulfone phenol (MSOOP, M05)	3	22.7	75.4
Methiocarb methoxy sulfone (MMS, M10)	3	49.8	165.5

[1] maximum of n values

MATERIAL AND METHODS

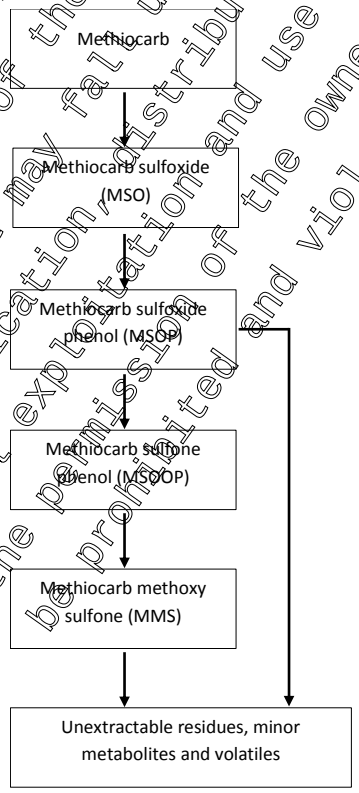
The aerobic degradation of methiocarb and its soil metabolites methiocarb sulfoxide (MSO, M01), methiocarb sulfoxide phenol (MSOP, M04), methiocarb sulfone phenol (MSOOP, M05) and methiocarb methoxy sulfone (MMS, M10) was kinetically evaluated based on the laboratory studies of [redacted] B.; 2002; M-053610-01-1 on the soils BBA 2.2, [redacted], [redacted] and [redacted] from Germany and [redacted] L.; 1989; M-004134-02-1 on the soil [redacted] from the US.

The kinetic evaluation was performed following the recommendation of FOCUS (2006) and FOCUS (2014a) to derive DT50 values for modelling purposes and trigger endpoints. The model fits and the statistical evaluation of the results was carried out with the software KinGUI version 2.1.

For the kinetic evaluation of the data a compartment model was developed based on the proposed metabolic pathway shown in Figure 7.1.1-1including the metabolites metabolites methiocarb sulfoxide (MSO, M01), methiocarb sulfoxide phenol (MSOP, M04), methiocarb sulfone phenol (MSOOP, M05) and methiocarb methoxy sulfone (MMS, M10).
Four different kinetic models were employed: single first-order (SFO), first-order multiple-compartment (FOMC, Gustafson-Holden), the hockey-stick model (HS, DFOS = double first order sequential), and the bi-exponential model (DFOP = double first order parallel). The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment, goodness of the fit (chi^2 square (χ^2) criterion, and significance of parameters (t-probability).

The aerobic soil metabolism of methiocarb can be characterized by the proposed metabolic pathway shown in Figure 7.1.2.1.1-1.

Figure 7.1.2.1.1-1 Metabolic pathway of methiocarb



Modelling endpoints: Pathway fits including parent and metabolites were considered for the derivation of modelling endpoints for parent and metabolites.

Values were normalized to the soil moisture corresponding to estimated field capacity (FC) and a temperature (T_{ref}) of 20 °C and Q_{10} = 2.58. The DT_{50} values were calculated from the resulting kinetic parameters.

Trigger endpoints:
For the parent substance methiocarb, trigger (persistence) endpoints were derived from the parent only fits considering SFO, FOMC, and DFOP. For the metabolites, trigger (persistence) endpoints were derived from pathway fits where possible or from decline fits in some cases. For this purpose the model selected from the parent only fits was used.

RESULTS

Modelling endpoints: As appropriate kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted] and [redacted] and first-order multiple-compartment (FOMC) for the soils [redacted] and [redacted] with results summarized in Table 7.1.2.1.1/03-3.

For use as modelling endpoint, the overall geometric mean of normalized half-lives of methiocarb was calculated to 1.8 days.

Table 7.1.2.1.1/03-3: Rate of degradation in soil (aerobic) laboratory studies for methiocarb (modelling endpoints) including normalisation.

methiocarb	**Dark aerobic conditions**						
Soil type	Label	pH[a)]	t, °C / % MWHC[c)]	DT_{50} / DT_{90}	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand[e)] (BBA 2.2)	phenyl	6.3	20 / 40	1.2 / 3.8	1.2	8.6	SFO
Silt loam[e)] ([redacted])	phenyl	7.6	20 / 40	1.0 / 3.4	0.7	10.8	SFO
Silt[e)] ([redacted])	phenyl	7.3	20 / 40	0.6 / 4.3	1.2[d)]	11.7	FOMC
Sandy loam[e)] ([redacted])	phenyl	6.4	20 / 40	1.1 / 3.8	1.0	9.8	SFO
Sandy loam[f)] ([redacted])	phenyl	6.7	24 / 75	16.5 / 76.6	17.7[d)]	6.4	FOMC
Geometric mean (if not pH dependent)					1.8		
pH dependence					No		

a) Measured in calcium chloride solution
b) Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
c) % of soil water content at pF=2.5 or 33 kPa matric potential
d) calculated as DT90/3.32
e) [redacted], 2002; M-053610-01-1
f) [redacted], 1989; M-004134-02-1

Trigger endpoints: Non-normalized values of the DT_{50} and the DT_{90} were derived from best fits kinetics which was DFOP in 4 soils and FOMC in one soil with results summarized in Table 7.1.2.1.1/03-4.
From tests at 20 to 24°C, non-normalized half-lives of methiocarb ranged from 0.4 days for silt soil ([redacted]) to 13.7 days for sandy loam soil ([redacted]) while values for the DT_{90} ranged from 3.1 days for silt soil ([redacted]) to 55.8 days for silt loam soil ([redacted]).

Table 7.1.2.1.1/03-4: Rate of degradation in soil (aerobic) laboratory studies for methiocarb (trigger endpoints)

methiocarb	**Dark aerobic conditions**						
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50} /DT_{90}	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand [e)] (BBA 2.2)	phenyl	6.3	20 / 40	1.1 / 4.7		1.3	DFOP
Silt loam [e)] ([redacted])	phenyl	7.6	20 / 40	0.8 / 3.7		1.1	DFOP
Silt [e)] ([redacted])	phenyl	7.2	20 / 40	0.4 / 3.1		4.6	FOMC
Sandy loam [e)] ([redacted])	phenyl	6.4	20 / 40	0.9 / 4.2		7	DFOP
Sandy loam [f)] ([redacted])	phenyl	6.7	24 / 75[c)]	13.7 / 55.8		2.2	DFOP
Geometric mean (if not pH dependent)							
pH dependence					No		

[a)] Measured in calcium chloride solution
[b)] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[c)] % of soil water content at pF=2.5 or 33 kPa matric potential
[d)] calculated as DT90/3.32
[e)] [redacted], B.; 2002; M-053610-01-1
[f)] [redacted], L.; 1989; M-004134-02-1

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

Report: KCA 7.1.2.1.2/01; [redacted]; 2002; M-038454-02-1
Title: Calculation of DT50 values in soil of methiocarb metabolites
Report No.: MR-038/02
Document No.: M-038454-02-1
Guideline(s): --
Guideline deviation(s): --
GLP/GEP: no

Previous evaluation: In DAR for original Annex I inclusion (2005).

[redacted]

Report: KCA 7.1.2.1.2/02; [redacted]; 2015; M-535501-01-1
Title: Methiocarb (MTC) and its metabolites - Kinetic Evaluation of Aerobic Metabolism in Soil According to FOCUS Kinetics
Report No.: EnSa-14-1290
Document No.: M-535501-01-1
Guideline(s): not applicable
Guideline deviation(s): not applicable
GLP/GEP: no

For method description see KCA 7.1.2.1.1/03.

RESULTS

methiocarb sulfoxide (M01)

Modelling endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], [redacted], and [redacted] and first-order multiple-compartment (FOMC) for the soil [redacted] with results summarized in Table 7.1.2.1.2/02-1.

For use as modelling endpoint, the overall geometric mean of normalized half-lives of methiocarb sulfoxide (M01) was calculated to 5.1 days and an arithmetic mean of 1.0 for the formation fraction derived from methiocarb.

Table 7.1.2.1.2/02-1: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfoxide (M01) (modelling endpoints) including normalisation.

methiocarb sulfoxide (M01)	Dark aerobic conditions The precursor from which the f.f. was derived was methiocarb							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50} - DT_{90} / k_{deg}	f. f. k_f	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ²)	Method of calculation
Loamy sand [e)] (BBA 2.2)	phenyl	6.3	20 / 40	6.3 - 21.0	1.0	6.3	13.2	SFO
Silt loam [e)] ([redacted])	phenyl	7.6	20 / 40	1.6 - 5.3	1.0	1.2	15.6	SFO
Silt [e)] ([redacted])	phenyl	7.2	20 / 40	3.3 - 10.8	1.0	3.1	9.0	SFO
Sandy loam [e)] ([redacted])	phenyl	6.4	20 / 40	8.1 - 49.4	1.0	12.4[d)]	10.2	FOMC
Sandy loam [f)] ([redacted])	phenyl	6.1	24 / 75[c)]	15.3 - 50.9	1.0	11.8	8.1	SFO
Geometric mean (if not pH dependent)						5.1		
Arithmetic mean					1.0			
pH dependence						No		

a) Measured in calcium chloride solution
b) Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
c) % of soil water content at pF=2.5 or 33 kPa matric potential
d) calculated as DT90/3.32
e) [redacted] B.; 2002; M-053610-01-1
f) [redacted] P. L.; 1989; M-004134-02-1

Trigger endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], and [redacted] and double first order parallel (DFOP) for the soil [redacted] with results summarized in Table 7.1.2.1.2/02-2.

Table 7.1.2.1.2/02-2: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfoxide (M01) (trigger endpoints)

methiocarb sulfoxide (M01)	Dark aerobic conditions							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/ DT_{90}	f. f. k_f / k_{dp}	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand [e)] (BBA 2.2)	phenyl	6.3	20 / 40	6.2 / 20.6			11.6	SFO
Silt loam [e)] ([redacted])	phenyl	7.6	20 / 40	1.6 / 5.3			15.6	SFO
Silt [e)] ([redacted])	phenyl	7.2	20 / 40	3.3 / 10.8			9.0	SFO
Sandy loam [e)] ([redacted])	phenyl	6.4	20 / 40	7.7 / 56.2			9.9	DFOP
Sandy loam [f)] ([redacted])	phenyl	6.7	24 / 75[c)]	15.3 / 51.0			8.1	SFO
Geometric mean (if not pH dependent)								
Arithmetic mean								
pH dependence						No		

[a)] Measured in calcium chloride solution
[b)] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[c)] % of soil water content at pF=2.5 or 33 kPa matric potential
[d)] calculated as DT90/3.32
[e)] [redacted]; 2002; M-053610-01-1
[f)] [redacted] L.; 1989; M-004134-02-1

methiocarb sulfoxide phenol (M04)

Modelling endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], [redacted], and [redacted] with results summarized in Table 7.1.2.1.2/02-3.
For use as modelling endpoint, the overall geometric mean of normalized half-lives of methiocarb sulfoxide phenol (M04) was calculated to 5.9 days and an arithmetic mean of 1.0 for the formation fraction derived from methiocarb sulfoxide (M01).

Table 7.1.2.1.2/02-3: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfoxide phenol (M04) (modelling endpoints) including normalisation

methiocarb sulfoxide phenol (M04)	**Dark aerobic conditions** **The precursor from which the f.f. was derived was methiocarb sulfoxide**							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/ DT_{90} k_{om} k_p	f.f. k_f	DT_{50} 20 °C, pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand [c)] (BBA 2.2)	phenyl	6.3	20 / 40	16.6 / 55.2	1.0	16.6	10.3	SFO
Silt loam [c)] ([redacted])	phenyl	7.6	20 / 40	3.4 / 11.3	1.0	2.5	14.5	SFO
Silt [c)] ([redacted])	phenyl	7.2	20 / 40	2.2 / 7.5	1.0	2.1	19.5	SFO
Sandy loam [c)] ([redacted])	phenyl	6.4	20 / 40	16.7 / 55.6	1.0	13.9	17.3	SFO
Geometric mean (if not pH dependent)						5.9		
Arithmetic mean					1.0			
pH dependence						No		

[a)] Measured in calcium chloride solution
[b)] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[c)] [redacted].; 2002; M-053610-01-1

Trigger endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], [redacted] and [redacted] with results summarized in Table 7.1.2.1.2/02-4.

Table 7.1.2.1.2/02-4: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfoxide phenol (M04) (trigger endpoints)

methiocarb sulfoxide phenol (M04)	**Dark aerobic conditions**							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/ DT_{90}	f. f. k_f / k_{dp}	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand [c)] (BBA 2.2)	phenyl	6.3	20 / 40	16.6 / 55.2			10.3	SFO
Silt loam [c)] ([redacted])	phenyl	7.6	20 / 40	3.4 / 11.3			14.7	SFO
Silt [c)] ([redacted])	phenyl	7.2	20 / 40	2.2 / 7.5			19.5	SFO
Sandy loam [c)] ([redacted])	phenyl	6.4	20 / 40	16.7 / 55.6			17.3	SFO
Geometric mean (if not pH dependent)								
Arithmetic mean								
pH dependence						No		

a) Measured in calcium chloride solution
b) Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
c) [redacted].; 2002; M-053610-01-1

methiocarb sulfone phenol (M05)

Modelling endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], and [redacted] with results summarized in Table 7.1.2.1.2/02-5.

For use as modelling endpoint, the overall geometric mean of normalized half-lives of methiocarb sulfone phenol (M05) was calculated to 9.9 days and an arithmetic mean of 0.491 for the formation fraction derived from methiocarb sulfoxide phenol (M04).

Table 7.1.2.1.2/02-5: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfone phenol (M05) (modelling endpoints) including normalisation.

methiocarb sulfone phenol (M05)	**Dark aerobic conditions** **The precursor from which the f.f. was derived was methiocarb sulfoxide phenol**							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/ DT_{90}	f. k_f / k_{dp}	DT_{50} 20 °C pF2/10kPa[b)]	st. (χ^2)	Method of calculation
Loamy sand [c)] (BBA 2.2)	phenyl	6.3	20 / 40	22.7 / 75.4	1.000	22.7	4.3	SFO
Silt loam [c)] ([redacted])	phenyl	7.6	20 / 40	8.6 / 28.5	0.147	6.3	9.2	SFO
Silt [c)] ([redacted])	phenyl	7.2	20 / 40	7.1 / 23.6	0.325	6.8	17.5	SFO
Geometric mean (if not pH dependent)						9.9		
Arithmetic mean					0.491			
pH dependence						No		

[a)] Measured in calcium chloride solution
[b)] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[c)] [redacted].; 2002; M-053610-01-1

Trigger endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], and [redacted] with results summarized in Table 7.1.2.1.2/02-6.

Table 7.1.2.1.2/02-6: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfone phenol (M05) (trigger endpoints)

methiocarb sulfone phenol (M05)	**Dark aerobic conditions**							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/ DT_{90}	f. f. k_f / k_{dp}	DT_{50} 20 °C pF2/10kPa[b)]	St. (%)	Method of calculation
Loamy sand [c)] (BBA 2.2)	phenyl	6.3	20 / 40	22.7 / 75.4			4.3	SFO
Silt loam [c)] ([redacted])	phenyl	7.6	20 / 40	8.6 / 28.7			9.2	SFO
Silt [c)] ([redacted])	phenyl	7.2	20 / 40	7.1 / 23.6			17.5	SFO
Geometric mean (if not pH dependent)								
Arithmetic mean								
pH dependence						No		

a) Measured in calcium chloride solution
b) Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
c) [redacted]; 2002; M-053610-01-1

methiocarb methoxy sulfone (M10)

Modelling endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], and [redacted] with results summarized in Table 7.1.2.1.2/02-7.

For use as modelling endpoint, the overall geometric mean of normalized half-lives of methiocarb methoxy sulfone (M10) was calculated to 27.6 days and an arithmetic mean of 1.0 for the formation fraction derived from methiocarb sulfone phenol (M05).

Table 7.1.2.1.2/02-7: Rate of degradation in soil (aerobic) laboratory studies for methiocarb sulfone phenol (M05) (modelling endpoints) including normalisation.

methiocarb methoxy sulfone (M10)	**Dark aerobic conditions** **The precursor from which the f.f. was derived was methiocarb sulfone phenol**							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/DT_{90}	f. f. k_f / k_{dp}	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand [c)] (BBA 2.2)	phenyl	6.3	20 / 40	23.5 / 78.2	1.0	23.5	12.5	SFO
Silt loam [c)] ([redacted])	phenyl	7.6	20 / 40	25.7 / 85.4	1.0	18.8	3.0	SFO
Silt [c)] ([redacted])	phenyl	7.2	20 / 40	49.8 / 165.4	1.0	47.5	8.5	SFO
Geometric mean (if not pH dependent)						27.6		
Arithmetic mean					1.0			
pH dependence						No		

[a)] Measured in calcium chloride solution
[b)] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[c)] [redacted].; 2002; M-053610-01-1

Trigger endpoints: As best fit kinetics were identified single first-order (SFO) for the soils BBA 2.2, [redacted], and [redacted] with results summarized in Table 7.1.2.1.2/02-8.

Table 7.1.2.1.2/02-8: Rate of degradation in soil (aerobic) laboratory studies for methiocarb methoxy sulfone (M10) (trigger endpoints)

methiocarb methoxy sulfone (M10)	**Dark aerobic conditions**							
Soil type	Label	pH[a)]	t. °C / % MWHC	DT_{50}/ DT_{90}	f. f. k_f / k_{dp}	DT_{50} 20 °C pF2/10kPa[b)]	St. (χ^2)	Method of calculation
Loamy sand [c)] (BBA 2.2)	phenyl	6.3	20 / 40	24.0 / 79.8		12.1		SFO
Silt loam [c)] ([redacted])	phenyl	7.6	20 / 40	24.1 / 93.5		1.6		SFO
Silt [c)] ([redacted])	phenyl	7.2	20 / 40	49.8 / 165.5		8.5		SFO
Geometric mean (if not pH dependent)								
Arithmetic mean								
pH dependence						No		

a) Measured in calcium chloride solution
b) Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
c) [redacted].; 2002; M-053610-01-1

CA 7.1.2.1.3 Anaerobic degradation of the active substance

This anaerobic soil degradation study was submitted for Annex I listing and has been summarized in the Baseline Dossier.

Report: KCA 7.1.2.1.3/01 [redacted] P. L.; 1989; M-004134-02-1
Title: Fate of methiocarb under aerobic and anaerobic soil conditions
Report No.: MR98/06
Document No: M-004134-02-1
Guideline(s): EPA Ref.: 162-1 Aerobic Soil Metabolism; 162-2 Anaerobic Soil Metabolism
Guideline deviation(s): not specified
GLP/GEP: no

Previous evaluation: In DAR for original Annex I inclusion (2005).

The anaerobic soil degradation study [redacted].; 1989; M-004134-02-1 was evaluated and summarized by the former RMS United Kingdom in Volume 3, Annex B, B.8 of the DAR, July 2005 (public version). A copy of this summary is given under CA 7.1.1.2.

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

The degradation behaviour of methiocarb under anaerobic conditions after application to soil surface is described in CA 7.1.1.2 (partly under aerobic soil metabolism CA 7.1.1.1. The major metabolites observed under anaerobic conditions were methiocarb sulfoxide (M01) and methiocarb phenol (M03).

CA 7.1.2.2 Field studies

CA 7.1.2.2.1 Soil dissipation studies

Due to the results of the laboratory soil degradation studies demonstrating the rapid degradation of methiocarb and its major degradation products in soil, field studies were not required.

CA 7.1.2.2.2 Soil accumulation studies

The accumulation potential of methiocarb was evaluated during the Annex I inclusion. Due to the short dissipation times, soil accumulation testing is not required for methiocarb.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

The adsorption and desorption behavior in soil of methiocarb and its major degradation products were studied in a number of soils in batch equilibrium experiments using either ^{14}C-labeled or unlabeled test items. Adsorption and desorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.
The calculated adsorption constants and correlation coefficients of methiocarb and its major degradation products are listed in CA 7.1.3.1.1 to CA 7.1.2.1.2. An overall summary is given Table 7.1.3.1- 1.

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

Compound	$K_{FOC(ads)}$ [a] [mL/g]	$K_{FOC(ads)}$ [b] [mL/g]
methiocarb	627	660
methiocarb sulfoxide (M01)	31[c)]	31[c)]
methiocarb sulfoxide phenol (M04)	43	51
methiocarb sulfone phenol (M05)	118	123
methiocarb methoxy sulfone (M10)	181	189

[a] geometric mean
[b] arithmetic mean
[c] Koc (HPLC)

CA 7.1.3.1.1 Adsorption and desorption of the active substance

The adsorption and desorption behaviour of methiocarb in soil in batch equilibrium experiments was evaluated during the Annex I Inclusion and was accepted by the European Commission Directive 2007/5/EC. The following study is included in the baseline dossier:

Report: KCA 7.1.3.1.1/01; [redacted]; 1987; M-013287-01-1
Title: Adsorption and desorption of (14C)-Mesurol by soil
Report No.: MR95032
Document No.: M-013287-01-1
Guideline(s): EPA guideline 163-1 Leaching and Adsorption/Desorption Studies
Guideline deviation(s): none
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

MATERIALS

1. Test Item

Test Item [phenyl-1-^{14}C]methiocarb
Description: Not stated
Lot/Batch: Not stated
Specific Activity: 33.7 mCi/mmole)
Radiochemical Purity: > 97 %
Chemical Purity: Not stated

Table 7.1.3.1.1- 2: Soil adsorption active substance (Regulation (EU) No 283/2013, Annex Part A, point 7.1.3.1.1 and Regulation (EU) No 284/2013, Annex Part A, point 9.1.2.1)

methiocarb							
Soil Type	OC %	Soil pH[a)]	K_d (mL/g)	K_{doc} (mL/g)	K_F (mL/g)	K_{Foc} (mL/g)	1/n
Sand [redacted], IN (USA)	0.42	4.3			5.3	1000	0.87
Sandy loam [redacted], IN (USA)	0.65	4.9			4.3	632	0.83
Silt loam [redacted], KS (USA)	1.53	6.9			9.0	600	0.82
Clay loam [redacted], MD (USA)	1.16	6.3			4.9	408	0.81
Geometric mean (if not pH dependent)*						627	
Arithmetic mean (if not pH dependent)						660	0.8325
pH dependence, *Yes or No*			No				

[a)] Measured in calcium chloride solution

* Only relevant after implementation of the published EFSA guidance.

An adsorption and desorption study was carried out on [phenyl-1-^{14}C]methiocarb. The adsorption and desorption constants were determined in four soils according to EPA Guideline 163-1(1982) and in compliance with the principles of GLP. The soil characteristics are given in Table 7.1.3.1.1- 3.

Table 7.1.3.1.1- 3: Characteristics of soils used for adsorption/desorption of [phenyl-1-^{14}C]methiocarb.

Soil Designation	Soil Type [a)]	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	CEC meq/100 g	pH ($CaCl_2$)
[redacted], IN (USA)	Sand	88	7	5	0.57	6	5.3
[redacted], IN (USA)	Sandy loam	72	21	7	0.68	12	4.9
[redacted], KS (USA)	Silt loam	17	66	17	1.53	25	5.9
[redacted], MD (USA)	Clay loam	20	50	30	1.16	21	6.1

[a)] = according to USDA scheme

Prior to the initiation of the study the soils were air-dried and sieved to <2 mm. Water to soil ratios were selected based on the data from a preliminary study. For the definitive study, adsorption/desorption tests were conducted in duplicate at nominal concentrations of 0.40, 0.80, 2.00 and 4.00 µg/L.

Following the shaking period the samples were centrifuged and the supernatant was decanted and radioassayed. The supernatant removed from each sample was replaced with an equal volume of 0.01 M calcium chloride. The tubes were sealed, shaken as described above for an additional 48 hours, and centrifuged to separate the phases. The supernatants were combined and extracted three times with two volumes of chloroform. The three extracts were combined, fortified with 1 mg of methiocarb and passed through anhydrous sodium sulfate. The dried extracts were reduced in volume and analysed by TLC. Mass balance was established on all samples from the definitive tests.
The results are summarized in Table 7.1.3.1.1- 4.

Table 7.1.3.1.1- 4: Adsorption and desorption of [phenyl-1-^{14}C]methiocarb on four different soils.

Soil Designation	Soil Type	Adsorption			Desorption		
		K_D (mL/g)	1/n	K_{OC} (mL/g)	K_D (mL/g)	1/n	K_{OC} (mL/g)
[redacted], In	Sand	3	0.8	1089	8.2	0.88	1547
[redacted], IN	Sandy loam	4.3	0.83	632	6.7	0.82	985
[redacted], KS	Silt loam	9.8	0.82	1600	16.2	0.82	1080
[redacted], MD	Clay loam	4.9	0.81	408	8.1	0.81	675

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

The adsorption and desorption behaviour of methiocarb sulfoxide, methiocarb sulfoxide phenol, methiocarb sulfone phenol, methiocarb methoxy sulfone in soil were evaluated during the Annex I Inclusion and were accepted by the European Commission Directive 2007/5/EC. The following studies are included in the Baseline Dossier.

Methiocarb sulfoxide

To determine the adsorption coefficient of methiocarb sulfoxide the batch equilibrium test according to OECD guideline for Testing of chemicals, No 106 could not be used as the test item was not stable under the study conditions. The adsorption coefficient was therefore estimated using high performance liquid chromatography and reference standards.

Report:	KCA 7.1.3.1.2/01; [redacted].; 2000; M-030161-01-1
Title:	Estimation of the adsorption coefficient (Koc) of methiocarb-sulfoxide on soil using high performance liquid chromatography (HPLC)
Report No.:	MR-474/00
Document No.:	M-030161-01-1
Guideline(s):	Proposal for a New Guideline Estimation onf the Adsorption Coefficient (Koc) on Soil using High Performance Liquid Chromatography (HPLC), Draft Document, August 1999 method used comparable to OECD Guideline for Testing of Chemicals, No 121 (2001
Guideline deviation(s):	not specified
GLP/GEP:	yes

Previous evaluation: In DAR for original Annex I inclusion (2005).

MATERIALS

1. Test Item

Test Item Description:	Methiocarb sulfoxide
Lot/Batch:	M00103
Specific Activity:	Not applicable
Radiochemical Purity:	Not applicable
Chemical Purity:	96.0 %

A batch adsorption study was not conducted on methiocarb sulfoxide (M01), because it was stated that this compound was not stable in calcium chloride solution. Instead an HPLC test was conducted according to the draft OECD Guideline for the Testing of Chemicals, Proposal for a New Guideline: Estimation of the Adsorption Coefficient (Koc) on Soil using High Performance Liquid Chromatography (HPLC), Draft Document, August 1999. The study was carried out in accordance with the principles of GLP.

Thirteen reference standard substances having known Koc values were chromatographed on an HPLC system to determine an average capacity factor (k'). The reference standards are listed in Table 7.1.3.1.2- 1. Sodium nitrate was used to determine the HPLC system dead time (t_0). A regression line was plotted with the determined k' values and the known Koc values (log k' vs. log Koc). Methiocarb sulfoxide (M01) was chromatographed on the same HPLC system during the same sample sequence as the reference standards, and average k' values were determined. The Koc value for the test substance was estimated by interpolation from the reference substance regression line. The linear regression of measured k' values yielded a line with a slope of 3.56, an intercept of 2.12 and a correlation coefficient R^2 of 0.8962.

Table 7.1.3.1.2- 1: Reference standards used to estimate Koc of methiocarb sulfoxide.

Substance	Koc
Acetanilide	17.8
N,N-dimethyl-benzamide	33.1
Atrazine	64.6
Isoproturon	72.4
Aniline	117
Triadimenol	251
Linuron	389
Methiocarb	1254
Fenthion	2042
Pyrazophos	4467
Phenanthrene	12303
Cyfluthrin	64300
Methiocarb sulfoxide	31.26

The estimated Koc value for methiocarb sulfoxide (M01) was 31 mL/g.

Methiocarb sulfoxide phenol

Report: KCA 7.1.3.1.2/02; [redacted]; 1996; M-013538-01-1
Title: Adsorption / desorption of 3,5-dimethyl-4-methylsulfinylphenol on four different soils
Report No.: IM1996
Document No.: M-013538-01-1
Guideline(s): EPA OPPTS 63-1 Leaching and adsorption/desorption (1982)
OECD Guideline for Testing of Chemicals, No 106 (2001)
Guideline deviation(s): not specified
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb sulfoxide phenol
Description:	solid
Lot/Batch:	THS 4504
Specific Activity:	3.02 MBq/mg (81.5 µCi/mg)
Radiochemical Purity:	> 99 % (HPLC)
Chemical Purity:	> 99 % (HPLC)

RESULTS AND DISCUSSION

Table 7.1.3.1.2- 2:Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

Methiocarb sulfoxide phenol							
Soil Type	OC %	Soil pH[a)]	K_d (mL/g)	K_{doc} (mL/g)	K_F (mL/g)	K_{Foc} (mL/g)	1/n
Loamy sand BBA 2.2	2.48	6.3			0.6611	26.7	0.894
Sand BBA 2.1	0.70	5.3			0.1855	26.9	0.9099
Silt loam [redacted]	0.90	7.3			0.4343	48.2	0.8902
Silty clay [redacted]	0.64	7.4			0.6466	101.0	0.9009
Geometric mean (if not pH dependent)*						43	
Arithmetic mean (if not pH dependent)					0.4826	50.7	0.9
pH dependence, *Yes or No*			No				

a) Measured in calcium chloride solution
* Only relevant after implementation of the published EFSA guidance.

An adsorption and desorption study was carried out on [phenyl-1-14C]methiocarb sulfoxide phenol (M04). The adsorption and desorption constants were determined in four soils according to OECD Guideline 106 (2000), EPA Guideline 163-1 (1982) and in compliance with the principles of GLP. The soil characteristics are given in Table 7.1.3.1.2-3.

Table 7.1.3.1.2- 3 Properties of the soils used in the methiocarb sulfoxide phenol (M04) adsorption/ desorption study

Soil Designation	Soil Type [a)]	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
BBA 2.2	Loamy sand	80.5	12.8	7.2	2.48	6.3
BBA 2.1	Sand	89.4	10.5	0.1	0.70	5.3
[redacted]	Silt loam	36.9	51.1	12.0	0.90	7.3
[redacted]	Silty clay	15.0	42.3	42.7	0.64	7.4

a) = according to USDA scheme

Just prior to the initiation of the study the soils were air-dried and sieved to < 2 mm. Based on the outcome of preliminary tests a soil/solution ratio corresponding to 12 g soil and 20 mL solution and a shaking period of 24 hours was used. For the definitive study, adsorption/desorption tests were conducted at concentrations of 5.1, 1.01, 0.21, and 0.04 mg/L $CaCl_2$ solution.
Following the shaking period the samples were centrifuged and the supernatant was decanted. The volumes were measured gravimetrically and recorded, and aliquots were taken for LSC. Two aliquots of 100 µL were taken for HPLC analysis. The pH was measured in all supernatants.
Following decantation of the adsorption phase, 20 mL of 0.01 M $CaCl_2$ solution was added to each sample. The samples were then shaken for the period and handled as described above. The pH was measured together with the stability of the test substance by radio-HPLC. The soil residual radioactivity was quantified by combustion. Mass balance was established on all samples from the definitive tests.

The results are summarized in Table 7.1.3.1.2- 4.

Table 7.1.3.1.2- 4: Adsorption and desorption coefficients for [phenyl-1-^{14}C]methiocarb sulfoxide phenol (M04)

Soil Designation	Soil Type [a)]	Adsorption			Desorption		
		K_D (mL/g)	1/n	K_{OC} (mL/g)	K_D (mL/g)	1/n	K_{OC} (mL/g)
BBA 2.2	Loamy sand	0.6611	0.8915	26.7	1.5240	0.9004	61.5
BBA 2.1	Sand	0.1885	0.9099	26.9	0.7384	1.0062	105.5
[redacted]	Silt loam	0.4343	0.8903	48.2	1.3828	0.9408	153.6
[redacted]	Silty clay	0.6466	0.9009	101.0	1.6438	0.9092	256.8

[a)] = according to USDA scheme

Methiocarb sulfone phenol

Report: KCA 7.1.3.1.2/03; [redacted], 2002; M-038460-01-1
Title: Adsorption/desorption of [1-14C]methiocarb sulfone phenol on four different soils
Report No.: IM 1993
Document No.: M-038460-01-1
Guideline(s): --
Guideline deviation(s): --
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005)

MATERIALS

1. Test Item

Test Item [1-^{14}C]methiocarb sulfone phenol
Description: Not specified
Lot/Batch: THS 6283
Specific Activity: 4.17 MBq/mg
Radiochemical Purity: 99 %
Chemical Purity: Not stated

RESULTS AND DISCUSSION

Table 7.1.3.1.2- 5: Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

Methiocarb sulfone phenol							
Soil Type	OC %	Soil pH[a)]	K_d (mL/g)	K_{doc} (mL/g)	K_F (mL/g)	K_{Foc} (mL/g)	1/n
Sand BBA 2.1	0.38	5.6			0.6195	163.0	0.8702
Sandy loam [redacted] AXXa	1.02	6.3			1.536	150.8	0.9022
Silt loam [redacted] AIII	0.98	7.4			0.905	92.4	0.8431
Silt [redacted] 4a	1.55	6.5			1.337	86.3	0.9386
Geometric mean (if not pH dependent)*						118	
Arithmetic mean (if not pH dependent)						123	0.88
pH dependence			No				

a) Measured in calcium chloride solution

* Only relevant after implementation of the published EFSA guidance.

An adsorption and desorption study was carried out with [1-^{14}C]methiocarb sulfone phenol (M05). The adsorption and desorption constants were determined in four soils according to OECD Guideline 106 (2000), EPA Guideline 163-1 (1982) and in compliance with the principles of GLP. The soil characteristics are given in Table 7.1.3.1.2-6.

Table 7.1.3.1.2- 6: Characteristics of soils used for adsorption/desorption of [phenyl-1-^{14}C]methiocarb sulfone phenol (M05)

Soil Designation	Soil Type a)	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
BBA 2.1	Sand	89.6	8.1	2.3	0.38	5.6
[redacted] AXXa	Sandy loam	72.4	22.6	5.0	1.02	6.3
[redacted] AIII	Silt loam	36.9	51.1	12.0	0.98	7.4
[redacted] 4a	Silt	8.2	81.3	10.2	1.55	6.5

a) = according to USDA scheme

Just prior to the initiation of the study the soils were air-dried and sieved to < 2 mm. Based on the outcome of preliminary tests a soil:solution ration of 1:1 corresponding to 20 g soil and 20 mL solution and a shaking period of 24 hours was used. For the definitive study, adsorption/desorption tests were conducted at concentrations of 1.006, 0.303, 0.101, 0.030 and 0.010 mg/L $CaCl_2$ solution.

Following the shaking period the samples were centrifuged and the supernatant was decanted. The volumes were measured gravimetrically and recorded, and aliquots were taken for LSC. Two aliquots of 100 µL were taken for HPLC analysis. The pH was measured in all supernatants.

Serial desorption cycles (including 3 desorptions) were then performed on the 1.00 mg/L concentration. Single point desorption was performed on the 0.30 mg/L, 0.10 mg/L, 0.03, and 0.01 mg/L concentrations. The volume of solution removed was replaced by an equal volume of stock

solution I. The test vessels were then shaken for the predetermined period and handled as described in the previous section. The pH was measured in the highest concentration specimens (1.00 mg/L.

The results are summarized in Table 7.1.3.1.2- 7.

Table 7.1.3.1.2- 7: Adsorption and desorption for [phenyl-1-^{14}C]methiocarb sulfone phenol (M05) on four different soils

Soil Designation	Soil Type [a)]	Adsorption			Desorption		
		K_D (mL/g)	1/n	K_{OC} (mL/g)	K_D (mL/g)	1/n	K_{OC} (mL/g)
BBA 2.1	Sand	0.6195	0.8704	163.0	0.7615	0.8683	200.4
[redacted] AXXa	Sandy loam	1.5386	0.9023	153.8	1.7420	0.8958	170.8
[redacted] AIII	Silt loam	0.9057	0.8431	92.4	1.0502	0.8383	107.2
[redacted] 4a	Silt	1.3377	0.8886	86.3	1.4998	0.8744	96.8

[a)] = according to USDA scheme

Methiocarb methoxy sulfone

Report: KCA 7.1.3.1.2/04; [redacted] 2002; M-038350-01-1
Title: Adsorption/desorption of [1-14C]methiocarb methoxy sulfone on four different soils
Report No.: IM 1992
Document No.: M-038350-01-1
Guideline(s): EPA OPPTS 163-1 Leaching and adsorption/desorption (1982)
OECD Guideline for Testing of Chemicals, No 106 (2000)
Guideline deviation(s): not specified
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

MATERIALS

1. Test Item

Test Item [1-^{14}C]methiocarb methoxy sulfone
Description: Not specified
Lot/Batch: THS 6284
Specific Activity: 3.9 MBq/mg
Radiochemical Purity: 98 %
Chemical Purity: Not stated

RESULTS AND DISCUSSION

Table 7.1.3.1.2- 8: Soil adsorption transformation products (Regulation (EU) N° 283/2013, Annex Part A, point 7.1.3.1.2 and Regulation (EU) N° 284/2013, Annex Part A, point 9.1.2.1)

Methiocarb methoxy sulfone							
Soil Type	OC %	Soil pH[a)]	K_d (mL/g)	K_{doc} (mL/g)	K_F (mL/g)	K_{Foc} (mL/g)	1/n
Sand BBA 2.1	0.38	5.6			0.9027	237.6	0.8402
Sandy loam [redacted] AXXa	1.02	6.3			2.5700	252.0	0.8586
Silt loam [redacted] AIII	0.98	7.4			1.207	122.2	0.8414
Silt [redacted] 4a	1.55	6.5			2.4881	145.4	0.9220
Geometric mean (if not pH dependent)*						181	
Arithmetic mean (if not pH dependent)						189	0.85
pH dependence			No				

a) Measured in calcium chloride solution

* Only relevant after implementation of the published EFSA guidance.

An adsorption and desorption study was carried out with [1-^{14}C]methiocarb methoxy sulfone (M10). The adsorption and desorption constants were determined in four soils according to OECD Guideline 106 (2000), EPA Guideline 163-1 (1982) and in compliance with the principles of GLP. The soil characteristics are given in Table 7.1.3.1.2-9.

Table 7.1.3.1.2- 9: Characteristics of soils used for adsorption/desorption of [phenyl-1-^{14}C]methiocarb methoxy sulfone (M10)

Soil Designation	Soil Type [a)]	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
BBA 2.1	Sand	89.6	8.1	2.3	0.38	5.6
[redacted] AXXa	Sandy loam	72.4	22.6	5.0	1.02	6.3
[redacted] AIII	Silt loam	36.9	51.1	12.0	0.98	7.4
[redacted] 4a	Silt	8[illegible]	81.3	10.2	1.55	6.5

a) = according to USDA scheme

Just prior to the initiation of the study the soils were air-dried and sieved to < 2 mm. Based on the outcome of preliminary tests a soil/solution ration of 1:1 corresponding to 20 g soil and 20 mL solution was used for soils BBA 2.1 and [redacted] AIII. A soil/solution ration of 1.2.22 was used for soils [redacted] AXXa and [redacted] 4a. A shaking period of 24 hours was used for soil [redacted] AXXa, [redacted] AIII and [redacted] 4a and 48 hours for soil BBA 2.1. For the definitive study, adsorption/desorption tests were conducted at concentrations of 1.000, 0.300, 0.100, 0.030 and 0.010 mg/L $CaCl_2$ solution.

Following the shaking period the samples were centrifuged and the supernatant was decanted. The volumes were measured gravimetrically and recorded, and aliquots were taken for LSC. Two aliquots of 100 µL were taken for HPLC analysis. The pH was measured in all supernatants.

Serial desorption cycles (including 3 desorptions) were then performed on the 1.00 mg/L concentration. Single point desorption was performed on the 0.30 mg/L, 0.10 mg/L, 0.03, and 0.01 mg/L concentrations. The volume of solution removed was replaced by an equal volume of stock solution I. The test vessels were then shaken for the predetermined period and handled as described in the previous section. The pH was measured in the highest concentration specimens (1.00 mg/L). The results are summarized in Table 7.1.3.1.2- 10.

Table 7.1.3.1.2- 10: Adsorption and desorption of [phenyl-1-14C]methiocarb methoxy sulfone (M10) on four different soils

Soil Designation	Soil Type [a)]	Adsorption			Desorption		
		K_D (mL/g)	1/n	K_{OC} (mL/g)	K_D (mL/g)	1/n	K_{OC} (mL/g)
BBA 2.1	Sand	0.9027	0.8405	237.6	1.0782	0.8383	283.8
[redacted] AXXa	Sandy loam	2.5700	0.8586	252.2	3.0122	0.8447	295.5
[redacted] AIII	Silt loam	1.2578	0.9414	126.2	1.4164	0.8379	144.5
[redacted] 4a	Silt	2.4881	0.8626	245.0	2.5988	0.8530	267.7

[a)] = according to USDA scheme

CA 7.1.3.2 Aged sorption

Aged desorption studies with the active substance methiocarb were only performed on slug pellet formulation as and aged column leaching study (see CA 7.1.4.1). This is, however, a formulation not further supported.

CA 7.1.4 Mobility in soil

CA 7.1.4.1 Column leaching studies

No column leaching studies were performed for the active substance and further metabolites. This requirement is covered by the adsorption and desorption studies covered under section CA 7.1.3.
For the previous submission an aged column leaching study was available with a slug pellet formulation in two soils.

CA 7.1.4.1.1 Column leaching of the active substance

Report: KCA 7.1.4.1.1/01 [redacted]; 2001; M-043847-01-1
Title: Leaching behavior of Mesurol R (methiocarb) DRAZA slug pellets in soil columns during aging
Report No.: MR-560/00
Document No: M-043847-01-1
Guideline(s):
Guideline deviation(s): --
GLP/GEP: yes

Previous evaluation: In DAR for original Annex I inclusion (2005).

This aged column leaching is specific to methiocarb formulated as slug pellets. Already the study report stated that in order to meet the specific release characteristic of the pellets the study design did

not comply with official guidelines. At the time it was felt that with such a study further understanding on the slug pellet formulation was to be gained.
From the data presented in this study it can be concluded that methiocarb and methiocarb sulfoxide do not have a potential to leach into deeper soil layers or to reach ground water if applied as DRAZA RB3 slug pellets.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

Report:	KCA 7.1.4.1.2/01; [redacted] O., 2001; M-043847-01-1
Title:	Leaching behavior of Mesurol® (methiocarb) DRAZA slug pellets in soil columns during aging
Report No.:	MR-360/00
Document No.:	M-043847-01-1
Guideline(s):	--
Guideline deviation(s):	--
GLP/GEP:	**yes**

See CA 7.1.4.1.1

CA 7.1.4.2 Lysimeter studies

No relevant studies are included in the Baseline Dossier, as they were not required. No additional studies are submitted within this renewal of approval.

CA 7.1.4.3 Field leaching studies

A field leaching study is not regarded as necessary. With the set of laboratory data on rate and route of degradation in soil which indicates that residues of methiocarb are readily degradable including mineralization. A comprehensive set of laboratory data on adsorption of methiocarb and its degradation products to soil allow for an assessment of the mobility of all significant residues under various environmental conditions by the use of computer simulations as given, for example, by the FOCUS scenario approach. Such transfer calculation is more flexible and allows for adaptation to crop, site or country specific climate and soil conditions such overcoming the limitations of a field leaching experiment.

CA 7.2 Fate and behaviour in water and sediment

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

CA 7.2.1.1 Hydrolytic degradation

Report:	KCA 7.2.1.1/01; [redacted]; 1988; M-013292-02-1
Title:	Mesurol hydrolysis in sterile buffers
Report No.:	MR69272
Document No.:	M-013292-02-1
Guideline(s):	EPA 161-1 Hydrolysis
Guideline deviation(s):	none
GLP/GEP:	**no**

Previous evaluation: In DAR for original Annex I inclusion (2005)

MATERIALS

1. Test Item

Test Item Description:	[phenyl-1-^{14}C]methiocarb
Lot/Batch:	Not stated
Specific Activity:	Not stated
Radiochemical Purity:	168.032 dpm/µg
Chemical Purity:	97 %
	Not stated

The hydrolysis of methiocarb was investigated according to US EPA guideline 161-1 (1982) and in accordance with the principles of GLP. The study was carried out with [phenyl-1-^{14}C]methiocarb labelled methiocarb in the dark at 25°C in three sterile phosphate buffered solutions pH 5, 7 and 9.
The test solutions were prepared with the test substance at a concentration of about 10 mg/L. The solutions were incubated for a maximum period of 30 days under sterile conditions in the dark at 25°C. Sampling intervals were 0, 1, 3, 7, 14, and 30 days. Analysis of the samples was performed by TLC in combination with authentic reference standards.

The results are summarized in Table 7.2.1.1/01-1.

The degradation kinetics were calculated based on first-order kinetics. The results are summarized in Table 7.2.1.1/01-2.

Table 7.2.1.1/01-1: Hydrolysis of [phenyl-1-^{14}C]methiocarb in three buffer solution at 25 °C [values are given in % of the applied radioactivity].

Sampling interval [days]	Methiocarb	M01	M03	M04	Others	TLC Origin	Recovery
pH **5**							
0	96.0	2.0	trace	trace	<1.0	trace	98.0
1	93.0	4.0	trace	trace	<1.0	trace	97.0
3	97.0	<1.0	trace	trace	<1.0	trace	97.0
7	92.0	5.5	trace	trace	<1.0	trace	97.5
14	95.0	2.0	trace	trace	<1.0	trace	97.0
30	91.0	5.0	trace	trace	<1.0	<1.0	96.0
51	93.0	3.5	trace	trace	<1.0	<1.0	96.5
pH **7**							
0	88.0	9.0	trace	trace	<1.0	trace	96.0
1	89.0	6.5	2.0	<1.0	<1.0	trace	97.5
3	87.0	3.0	6.5	<1.0	<1.0	<1.0	97.5
7	83.0	3.0	5.0	2.5	3.5	<1.0	97.5
14	71.0	2.0	19.0	3.5	1.5	1.5	95.5
30	48.0	trace	46.0	3.0	1.0	1.0	97.0
pH **9**							
0	67.0	3.5	21.5	4.0	<1.0	<1.0	97.0
1	9.0	<1.0	70.5	10.5	3.0	3.0	96.0
3	4.5	trace	82.0	4.5	2.5	1.0	96.0
7	2.0	<1.0	78.5	9.5	4.5	2.5	97.0

M01 = methiocarb sulfoxide; M03 = methiocarb phenol; M04 = methiocarb sulfoxide phenol.

Table 7.2.1.1/01-2: Estimated DT$_{50}$-values of [ring-1-^{14}C]methiocarb under hydrolytic conditions.

pH	Half-life [days]	
	25 °C	Order
5	32	1st
7	24	
9	0.21	1st

Report: KCA 7.2.1.1/02[redacted]; 2001; M-069229-01-1
Title: Hydrolysis of [phenyl-1-14C]methiocarb-sulfoxide in sterile buffer solutions
Report No.: MR-274/01
Document No.: M-069229-01-1
Guideline(s): SETAC procedures for assessing the environmental fate and ecotoxicity of pesticides 1995, OECD 111, Commission directive 95/36/EC, 1995
Guideline deviation(s): --
GLP/GEP: **yes**

Previous evaluation: No previous evaluation, submitted for the purpose of active substance renewal.

This study does not seem to have been submitted in the previous evaluation. The assessment of the full hydrolysis of methiocarb sulfoxide (M01) at pH 5, 7 and 9 was not triggered by the results on the hydrolysis of methiocarb [redacted]; 1988; M-013292-02-1. [redacted]ver, understanding on the rate of hydrolysis at pH 5, 6 and 7 was considered useful.

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb sulfoxide
Description:	solid
Lot/Batch:	KML 2837
Specific Activity:	3.48 MBq/mg (94.1 µCi/mg)
Radiochemical Purity:	> 98 %
Chemical Purity:	> 98 %

STUDY DESIGN AND METHODS

The hydrolysis of methiocarb sulfoxide (M01) was investigated in sterile 0.01 M buffer solutions, which were adjusted to pH 5, 6, and 7. The test solutions were prepared with radiolabelled [phenyl-1-^{14}C]methiocarb sulfoxide at a concentration of approximately 10 mg/L.
The solutions in the pre-test were incubated for a maximum period of 7 days under sterile conditions in the dark at 50 °C, and the sampling intervals were 0, 2, 5 and 6 hours and 1, 2, 5 and 7 days.
The solutions in the main-test (pH 5 and pH 6) were incubated for a maximum period of 30 days under sterile conditions in the dark at 25 °C and the revised sampling intervals were 0, 2 and 6 hours and 1, 2, 4, 7, 14, 21 and 30 days as deduced from the results of the pre-test. The maximum incubation period for the pH 7 samples was 4 days with sampling intervals after 0, 2, 6, 24 and 30 hours as well as 2, 3 and 4 days.
Duplicate samples were taken for analysis. Analysis of the samples was performed by measurement of radioactivity and using thin layer chromatography (TLC) in combination with authentic reference standards. HPLC was used as a confirmatory system. Based on the LSC results a radioactivity balance was established for both tests for each buffer solution at each sampling interval.

RESULTS AND DISCUSSION

The complete material balances found in all solutions demonstrated that no radioactivity dissipated from the solutions by means of volatilisation.
Under the hydrolytic conditions of pH 5, 6 and 7 at 50 °C (pre-test) as well as at 25 °C (main test) the test substance showed rapid degradation and was clearly dependent on the pH. The degradation rates in both tests were increasing with increasing pH. After 30 days of incubation at 25 °C, the remaining level of the test substance amounted to 65.6% (pH 5) and 2.4% (pH 6) of the applied radioactivity. In the main test at pH 7 the remaining level of the test substance amounted to 0.8% of the applied radioactivity after 4 days of incubation.

At all three pH values methiocarb sulfoxide phenol (M04), was formed resulting at pH 7 in 97 % of the applied radioactivity after 3 days at 25 °C.

No further hydrolysis products were found to be relevant, individual peaks resulting in less than 0.5 % of the applied radioactivity.

For calculation of the DT$_{50}$ values the evaluation program ModelManager® was used (simple first-order model [SFO]). Table 7.2.1.1/02-1 and Table 7.2.1.1/02-2 contain the kinetic results of methiocarb sulfoxide hydrolysis at 50 °C and 25°C, respectively.

Table 7.2.1.1/02-1: Kinetics results of methiocarb sulfoxide (M01) hydrolysis at 50 °C.

Test Solution	Half-life [days]	Order of Function	R^2
pH 5 (0.01 M citrate buffer)	1.19	SFO	0.999
pH 6 (0.01 M citrate buffer)	0.09	SFO	0.995
pH 7 (0.01 M phosphate buffer)	0.01	SFO	1.000

Table 7.2.1.1/02-2: Kinetics results of methiocarb sulfoxide (M01) hydrolysis at 25 °C

Test Solution	Half-life [days]	Order of Function	R^2
pH 5 (0.01 M citrate buffer)	54.8	SFO	0.994
pH 6 (0.01 M citrate buffer)	6.1	SFO	0.996
pH 7 (0.01 M phosphate buffer)	0.5	SFO	0.999

At 20 °C the DT_{50} values calculated via Arrhenius plots (lnk versus 1/T) were 122, 15 and 1 days for the pH of 5, 6 and 7, respectively.

Conclusion: Considering the hydrolytic behaviour determined under environmental pH conditions it is expected that hydrolytic processes will significantly contribute to the degradation of methiocarb sulfoxide in the environment.

CA 7.2.1.2 Direct photochemical degradation

Report: KCA 7.2.1.2/01; [redacted]; 1991; M-013352-01-2
Title: Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation of methiocarb in water
Report No.: PF3469
Document No.: M-013352-01-2
Guideline(s): --
Guideline deviation(s): --
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

A quantum yield Φ of 0.2828 was calculated. The quantum yield and UV absorption were used to estimate the environmental half-life of methiocarb in water by two simulation models (GC-SOLAR and Frank&Klopffer). The estimates based on these models resulted in environmental direct photolysis half-lives of about 6 to 16 days for all relevant scenarios investigated (i.e. spring and summer application at the 50th degree of latitude). The direct photodegradation in water was concluded only to contribute to a small proportion of the elimination of methiocarb from the environment.

Report:	KCA 7.2.1.2/02; [redacted].; 2002; M-053504-01-1
Title:	Photolysis of [phenyl-1-14C]methiocarb in sterile aqueous buffer pH 5
Report No.:	MR-614/01
Document No.:	M-053504-01-1
Guideline(s):	SETAC Guidelines (1995), US EPA Guideline 161-2
Guideline deviation(s):	none
GLP/GEP:	**yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb
Description:	solid
Lot/Batch:	13824/1
Specific Activity:	3.73 MBq/mg (100.9 µCi/mg)
Radiochemical Purity:	> 99 %
Chemical Purity:	> 99 %

An aqueous photolysis study was carried out at 25°C using phenyl-1-^{14}C methiocarb. The study followed SETAC Guidelines (1995), US EPA Guideline 161-2 (1982) and was conducted in accordance with the principles of GLP. The test solutions were made up in sterile aqueous solution (pH 5, acetate buffer) to a concentration of 0.989 mg/l. The solutions were continuously exposed to simulated sunlight using a xenon lamp with 290nm UV filter. The maximum period of continuous light exposure amounted to 10 days (240 hours). This was equated to 11 or 18 solar midsummer days in [redacted], Arizona (USA, latitude 33.3°N) or in [redacted] (Greece, latitude 37°58'N).
An aliquot of 10 ml test solution filled in a glass quartz test vessel with a maximum capacity of 25ml (inside length 65mm, width 25mm, height 39mm). Trap attachments were fitted and filled with soda lime granules for absorption of CO_2 and fitted with a polyurethane plug for absorption of any volatile organic compounds generated. The distance of the light source to the cooling platform was 230mm; to the radiometer measuring cell was 210mm; to the water surface was 220mm; and to the top of the vessel was 210mm. Irradiated samples were taken for analysis at 1, 2, 3, 6, 8 and 10 days. The dark controls were sampled at 0, 5 and 10 days.
Volatile organic compounds possibly contained in the PU foam plug were extracted with acetonitrile and analysed by LSC. Further chromatographic analyses of these extracts were not performed because the ^{14}C content was considerably lower than 1 % AR. The radioactivity absorbed by the soda lime was liberated with 18 % HCl and analysed by LSC. At each sampling interval aliquots of 500 µl were sampled for LSC measurements, then all test solutions were analysed within a few days by means of HPLC.
The results are presented in Table 7.2.1.2/02-1.

Table 7.2.1.2/02-1: Material balance of the photolysis of [phenyl-1-^{14}C]methiocarb in aqueous buffer solution under artificial light conditions (in % of the applied radioactivity, mean of two samples).

Time of irradiation [days]	AS	M01	M04	Unknown #1	Unknown #2	Others (> 2)	CO2	Total
0	99.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	99.4
1	98.2	2.4	n.d.	n.d.	n.d.	n.d.	0.1	100.8
2	93.8	4.5	n.d.	n.d.	n.d.	n.d.	0.6	98.9
3	89.9	6.2	n.d.	n.d.	1.7	n.d.	1.3	99.1
6	62.1	20.2	2.1	3.7	2.8	3.5	4.3	99.5
8	56.1	18.0	2.7	5.3	5.5	6.8	6.3	101.0
10	39.3	25.1	3.4	5.7	5.7	8.9	9.0	99.6
Dark control [days]								
6	103.0	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	103.1
10	103.3	n.d.	n.d.	n.d.	n.d.	n.d.	<0.1	103.4

AS = methiocarb n.d. = not detected
M01 = methiocarb sulfoxide M04 = methiocarb sulfoxide phenol

The degradation curve and regression analysis of methiocarb was calculated with Model Manager (v1.1). Based on an experimental half-life of 8.7 days the half-life under experimental conditions was calculated to be 31 solar summer days at [redacted], Arizona (USA) and 48 solar summer days at [redacted] (Greece).

Report: KCA 7.2.1.2/03; [redacted]; 1988; M-013358-01-1

Title: Photochemical degradation of [14C] mesurol in aqueous solutions
Report No.: M1053
Document No.: M-013358-01-1
Guideline(s): 161-2 Photodegradation in Aqueous Solution
Guideline deviation(s): The TLC system used to confirm the identities of [14C]Mesurol and its degradates was Isopropyl EtherMethanol (8:1) rather than the system stated in the protocol, Isopropyl EthenMethanol (3:2).

GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

MATERIALS

1. Test Item

Test Item Description: [phenyl-1-14C]methiocarb
Lot/Batch: Not stated
Specific Activity: 29.7 mCi/mmole
Radiochemical Purity: 99.4 %
Chemical Purity: Not stated

An aqueous photolysis study was carried out for 30 days under natural sunlight conditions using 14C methiocarb. The study followed US EPA Guideline 161-2 (1982) and was not conducted in accordance with the principles of GLP. The test solutions were made up in sterile aqueous solution

(pH 5, acetate buffer) to a concentration of 0.91 mg/L and placed in quartz tubes with a flow-through system to collect volatiles. The tubes were immersed in a bath of deionised water and exposed to direct sunlight in [redacted], Kentucky, USA (38.05°N, 84.30°W) in January and February 1988. Dark controls were maintained at the same location. The mean temperature of the solutions was 25.9°C. Duplicate samples were taken for analysis at 0.25, 6, 12, 20 and 30 days post-treatment.
At each sampling interval aliquots were sampled for LSC measurements, then all test solutions were analysed by means of HPLC. TLC was used to confirm the HPLC characterisation of 14C methiocarb and metabolites.
The results are presented in Table 7.2.1.2/03-1.
The half-lives for degradation in both the irradiated and dark control samples were calculated to be greater than 30 days. The dark controls had a half-life of 238 days and irradiated samples had a half-life of 88 days ([redacted], Kentucky, USA, 38.05°N, 84.30°W, in January and February).

Table 7.2.1.2/03-1: Material balance of the photolysis of [^{14}C]methiocarb in aqueous buffer solution under natural sunlight conditions (in % of the applied radioactivity, means of two values).

Time of irradiation [days]	Methiocarb	M01	M04	Unknown	Recovery
0	103.5	n.d.	n.d.	n.d.	103.5
0.25	107.8	0.3	n.d.	n.d.	108.1
6	107.1	2.0	n.d.	n.d.	109.0
12	101.5	4.6	n.d.	n.d.	106.0
20	97.4	10	n.d.	n.d.	107.5
30	83.8	9.8	2.4	5.8	102.0
Dark controls [days]					
0	96.5	n.d.	n.d.	n.d.	96.5
0.25	105.9	1.2	n.d.	n.d.	107.0
6	108.0	0.5	n.d.	n.d.	108.0
12	92.4	0.6	n.d.	n.d.	93.0
20	99.0	0.6	n.d.	n.d.	99.5
30	94.7	2.4	0.8	5.2	103.0

n.d. = not detected
M01 = methiocarb sulfoxide M04 = methiocarb sulfoxide phenol

CA 7.2.1.3 Indirect photochemical degradation

No studies are submitted under the indirect photochemical degradation. No study is needed as there was no indication from other available data that route and rate of degradation in the water phase can be significantly influenced by indirect photodegradation.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

A test on the "ready biodegradability" was not performed since methiocarb is not regarded as ready biodegradable. This was indicated by the overall results of the water/sediment study see section CA 7.2.2.3.

CA 7.2.2.2 Aerobic mineralisation in surface water

This topic was not part of and thus not evaluated by the European Commission during the last Annex I inclusion of methiocarb, no respective study is therefore included in the Baseline Dossier. [redacted]ver, the applicant believes that the circumstances in which the study is required are not fulfilled for methiocarb, 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).

Methiocarb is a fast degrading active substance in soil and water/sediment systems. Based on the laboratory data the PECsw for methiocarb was determined according to FOCUS SW guidances (see MCP section 9.2.5)

For application as maize seed treatment the FOCUS crop group "no drift (incorporation or seed treatment) applies. According to FOCUS SW this leaves possible entry routes of methiocarb into surface water as runoff or entry via drainage. [redacted]ver, due to the incorporation of the treated seeds into the soil an entry via run-off does not occur. All relevant step 3 scenarios, without any further mitigation options lead to concentrations PECsw <0.001 µg/L (see MCP section 9.2.5) thus showing that entry into open water will not occur.

CA 7.2.2.3 Water/sediment study

Report: KCA 7.2.2.3/01; [redacted]; 1979; M-013362-01-1
Title: Metabolic fate of [redacted] in aerobic and anaerobic aquatic environments
Report No.: MR667/5
Document No.: M-013362-01-1
Guideline(s): not specified
Guideline deviation(s): not specified
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Assessment on suitability of study: the data presented are from a non-GLP study, evaluated for the original Annex I inclusion (2005), assessing the degradation of radiolabeled methiocarb in aerobic pond water, a route that is not relevant for seed treatment only (see CA 7.2.2.2). The second part of the study - anaerobic aquatic system – is not a European data requirement.
The study set up from 1979, although well conducted for the time of performance, would have some shortcomings when compared with modern guideline studies (e.g. conducted at elevated temperature

(mean temperature 89°F = 32°C) with no record of the actual temperatures over the course of the study, lack of material balance, no record of redox potentials).

Two water/sediment studies on [phenyl-1-^{14}C]methiocarb were conducted on an aerobic water and anaerobic water/sediment system in the dark under non-sterile conditions. The study was carried out similar to but pre US EPA Guideline 162-3 (1982), and was not in compliance with GLP.

MATERIALS

1. Test Item

Test Item	[phenyl-1-^{14}C]methiocarb
Description:	Not stated
Lot/Batch:	Not stated
Specific Activity:	2.38 MBq/mg (14.876 dpm/µg; 14.5 mCi/mmol)
Radiochemical Purity:	Not stated
Chemical Purity:	Not stated

2. Sediment and water

The sediment and water were taken from a natural pond in [redacted], [redacted], USA. The pond water is very scarcely characterized only mentioning pH 8 at one point of the experimental set up. Dissolved oxygen content at day zero is 8.0 ppm in the pond water.

Soil characteristics are summarised in Table 7.2.2.3/01-1.

Table 7.2.2.3/01-1: Physico-chemical properties of test sediment

Parameter	Results/Units Research Center, [redacted], [redacted], USA
Geographic location	
Mapping unit	
Type of aquatic system	
Taxonomic classification	
Texture class [USDA]	Silty Clay Loam
Sand (2000-50 µm); [%]	16
Silt (50-2 µm); [%]	54
Clay (< 2 µm); [%]	30
pH: CaCl$_2$	6.3
Organic matter [%] [1]	1.4
Organic carbon [%]	0.74
Microbial activity	No data
Cation exchange capacity [meq Ba^{2+}/100 g sediment]	8.2
Total nitrogen [% N]	No data
Total phosphorous [mg P/g DM]	No data
CaCO$_3$ [%]	No data
Water content [%]	No data
Redox potential [mV]	No data
Particle density [g/cm^3]	2.6

USDA: United States Department of Agriculture
[1] calculated as: OM [%] = OC [%] x 1.9

STUDY DESIGN AND METHODS

In the aerobic study, pond water (100 ml) only was placed in jars. In the anaerobic study, pond water (100 mL) and sediment (100 g) were placed in the jars. Anaerobic conditions were established in the sediment by adding 100 mL of pond water (pH 8) containing 2 mg/mL glucose plus 8.4 mg/mL calcium nitrate to each soil sample. After 33 days the water was discarded and fresh pond water was added to each sample prior to fortification with [phenyl-1-14C]methiocarb. The concentration of the test substance was 2 mmm in both studies

The test jars were maintained in a greenhouse environment (mean temperature 69°F = 22°C) and samples were removed in duplicate from at 0, 3, 7 14, 21, and 32 days after application (aerobic study) and 0, 3, 7, 14, 21, 28, 56, and 112 days (anaerobic study). For analysis, pond water was extracted 3 times with ethyl acetate (200 mL) and the organic phase was analyzed by thin-layer chromatography (TLC). Sediment was Soxhlet extracted with chloroform/methanol (7:3 v/v) for 16 hours and the extracts were analyzed by TLC.
The extracted soil solids were further extracted with NaOH and HCl to separate the bound radioactivity into humin, humic acid and fulvic acid fractions. The radioactivity content was determined by liquid scintillation measurements after combustion.

RESULTS AND DISCUSSION

Table 7.2.2.3/01-2: Distribution and total recovery after degradation [phenyl-1-^{14}C]methiocarb in aerobic pond water and anaerobic water/sediment systems (% of applied radioactivity).

Sampling interval [days]	Aerobic aquatic			Anaerobic aquatic					
	Water			Water		Sediment			
	Organo-soluble	water soluble	Loss	Organo-soluble	water soluble	Organo-soluble	water soluble	Bound	Loss
0	99	1	0	99	1	0	0	0	0
3	100	0	0	64	1	23	<1	7	5
7	100	0	0	42	1	41	<1	9	2
14	98	1	1	<1	1	41	<1	10	11
21	95	2	3	29	1	35	<1	10	5
28	snt	snt	snt	22	1	58	<1	11	8
32	88	1	11	snt	snt	snt	snt	snt	snt
56	snt	snt	snt	3	1	30	<1	42	22
112	snt	snt	snt	<1	2	5	<1	72	21

snt - sample not taken at this interval

Table 7.2.2.3/01-3: Distribution of parent compound and metabolites after application of [phenyl-1-^{14}C]methiocarb in aerobic and anaerobic water/sediment systems (% of applied radioactivity).

Sampling Interval (days)	Aerobic aquatic Water Organosoluble part				Anaerobic aquatic Water Organosoluble part			Sediment Organosoluble part		
	as	M01	M03	M04	as	M01	M03	as	M03	M04
0	97	1	1	0	97	1	1	na	na	na
3	0	0	80	20	18	0	45	10	12	<1
7	0	0	83	17	5	0	42	9	32	<1
14	0	na	34	63	2	0	30	6	34	<1
21	na	na	na	na	<1	0	28	5	48	1
28	na	na	na	na	<1	0	21	4	51	2
32	na	na	na	na	snt	snt	snt	snt	snt	snt
56	na	na	na	na	<1	0	9	2	26	1
112	na	na	na	na	0	0	0	1	3	<1

as = methiocarb
M01 = methiocarb sulfoxide
M03 = methiocarb phenol
snt = sample not taken at this interval
na = not analysed
M04 = methiocarb sulfoxide phenol

Report: KCA 7.2.2.3/04; [redacted]; 2005; M-259880-01-1
Title: [Phenyl-1-14C]methiocarb: Aerobic aquatic metabolism in two water-sediment systems
Report No.: MEF-05/365
Document No.: M-259880-01-1
Guideline(s): EU 95/36/EC amending 91/414/EEC Annexes I and II; OECD 308; US EPA Subdivision N, 161-4
Guideline deviation(s): none
GLP/GEP: **yes**

Previous evaluation: No previous evaluation, submitted for the purpose of active substance renewal.

MATERIALS

1. Test Item

Test Item [phenyl-1-^{14}C]methiocarb
Description: Not stated
Lot/Batch: BECH 1665, KML 2833
Specific Activity: 3.73 MBq/mg (100.9 µCi/mg)
Radiochemical Purity: 98 %
Chemical Purity: > 98 %

2. Water and Sediment

Sediment and corresponding supernatant water were taken from a reclaimed gravel pit ([redacted]) and an artificially dammed pont ([redacted]). Properties and characteristics are summarized for the sediment in Table 7.2.2.3/04-1 and for the water Table 7.2.2.3/04-2.

Table 7.2.2.3/04-1: Physico-chemical properties of test sediment

Parameter	Results/Units	
	[redacted]	[redacted]
Geographic location	[redacted], Northrhine-Westfalia, Germany	[redacted];, Northrhine-Westfalia, Germany
Mapping unit	[redacted]	[redacted]
Type of aquatic system	oligotrophic	meso-/oligotrophic
Taxonomic classification	Sand	Loam
Texture class [USDA]	Sand	Silt loam
Sand (2000-50 µm); [%]	93.8	14.7
Silt (50-2 µm); [%]	4.3	62.6
Clay (< 2 µm); [%]	1.9	22.7
pH: Water	8.46	7.30
$CaCl_2$	7.14	6.61
Organic matter [%] [1]	0.64	5.19
Organic carbon [%]	0.37	3.01
Microbial activity [mg CO_2/h*kg of sediment DM]		
Initial (at date of sampling)	7.9	26
Final (at latest processing date)	0.8	10.8
Cation exchange capacity [meq Ba^{2+}/100 g sediment]	2.2	11.2
Total nitrogen [% N]	0.03	0.23
Total phosphorous [mg P/kg DM]	474.5	474.5
$CaCO_3$ [%]	< 0.1	<0.1
Water content [%][2]	19.0	51.9
Redox potential [mV][2]	197	174

[1] % organic matter = % organic carbon*1.724
[2] determined within this study, just before filling the test vessels

Table 7.2.2.3/04-2: Physico-chemical properties of test supernatant water

Parameter	Results/Units	
	[redacted]	[redacted]
Temperature at sampling [°C]	12.0	10.2
pH at sampling	7.6	8.0
Hardness [° dH]	9.8	3.1
Electrical conductivity	N/A	N/A
Oxygen concentration [mg/L][1]		
Initial (at date of sampling)	10.9	10.8
Final (at latest processing date)	6.3	6.2
Dissolved organic carbon, DOC [mg C/L]	< 2	< 2
Total organic carbon, TOC [mg C/L]	< 2	< 2
Total nitrogen [mg N/L]	5.5	4.0
Total phosphorous [mg P/L]	< 0.03	< 0.03
Redox potential [mV]		
Initial (at date of sampling)	190	204
Final (at latest processing date)	217	227

[1] Definition of O_2 saturation: 100 % saturation (20 °C) is equivalent to 9.17 mg/L

STUDY DESIGN AND METHODS

The aerobic biotransformation of methiocarb was studied in two water/sediment systems for a maximum of 90 days in the dark at 20 °C.
A study application rate of 12.5 µg per test system (corresponding to 24 µg/L, calculated to a water depth of 100 cm) was applied based on a maximum single field application rate of methiocarb of 240 g/ha.
The test was performed in systems consisting of cylindrical glass containers containing a water-to-sediment volume ratio of 3/1 (v/v) and equipped with traps for the collection of carbon dioxide and volatile organic compounds. During incubation, the water was in smooth motion. The test item was applied onto the water surface.
Duplicate samples were analysed at 0, 1, (2,) 3, 7, 14, 30, 62, and 90 days of incubation. At each sampling interval, the water was separated from the sediment by decantation. The sediment was extracted twice at ambient temperature using acetonitrile/water/glacial acetic acid (50/50/0.1, v/v/v), followed by a single extraction with pure acetonitrile and finally by an aggravated microwave extraction with acetonitrile/water/glacial acetic acid (8/2/1, v/v/v) at 60 °C.
The amounts of test item and degradation products in water and sediment extracts were determined by liquid scintillation counting (LSC) and by HPLC-radiodetection analysis. The water and sediment extracts were concentrated prior to HPLC-radiodetection analysis. The amount of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. Test item and degradation products were identified by HPLC-MS(/MS) including accurate mass determination, by ^{1}H-NMR and/or by co-chromatography with reference items.
The limit of quantitation (LOQ) for the HPLC method was set to three times the LOD, which was 2.1% of the AR. The results were confirmed by normal phase radio AMD-TLC for representative samples. The limit of quantitation (LOQ) for the HPTLC method was set to three times the LOD, which is 3% of the AR. Identification of the transformation products was achieved by co-chromatography with reference compounds.

RESULTS AND DISCUSSION

The material balances of the water/sediment systems ranged from 97.7 % to 103.7 % and from 92.0 % to 101.9 % of the applied radioactivity (AR) for [redacted] and [redacted], respectively, with overall mean ± standard deviations of 100.7 ± 2.0 % and 97.1 ± 2.8 %, respectively.

Residues in water decreased from day 0 to study termination from 97.5 % to 13.8 % AR for [redacted] and from 97.5 % to 2.5 % AR for [redacted]. Extractable residues in sediment increased from day 0 to study termination from 2.6 % to 13.6 % for [redacted] and from 2.7 % to 20.7 % AR for [redacted]. Non-extractable residues (NER) in the sediment of [redacted] increased from day 0 to study termination from 9.3 % to 45.2 % AR and in the sediment of [redacted] from 0.5 % to 58.6 % AR.
The formation of $^{14}CO_2$ was detectable first one day after application in both systems. Afterwards the amount of $^{14}CO_2$ steadily increased to values of 25.3 % AR in [redacted] and 12.3 % AR in [redacted] at study termination. The radioactivity found in the PU traps amounted to <0.1 % AR for both systems.

Methiocarb dissipated from the water due to degradation and translocation into the sediment. Shortly after application, processed after 60 min, the amount of methiocarb in water was 91.5 % AR in [redacted] and 93.7 % AR in [redacted]. Methiocarb had disappeared completely from the supernatant water 14 and 30 days after application from [redacted] and [redacted], respectively. The amount of methiocarb in the sediment, processed 60 min after application, was 2.6 % and 2.7 % AR and increased up to 22.3 % AR by day 14 in [redacted] and 46.1 % AR by day 7 in [redacted]. At study termination, 90 days after application, methiocarb had disappeared completely in the entire water/sediment system of [redacted] and declined to 7.7 % of the AR in [redacted].

At study termination 90 days post application, methiocarb disappeared completely in the entire water/sediment system of [redacted] and declined to 7.7 % of the AR in [redacted], respectively.
Three degradation products were identified with the following maximum occurances in water : Methiocarb phenol with 15.2 % AR by day 3 in the water of [redacted] and 6.8 % AR by day 7 in the water of [redacted] and methiocarb sulfoxide phenol with 34.1 % AR by day 7 in the water of [redacted] and 12.6 % AR by day 7 in the water of [redacted]. One minor degradation product identified in the water was methiocarb sulfone phenol, formed at a maximum of 4.2 % AR by day 90 in [redacted] and 0.4 % of the AR by day 30 in [redacted].
The only major degradation product found in the sediments was methiocarb phenol formed at a maximum of 13.7 % AR by day 30 in [redacted] and 16.5 % AR by day 14 in [redacted]. Two minor degradation products were detected in the sediment: Methiocarb sulfone phenol at a maximum of 1.5 % by day 62 in [redacted] and 0.9 % AR by day 30 in [redacted] and methiocarb sulfoxide phenol at a maximum of 7.0 % and 5.9 % AR by day 62 in [redacted] and [redacted].
Three major degradation products were detected in the entire water/sediment system, methiocarb phenol, methiocarb sulfoxide phenol and methiocarb sulfone phenol. Methiocarb phenol formed at a maximum of 19.2 % AR by day 3 in [redacted] and 18.4 % AR by day 14 in [redacted].
Methiocarb sulfoxide phenol formed at a maximum of 40.2 % AR by day 14 in [redacted] and 14.7 % AR by day 7 in [redacted]. Methiocarb sulfone phenol formed at a maximum of 5.2 % AR at study termination in [redacted] and 1.3 % of the AR by day 30 in [redacted].
The maximum amount of unidentified radioactivity was 4.4 % AR in [redacted] and 0.9 % AR in [redacted].

Table 7.2.2.3/04-3: Biotransformation of methiocarb, HPLC components expressed as % of AR (mean) in water/sediment system [redacted] under aerobic conditions

Compound	Source	DAT [days] 0	1	2	3	7	14	30	62	90
Methiocarb	Water	91.5	54.2	31.2	20.0	2.7				
	Sediment	2.6	14.9	14.5	14.6	6.9	3.0	0.7		
Methiocarb phenol	Water	5.7	11.7	13.6	15.2	3.9				
	Sediment		1.1	2.5	4.0	8.4	12.4	13.7	7.8	7.5
ROI2	Water			1.2	1.4	1.0				
	Sediment									
ROI3	Water					2.5	2.1	1.7	0.5	
	Sediment									
ROI4	Water					0.7				
	Sediment									
Methiocarb sulfone phenol	Water				0.5	2.4	1.1	2.3	3.1	4.2
	Sediment							1.1	1.5	2.4
ROI6	Water									
	Sediment			1.5	4.1					
Methiocarb sulfoxide phenol	Water		10.0	20.9	25.5	34.1	33.3	20.4	11.3	9.7
	Sediment		1.1	3.0	3.0	4.3	6.9	6.3	7.0	3.8
ROI8	Water				0.7	1.9	2.1	1.2		
	Sediment									
Diffuse radioactivity	Water						0.6	1.2	3.5	
	Sediment								0.9	
TER	Water	97.2	75.9	67.2	63.3	49.3	39.2	26.7	18.4	13.8
	Sediment	2.6	18.5	21.3	21.6	19.6	22.3	21.8	17.3	13.7
Total $^{14}CO_2$	Entire System	n.a.	0.2	1.7	1.4	1.9	8.5	14.9	20.8	25.3
Total volatile organics	Entire System	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NER	Sediment	0.3	4.3	11.3	15.1	27.2	32.6	37.9	46.3	45.2
Total % recovery	Water	97.2	75.9	67.2	63.3	49.3	39.2	26.7	18.4	13.8
	Sediment	2.6	18.5	21.3	21.6	19.6	22.3	21.8	17.3	13.7
	Entire System	100.2	99.5	101.5	101.3	98.0	102.6	101.4	102.7	97.9

blank boxes: values < LOD, DAT: days after treatment, NER: Non-extractable residues, TER: total extracted residues, ROI: regions of interest

Table 7.2.2.3/04-4: Biotransformation of methiocarb, HPLC components expressed as % of AR (mean) in water/sediment system [redacted] under aerobic conditions

Compound	Source	DAT [days] 0	1	3	7	14	30	62	90
Methiocarb	Water	93.7	60.5	38.8	16.7	4.0	0.4		
	Sediment	2.7	27.8	36.7	33.9	25.0	15.3	8.7	7.7
Methiocarb phenol	Water	3.8	3.6	6.1	6.8	1.9			
	Sediment			2.9	9.6	16.5	15.5	14.1	11.8
ROI2	Water			0.4	0.9				
	Sediment								
Methiocarb sulfone phenol	Water					0.4	0.3		
	Sediment						0.9	0.6	
ROI6	Water		1.4	1.2					
	Sediment		1.6	1.2	0.4				
Methiocarb sulfoxide phenol	Water		2.2	5.5	12.6	9.5	5.7	3.7	1.1
	Sediment			1.1	2.1	2.9	4.6	5.9	6.3
ROI8	Water					0.4			
	Sediment								
Diffuse radioactivity	Water					0.5	0.4		0.9
	Sediment								
TER	Water	97.5	67.6	52.1	37.4	16.7	6.5	3.7	2.0
	Sediment	2.7	29.4	41.8	46.1	44.4	35.7	29.3	20.7
Total $^{14}CO_2$	Entire System	n.a.	0.1	0.3	1.1	3.6	7.0	9.4	12.3
Total volatile organics	Entire System	n.a.	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
NER	Sediment	0.3	1.5	5.1	12.3	30.7	47.9	52.5	58.6
Total % recovery	Water	97.5	67.6	52.1	37.1	16.7	6.5	3.7	2.0
	Sediment	2.7	29.4	41.8	46.1	44.4	35.7	29.3	20.7
	Entire System	100.6	98.6	99.3	96.5	95.2	97.0	94.8	93.6

blank boxes: values < LOD, DAT: days after treatment, NER: Non-extractable residues, TER: total extracted residues, ROI: regions of interest

Both water/sediments s[redacted]d an excellent potential for the degradation of the test item. This also was supported by the high $^{14}CO_2$ formation rates. There is no potential for accumulation of methiocarb neither in the supernatant water nor in the submerged sediments.
The three degradation products were detected, methiocarb phenol, methiocarb sulfoxide phenol and methiocarb sulfone phenol. The major degradation products methiocarb phenol and methiocarb sulfoxide phenol declined until study termination not exceeding 11.8% of AR in all compartments, the minor transformation product Methiocarb sulfone phenol remained in [redacted] at a very low level (below 5% of AR until study termination).

The kinetic evaluation of methiocarb and its metabolites is covered under [redacted], K.; [redacted], S.; 2015; M-535504-01-1

Report: KCA 7.2.2.3/05 [redacted] S.; 2015; M-535504-01-1
Title: Methiocarb (MTC) and its metabolites - Kinetic Evaluation of Degradation and Dissipation Behaviour in Water-Sediment Systems According to FOCUS Kinetics Using the KinGUI 2.1 Tool
Report No.: EnSa-15-0603
Document No.: M-535504-01-1
Guideline(s): not applicable
Guideline deviation(s): not applicable
GLP/GEP: **no**

Previous evaluation: No previous evaluation, submitted for the purpose of active substance renewal.
Executive Summary

The degradation and dissipation behavior of methiocarb and its metabolites methiocarb phenol (MP, M03), methiocarb sulfoxide phenol (MSOP, M04), and methiocarb sulfone phenol (MSOOP, M05) in

the aquatic environment was investigated by kinetic evaluation of the aerobic water/sediment study [redacted], O.; 2005; M-259880-01-1.

The modelling and trigger endpoint DT50 values and formation fractions for methiocarb and its metabolites as they can be used in exposure assessments are summarized in Table 7.2.2.3/05-1 and Table 7.2.2.3/05-2.

Table 7.2.2.3/05-1: Modelling endpoints of methiocarb and its metabolites (dis. denotes dissipation)

	Compartment	Compound	Model (parent/ metabolite)	DT50$_{SFO}$ (days)
[redacted]	total system	methiocarb	SFO	1.9
	total system	methiocarb	DFOP	17.9 [3]
Geometric mean	total system	methiocarb		5.8
[redacted]	total system	methiocarb phenol	…/DFOP [4]	96.7 [5]
	total system	methiocarb phenol	DFOP/SFO [2]	54.1
Geometric mean	total system	methiocarb phenol		72.3
[redacted]	total system	methiocarb sulfoxide phenol	SFO/SFO [2]	46.2
	total system	methiocarb sulfoxide phenol	DFOP/SFO [2]	27.7
Geometric mean	total system	methiocarb sulfoxide phenol		35.7
[redacted]	dis. water	methiocarb	SFO	1.2
	dis. water	methiocarb	DFOP	2.8 [3]
Geometric mean	dis. water	methiocarb		1.9
[redacted]	dis. sed.	methiocarb	DFOP	6.2 [3]
	dis. sed.	methiocarb	HS	52.5 [5]
Geometric mean	dis. sed.	methiocarb		18.1

[1] endpoint from parent-only fit
[2] pathway fit, including all data, total system for methiocarb fit was conducted with model mentioned first
[3] back calculated from DFOP DT90 (DT90/3.32) since final residue < 10 % of applied
[4] parameter estimated from the decline from maximum
[5] slow phase

Table 7.2.2.3/05-2: Trigger endpoints of methiocarb and its metabolites (dis. denotes dissipation)

	Compartment	Compound	Model (parent/ metabolite)	DT50 (days)	DT90 (days)
[redacted]	total system	methiocarb	DFOP [1)]	1.8	7.0
[redacted]	total system	methiocarb	DFOP [1)]	7.2	58.1
[redacted]	total system	methiocarb phenol	…/DFOP[3)]	51.5	276.1
[redacted]	total system	methiocarb phenol	DFOP/SFO[2)]	54.1	179.8
[redacted]	total system	methiocarb sulfoxide phenol	SFO/SFO[2)]	45.7	151.7
[redacted]	total system	methiocarb sulfoxide phenol	DFOP/SFO[2)]	22.7	91.9
[redacted]	dis. water	methiocarb	DFOP	1.1	4.4
[redacted]	dis. water	methiocarb	DFOP	1.8	9.5
[redacted]	dis. sed.	methiocarb	DFOP	3.7	20.6
[redacted]	dis. sed.	methiocarb	HS	20.5	131.9

[1)] endpoint from parent-only fit
[2)] pathway fit, including all data, total system, for methiocarb fit was conducted with model mentioned first
[3)] Parameter estimated from the decline from maximum
[4)] Fit based on four datapoints only, no bi-phasic model considered

Table 7.2.2.3/05-3: Maximum occurrences of methiocarb and its metabolites as given by [redacted], O.; 2005; M-259880-01-1 in (%) of applied radioactivity (based on mean of replicates)

	Total system	Water	Sediment
methiocarb	-	36.7	
methiocarb sulfoxide phenol	40.2	34.1	7.0
methiocarb sulfone phenol	6.5	4.2	2.4
methiocarb phenol	19.1	15.2	16.5

The metabolite methiocarb sulfone phenol (MSOOP, M05) was not considered for kinetic analysis because it occurred only at marginal amounts (< 1 % of applied radioactivity) in the system [redacted] or at small amounts (≤10 % of applied radioactivity) which were increasing until the end of the study for the system [redacted].

MATERIAL AND METHODS

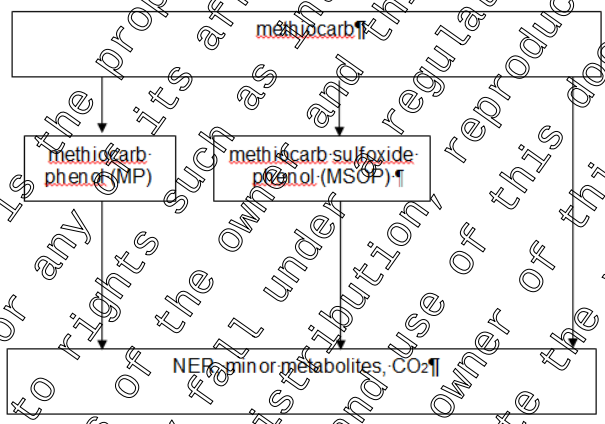
Residue data from the aerobic water/sediment degradation study [redacted], O.; 2005; M-259880-01-1 were used. The test substance was applied to two water/sediment systems [redacted] and [redacted] under aerobic conditions in the dark in the laboratory for up to 90 days in the dark at 20 °C.

The kinetic evaluation was performed following the recommendation of FOCUS (2006), FOCUS (2011), and FOCUS (2014) according to the respective decision flowcharts for the determination of trigger and modelling endpoints (Level I). Evaluations were performed for degradation in the total system and dissipation in the water and in the sediment phase. The dissipation and degradation rates were evaluated as modelling endpoints and as trigger endpoints.

The model fits and the statistical evaluation of the results was carried out with the software KinGUI version 2.1.
For the kinetic evaluation of the data a compartment model was developed Figure 7.2.2.3-1 including the metabolites methiocarb phenol (MP) and methiocarb sulfoxide phenol (MSOP).). The metabolite methiocarb sulfoxide (MSO) did not occur at all and was therefore not considered for kinetic analysis
The metabolite methiocarb sulfone phenol (MSOOP) was not considered for kinetic analysis because it occurred only at marginal amounts (< 1 % of applied radioactivity) in the system [redacted] or at small amounts (< 10 % of applied radioactivity) which were increasing until the end of the study for the system [redacted].

Four different kinetic models were employed: single first-order (SFO), first-order multiple-compartment (FOMC, Gustafson-Holden), the hockey-stick model (HS, DFOS = double first order sequential), and the bi-exponential model (DFOP = double first order parallel). The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fit, chi^2 (χ^2) test, t-test significance, correlation analysis and standard deviation.

Figure 7.2.2.3-1: Compartment model used for the kinetic analysis



Modelling endpoints: For the derivation of modelling endpoints, simple first-order (SFO) kinetics were tested first, then bi-phasic models. Finally the model was chosen which is visually acceptable and provides a significantly better fit in terms of chi^2-error.
Modelling endpoints for parent and metabolites were derived from pathway fits. This method was chosen to safeguard consistency between parent degradation and metabolite formation. Typically higher tier exposure calculations consider the relevant metabolic pathway including simultaneous degradation and formation of the compounds. Thus pathway fits are preferred to ensure also consistency between kinetic evaluation and use in exposure calculations. If a pathway fit did not deliver an acceptable fit for a metabolite, decline fits from maximum were considered where feasible.

Trigger endpoints:
For the parent substance methiocarb, trigger endpoints were derived from the parent only fits considering SFO, FOMC and DFOP. For the metabolites, trigger endpoints were derived from pathway fits using the model derived from the parent-only fits for parent. If a pathway fit did not deliver an acceptable fit for a metabolite, decline fits from maximum were considered where feasible.

RESULTS

Model selection, degradation kinetics total system

Methiocarb

Parent only fits were considered for the derivation of trigger endpoints. Pathway fits were considered for the derivation of modelling endpoints to safeguard consistency between the degradation of the parent and the formation of the metabolites. Generally, the differences obtained between parent only, and pathway fits for parent were marginal.

[redacted]: The SFO fit provided a good fit to the measured residue data of methiocarb and a statistically significant degradation rate. The residuals did not show systematic deviations and the chi^2-error was far below the recommended value of 15 %. Thus, the SFO model was selected as the appropriate model to obtain modelling endpoints.
All bi-phasic models yielded a slightly higher goodness of fit than SFO where DFOP was selected as best fit model with minimum chi^2-error to derive trigger endpoints.

[redacted]: The residues show a relatively clear bi-phasic pattern with a reduced decline in the later experimental period. The SFO fit could not describe this behavior and therefore was not considered visually acceptable. All bi-phasic models yielded a substantially higher goodness of fit than SFO where DFOP was selected as best fit model with minimum chi^2-error to derive both, modelling and trigger endpoints. Both DFOP rate parameters were highly significant (pathway and parent only fit).

Table 7.2.2.3/05-4 Rate of degradation/dissipation in aquatic (aerobic) laboratory studies methiocarb, Modelling endpoints according to FOCUS Level I

methiocarb	Distribution (max. sed 36.7 % after 3 d)									
Water / sediment system	pH water phase	pH sed [a]	t. °C	DT_{50} /DT_{90} whole sys.	St. (χ^2)	DT_{50} /DT_{90} water	St. (χ^2)	DT_{50} /DT_{90} sed	St. (χ^2)	Method of calculation whole sys/ water/sed
[redacted] [d]	7.6	7.1	20	1.9/6.3	3.8	1.2/4.0	3.0	6.2[b]/20.6	0.7	SFO/SFO/ DFOP
[redacted] [d]	8.0	6.6	20	17.9[b]/59.4	2.0	2.8[b]/9.5	0.6	52.5[c]/174.2	4.2	DFOP/ DFOP/HS
Geometric mean at 20°C				5.8/19.4		1.9/6.2		18.1/59.9		

[a] Measured in calcium chloride solution
[b] DT_{50} back-calculated from $DT90/DisT_{90}$ as DT90/3.32
[c] Slow phase DT50/DisT50
[d] [redacted]; 2005; M-259880-01-1

Table 7.2.2.3/05-5 Rate of degradation/dissipation in aquatic (aerobic) laboratory studies methiocarb, Trigger endpoints according to FOCUS Level I

methiocarb	Distribution (max. sed 36.7 % after 3 d)									
Water / sediment system	pH water phase	pH sed [a]	t. °C	DT_{50} /DT_{90} whole sys.	St. (χ^2)	DT_{50} /DT_{90} water	St. (χ^2)	DT_{50} /DT_{90} sed	St. (χ^2)	Method of calculation whole sys/ water/sed
[redacted] [b]	7.6	7.1	20	1.8/7.0	2.2	1.1/4.4	1.0	3.7/20.6	0.7	all DFOP
[redacted] [b]	8.0	6.6	20	7.2/58.1	2.0	1.8/9.5	0.6	20.3/131.9	4.2	DFOP/ DFOP/HS
Geometric mean at 20°C										

[a] Measured in calcium chloride solution
[b] [redacted].; 2005; M-259880-01-1

methiocarb phenol (MP)

Table 7.2.2.3/05-6 Rate of degradation/dissipation in aquatic (aerobic) laboratory studies methiocarb phenol (MP), Modeling endpoints according to FOCUS Level I

methiocarb phenol (MP)	Distribution(max in water 15.2 % after 3 d, max. sed 16.5 % after 14 d. max in total system 19.1 % after 3 days)									
Water / sediment system	pH water phase	pH sed [a]	t. °C	DT_{50} /DT_{90} whole sys.	St. (χ^2)	DT_{50} /DT_{90} water	St. (χ^2)	DT_{50} /DT_{90} sed	St. (χ^2)	Method of calculation whole sys/ water/sed
[redacted] [d]	7.6	7.1	20	96.7 [b] [c]/321.1	9.5					DFOP
[redacted] [d]	8.0	6.6	20	54.1/179.7	10.3					SFO
Geometric mean at 20°C [b]				72.3/240.2						

[a] Measured in calcium chloride solution
[b] Parameter estimated from the decline from maximum
[c] Slow phase DT50/DisT50
[d] [redacted].; 2005; M-259880-01-1

Table 7.2.2.3/05-7 Rate of degradation/dissipation in aquatic (aerobic) laboratory studies methiocarb phenol (MP), Trigger endpoints according to FOCUS Level I

methiocarb phenol (MP)										
Water / sediment system	pH water phase	pH sed [a]	t. °C	DT_{50} /DT_{90} whole sys.	St. (χ^2)	DT_{50} /DT_{90} water	St. (χ^2)	DT_{50} /DT_{90} sed	St. (χ^2)	Method of calculation whole sys/ water/sed
[redacted] [b]	7.6	7.1	20	51.5[c]/276.1	9.5					DFOP
[redacted] [b]	8.0	6.6	20	54.1/179.8	10.3					SFO
Geometric mean at 20°C										

[a] Measured in calcium chloride solution
[b] [redacted] 2005; M-259880-01-1
[c] Parameter estimated from the decline from maximum

Methiocarb sulfoxide phenol (MSOP)

Table 7.2.2.3/05-8 Rate of degradation/dissipation in aquatic (aerobic) laboratory studies methiocarb sulfoxide phenol (MSOP), modelling endpoints according to FOCUS Level I

methiocarb sulfoxide phenol (MSOP)	Distribution(max in water 34.1 % after 7 d, max. sed 7.0 % after 62 d, max in total system 40.2 % after 14 days) kinetic formation fraction (k_f/k_{dp}):									
Water / sediment system	pH water phase	pH sed [a]	t. °C	DT_{50} /DT_{90} whole sys.	St. (χ^2)	DT_{50} /DT_{90} water	St. (χ^2)	DT_{50} /DT_{90} sed	St. (χ^2)	Method of calculation Whole sys/ water/sed
[redacted] [d]	7.6	7.1	20	46.2/153.3	5.7					SFO
[redacted] [d]	8.0	6.6	20	27.7/91.9	20.6					SFO
Geometric mean at 20°C				35.7/118.7						

[a] Measured in calcium chloride solution
[b] Parameter estimated from the decline from maximum
[c] Slow phase DT50/Dis150
[d] [redacted].; 2005; M-259880-01-1

Table 7.2.2.3/05-9 Rate of degradation/dissipation in aquatic (aerobic) laboratory studies methiocarb sulfoxide phenol (MSOP), Trigger endpoints according to FOCUS Level I

methiocarb sulfoxide phenol (MSOP)										
Water / sediment system	pH water phase	pH sed [a]	t. °C	DT_{50} /DT_{90} whole sys.	St. (χ^2)	DT_{50} /DT_{90} water	St. (χ^2)	DT_{50}/DT_{90} sed	St. (χ^2)	Method of calculation Whole sys./ water/sed
[redacted] [b]	7.6	7.1	20	45.7/151.7	6.3					SFO
[redacted] [b]	8.0	6.6	20	27.7/91.9	20.6					SFO
Geometric mean at 20°C										

[a] Measured in calcium chloride solution
[b] [redacted]; 2005; M-259880-01-1

Modelling endpoints – Degradation and dissipation Kinetics

The resulting SFO modelling half-lives ($DT50_{SFO}$) of methiocarb and its metabolites have been reported in the above tables and are listed again in Table 7.2.2.3/05-10 to Table 7.2.2.3/05-12 for the total system, in Table 7.2.2.3/05-13 for the dissipation in the water phase and in Table 7.2.2.3/05-14 for dissipation in the sediment phase with the optimized degradation parameters.

Degradation Kinetics Total System

Methiocarb

Table 7.2.2.3/05-10 Optimized degradation parameters of methiocarb total system

	Model	k1 (1/days)	k2 (1/days)	g	$DT50_{SFO}$ (days)
[redacted]	SFO	0.3648	-	-	1.9
[redacted]	DFOP	0.1340	0.0124	0.7923	17.9[1)]

[1)] back calculated from DFOP DT90 (DT90/3.32) since final residue < 10 % of applied

Methiocarb phenol (MP)

Table 7.2.2.3/05-11 Optimized degradation parameters of methiocarb phenol total system. The term ff_{MTC-MP} denotes the formation fraction from compound methiocarb to methiocarb phenol

	Model	k1 (1/days)	k2 (1/days)	$DT50_{SFO}$ (days)	ff_{MTC-MP}
[redacted]	./DFOP[1)]	5.8340	0.0072	96.7[3)]	-[2)]
[redacted]	DFOP/SFO	0.0128		54.1	0.295

[1)] decline fit from maximum
[2)] was not considered valid since pathway fit for metabolite was rejected
[3)] slow phase

Methiocarb sulfoxide phenol (MSOP)

Table 7.2.2.3/05-12 Optimised degradation parameters of MSOP total system. The term $ff_{MTC-MSOP}$ denotes the formation fraction from compound methiocarb to methiocarb sulfoxide phenol

	Model	k (1/days)	DT50SFO (days)	$ff_{MTC-MSOP}$
[redacted]	SFO/SFO	0.0150	46.2	0.449
[redacted]	DFOP/SFO	0.0251	27.7	0.250

Dissipation Kinetics Water Phase

Methiocarb

Table 7.2.2.3/05-13 Optimised degradation parameters of methiocarb water phase, decline fit from maximum

	Model	k1 (1/days)	k2 (1/days)	g	DT90 (days)	$DT50_{SFO}$ (days)
[redacted]	SFO	0.5743			4.0	1.2
[redacted]	DFOP	2.8570	0.2091	0.2785	9.5	2.8[1)]

[1)] Back calculated from DFOP DT90 (DT90/3.32) since final residue <10 % of applied

Dissipation Kinetics Sediment Phase

Methiocarb

Table 7.2.2.3/05-14 Optimised degradation parameters of methiocarb, decline fit from maximum

	Model	k1 (1/days)	k2 (1/days)	g/f	DT90 (days)	$DT50_{SFO}$ (days)
[redacted]	DFOP	0.3109	0.0664	0.6105	20.6	6.2[1)]
[redacted]	HS	0.0342	0.0132	26.6	131.9	52.5[2)]

[1)] Back calculated from DFOP DT90 (DT90/3.32) since final residue <10 % of applied
[2)] Slow phase

CA 7.2.2.4 Irradiated water/sediment study

Report: KCA 7.2.2.3/02; [redacted]; 2000; M-027403-02-1
Title: Aerobic metabolism of methiocarb in an aquatic model ecosystem
Report No.: MR-64/99
Document No.: M-027403-02-1
Guideline(s): BBA Guideline for Testing of Plant Protectants in the Registration Procedure, Part IV, 5-1, 1990; Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behaviour in the Environment), July 14, 1995; FOCUS Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995
Guideline deviation(s): not specified
GLP/GEP: **yes**

Previous evaluation: In DAR for original Annex I inclusion (2005).

Assessment on suitability of study: The recommendation is to withdraw this study from the European evaluation.
The study was conducted with methiocarb slug pellet, a formulation not further supported. The study design was trying to use the conditions of the water /sediment study with irradiation to imitate the behavior of the methiocarb pellet under environmental conditions. At the previous evaluation the

endpoint used from this study in the risk assessment was the DT50 value of 5.7 days for pellet degradation used in the PECsoil assessment. At the time no data towards the exposure in surface water were taken from this study. Subsequently a new guideline study [redacted].; 2005; M-259880-01-1 was conducted to address this requirement.

MATERIALS

1. Test Item

Test Item	Methiocarb
Description:	Formulated as pellet RB3
Lot/Batch:	H 3213 GR 00313/2015
Specific Activity:	n/a
Radiochemical Purity:	n/a
Chemical Purity:	n/a
Amount of ai/pellet:	3%

2. Water/sediment

The sediment characteristics are summarised in Table 7.2.2.3/02-1.

Table 7.2.2.3/02-1: Physico-chemical properties of test sediment

Origin	[redacted]
Textural class	Loam
Textural analysis (USDA)	
2000 - 50 µm	36.0%
50 - 2 µm	48.1%
< 2 µm	15.9%
pH (KCl)	6.5
Organic carbon (%)	4.4
Total N [mg/100 g dry soil]	400
Total P [mg/kg dry soil]	920
$CaCO_3$ [%]	<0.01
Moisture content [%]	50.1%
Cation Exchange Capacity [meq/100 g dry soil]	14

The sediment was sampled and stored in mesocosm ponds. The aqueous sediment was passed through a 2mm mesh sieve, mixed and stored frozen. The water used was from the research laboratory carrying out the study (deionized, pH 7.9).

STUDY DESIGN AND METHODS

A water/sediment study on methiocarb formulated as pellet RB3 was conducted on a water/sediment system of a pond ([redacted], Germany). Incubation took place in bright/dark aerobic conditions with periods of 16:8 hours, respectively, using a light intensity of approximately 1000 lux. The lamp used was stated to be a fluorescent tube with the brand name "Philips TLD Secura 18W/840". No further information was available on the light source.

The sediment was filled into test vessels to a height of 3 cm. Water was added to a total height of 30 cm. The vessels were incubated for 27 days prior to the application of the active substance. The applied amount of the test product was 1, 2, 5 or 9 non-radiolabelled pellets per test vessel, corresponding to 20, 50, 100 and 200 % of an application rate of 5 kg/ha of the formulated product. Aerobic conditions were maintained throughout the study. Sampling dates were 1, 3, 7, 14, 28, 56 and

98 days after application. At each interval the water/sediment samples were analysed by HPLC/MS/MS for methiocarb and metabolites methiocarb sulfoxide (M01), methiocarb sulfone (M02), methiocarb sulfoxide phenol (M04), methiocarb sulfone phenol (M05) and methiocarb phenol (M03). Sediment samples were extracted with acetonitrile/water/acetic acid. Water samples were directly injected into the HPLC instrument. The mean recoveries for all compounds were in the range 91.2 to 98.5 % of the applied amount. The limit of quantification was stated as 0.1 µg/kg for all compounds in the sediment phase, with the exception of methiocarb phenol (M03) where the LOQ in sediment was stated to be 0.3 µg/kg. The sediment LOQ values were theoretical due to fortified tests only being carried out at 1 µg/kg for all compounds except methiocarb phenol (M03). The mean recoveries for compounds tested in sediment at 1 µg/kg were in the range 91.2 – 98.5 %. The mean recovery for methiocarb phenol (M03) in sediment at 0.3 µg/kg was 82.6 %. No specific concurrent recovery tests were carried out in the water phase. The LOQ was stated to be 0.1 µg/kg for all compounds analysed based on a repeatability test using standard injections in the range 0.1 to 1.0 µg/kg. Based on the lowest application rate of the test substance at 1 kg/ha the LOQ was equivalent to a maximum of 0.0002% of the amount of active substance estimated to reach the sediment.

RESULTS AND DISCUSSION

The results are presented in Table 7.2.2.3/02-2. In the exaggerated dose experiment (application rate corresponding to 200 %) they amounted to a maximum value of 22.1 % (methiocarb phenol (M03), day 14) and to 23.6 % (methiocarb sulfoxide phenol (M04), day 28). In the sediment methiocarb phenol (M03) was observed with a maximum amount of 9.2 % (day 56) of the applied methiocarb. All other metabolites included in the analytical method were near or at the limit of quantification (LOQ).

Table 7.2.2.3/02-2 Distribution of methiocarb and metabolites after application of the formulated product (P03) at an exaggerated use rate of 200 % in an aerobic water/sediment system (% of applied amount)

Sampling Interval [days]	Water			Sediment	
	methiocarb	methiocarb phenol (M03)	methiocarb sulfoxide phenol (M04)	methiocarb	methiocarb phenol (M03)
[redacted]					
7	30.1	6.1	3.0	9.5	0.6
14	33.7	22.1	8.0	15.6	1.5
28	23.1	15.6	21.3	18.6	5.1
56	0.5	1.3	23.6	9.4	9.2
98	0.1	0.2	8.8	4.1	5.9

Degradation kinetics were calculated assuming first order kinetics using ACSL Optimize version 1.2. The results are presented in Table 7.2.2.3/02-3.

Table 7.2.2.3/02-3 DT_{50}- and DT_{90} values for the surface water and the entire water/sediment system

System [redacted]	Compartment	DT50 [days]	Order
Methiocarb	Surface water	7.8	1st
	Entire system	15.3	1st
Methiocarb phenol (M03)	Surface water	5.1	1st
	Entire system	12.0	1st

Report: KCA 7.2.2.3/03; [redacted]; 2000; M-029744-01-1
Title: Calculation of DT-50 values of methiocarb and its metabolite methiocarb-phenol in water and sediment based on results of a water/sediment study
Report No.: MR-108/00
Document No.: M-029744-01-1
Guideline(s): not applicable
Guideline deviation(s): not applicable
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005)

Assessment on suitability of study: This kinetic evaluation will be redundant. It was conducted on the basis of [redacted], H.; 2000; M-027403-02-1, the irradiated water/sediment study using formulated methiocarb pellet RB 3 as test material. [redacted], H.; 2000; M-027403-02-1 will not be resubmitted as the formulation will not be supported (see KCA 7.2.2.3/2).

METHODS

Mathematical evaluation of the study [redacted]; 2000; M-027403-02-1 was carried out using the ACSL Optimize Software package. The experimental results were analysed in two different ways. First a simplified scheme was utilized aiming at the generation of dissipation times for the total system or water phase only. Additionally a more complex system was used, which took the concentrations in both the water and sediment phases into account.

RESULTS AND DISCUSSION

The calculation resulted in the rate constants and DT50 values presented in Table 7.2.2.3/03-1.

Table 7.2.2.3/03-1 DT50 values of pellets, methiocarb and methiocarb phenol in a water/sediment study

"simplified approach"	Whole system			Water phase		
	Pellets	methiocarb	Methiocarb phenol (M03)	Pellets	methiocarb	Methiocarb phenol (M03)
Rate constant (d^{-1})	0.093548	0.0454	0.0580	0.093548	0.0883	0.135
DT50	7.4	15.3	12.0	8.8	7.9	5.1
"complex approach"	Whole system			Water phase		
	Pellets	methiocarb	Methiocarb phenol (M03)	Pellets	methiocarb	Methiocarb phenol (M03)
Rate constant (d^{-1})	0.12149	0.0765	0.101	-	0.0345	0.0319
DT50	5.7	9.1	6.9	-	20.1	21.7

Summary of the fate and behavior in water and sediment

Based on the results of the laboratory degradation studies investigating methiocarb it was clearly demonstrated that methiocarb is rapidly degraded in aquatic systems and thoroughly metabolised to the final degradation product carbon dioxide. Major metabolites involved in the degradation are, methiocarb phenol (M03), methiocarb sulfoxide phenol (M04) and methiocarb sulfoxide (M01)

The degradation pathway of methiocarb in the aquatic environment is shown in Figure 7.2.2.4-1. A summary of maximum occurrences in soil of major degradation products derived from laboratory studies is shown in Table 7.2.2.4-1.

Figure 7.2.2.4-1 Proposed degradation pathway of methiocarb in water and sediment

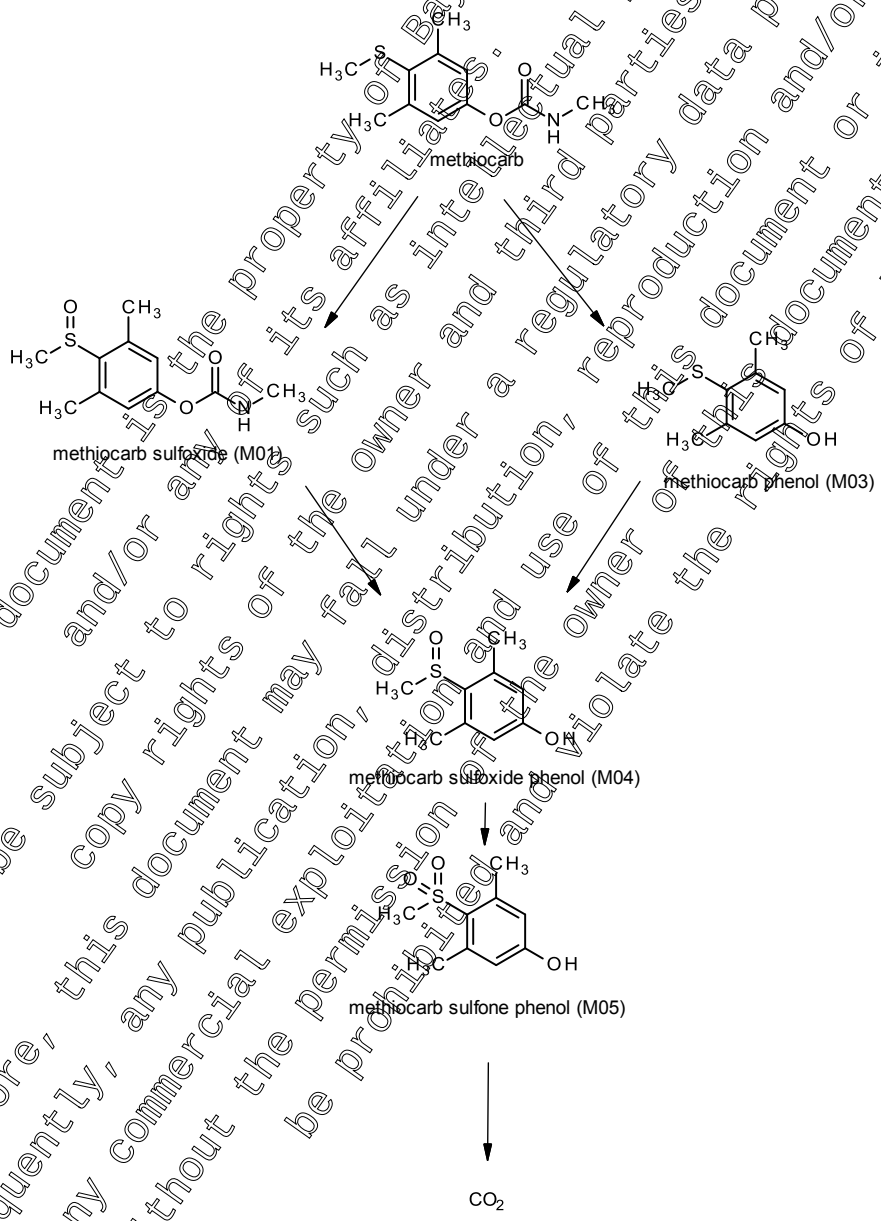


Table 7.2.2.4-1: Summary of maximum occurrences in soil of major methiocarb degradation products derived from laboratory studies (in percentage of applied radioactivity [% AR])

Degradation Product	Hydrolysis [% AR]	Aqueous photolysis [% AR]	Aerob water /sediment [% AR]	Anaerob water /sediment [% AR]
methiocarb sulfoxide (M01)	9.0	25.1	-	
methiocarb phenol (M03)	82	-	15.2 (water), 16.5 (sediment), 19.1 (total system)	45 (water), 48 (sediment), 76 (total system)
methiocarb sulfoxide phenol (M04)	10.5	3.4	34.1 (water), 7.0 (sediment), 40.2 (total system)	
methiocarb sulfone phenol (M05)	-		4.2 (water), 2.4 (sediment), 6.5 (total system)	

CA 7.2.3 Degradation in the saturated zone

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

CA 7.3 Fate and behaviour in air

CA 7.3.1 Route and rate of degradation in air

Report: KCA 7.3.1/01; [redacted], 2000, M-040706-01-1
Title: Calculation of the chemical lifetime of methiocarb in the troposphere
Report No.: MR-14/00
Document No.: M-040706-01-1
Guideline(s):
Guideline deviation(s): --
GLP/GEP: **no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

The chemical lifetime methiocarb in the air was calculated to the model of Atkinson, using AOPWIN-software (version 1.87).
The half-life of methiocarb in air was calculated to be 9.5 hours. This corresponded to a chemical lifetime in air of 13.8 hours with respect to the OH radical reaction only. These calculations assumed an OH radical concentration of 1.5 x 10^6 radicals cm^{-1}. A more conservative assessment of the overall OH radical rate constant, i.e. only considering half of the estimated rates in case of the assumed values for modelling would result in a maximum chemical life time for methiocarb of 20 hours in the air.
These estimates do not consider any contribution of attack by other radicals (e.g. nitrate radicals).

CA 7.3.2 Transport via air

Report:	KCA 7.3.2/01; [redacted].; 2000; M-040706-01-1
Title:	Calculation of the chemical lifetime of methiocarb in the troposphere
Report No.:	MR-314/00
Document No.:	M-040706-01-1
Guideline(s):	--
Guideline deviation(s):	--
GLP/GEP:	**no**

Previous evaluation: In DAR for original Annex I inclusion (2005).

See summary under CA 7.3.1

Methiocarb has a vapour pressure < 10^{-4} Pa (see CA 2.2.2). It is not expected to significantly volatilise. Furthermore its vapour pressure is below the trigger value of 10^{-4} Pa applicable for a substance applied as seed treatment only to soil.
The calculated photochemical oxidative degradation half-life of 3.8 hours indicates that methiocarb is unlikely to be subject to long-range transport, even if it were emitted into the atmosphere.

CA 7.3.3 Local and global effects

Local and global effects of methiocarb were not considered since its half-life in air is < 2 days.

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The route and rate of degradation of methiocarb had been investigated after application of radiolabeled active substance to various soil and aquatic test systems in the laboratory. Following the observation of metabolites and degradation products above the trigger values set in the relevant tests, those are potential residues to occur in the environment thus to be considered in the corresponding environmental risk assessments.

Soil/ground water:	methiocarb, methiocarb sulfoxide (M01), methiocarb sulfoxide phenol (M04), methiocarb sulfone phenol (M05), methiocarb methoxy sulfone (M10),*
Surface water/sediment:	methiocarb, methiocarb sulfoxide (M01),methiocarb phenol (M03), methiocarb sulfoxide phenol (M04), methiocarb sulfone phenol (M05), methiocarb methoxy sulfone (M10)
Air:	methiocarb

* The metabolite methiocarb phenol (M03) occurs in soil only under strictly anaerobic conditions. Under aerobic conditions methiocarb phenol (M03) is a metabolite detected in one soil with 2 % on day 0 only and not detected at all in 4 further soils.
It was considered whether or not a calculation of predicted environmental concentrations in soil and groundwater was required for methiocarb phenol (M03) whenever prolonged strictly anaerobic conditions could be present shortly after application.
The intended use of methiocarb is a seed treatment in maize. Growth of the maize seed will be severely inhibited under anaerobic conditions due to shortage of oxygen. Sites where anaerobic conditions may occur during the early vegetation period of maize in late spring and summer will produce uneconomic yields and are consequently not used to grow maize. It is therefore extremely unlikely that metabolites which are only formed in an anaerobic environment occur under realistic use conditions. Therefore the metabolite methiocarb phenol (M03) is not considered relevant for soil and groundwater risk assessment.

CA 7.4.2 Definition of the residue for monitoring

The residue definition for monitoring purposes in soil is methiocarb and methiocarb sulfoxide (M01). (methiocarb sulfoxide (M01) cannot be concluded as sufficiently less toxic than parent methiocarb in the terrestrial environment, please refer to MCP 10.4.1).

The residue definition for monitoring purposes in groundwater is methiocarb and methiocarb sulfoxide (M01). (methiocarb sulfoxide (M01) cannot be concluded as sufficiently less toxic than parent methiocarb in the terrestrial environment, please refer to MCP 10.4.1).

The residue definition for monitoring purposes in surface water is methiocarb and methiocarb sulfoxide (M01). (methiocarb sulfoxide (M01) cannot be concluded as sufficiently less toxic than parent methiocarb in the aquatic environment, please refer to MCP 10.2).

The residue definition for monitoring purposes in sediment is methiocarb and methiocarb sulfoxide (M01). Methiocarb sulfoxide (M01) cannot be concluded as sufficiently less toxic than parent methiocarb in the aquatic environment, please refer to CP 10.2.

The residue definition for monitoring purposes in air is methiocarb only.

CA 7.5 Monitoring data

No formal monitoring program was requested or required to address this point for methiocarb or its major residue methiocarb sulfoxide in soil and water in the EU.

[redacted]ver, there are some published data outside Bayer CropScience available.

The literature review on methiocarb and its degradation products resulted in a list of 5 peer reviewed articles that are briefly summarised here.

	Short method	Short evaluation
[redacted].; 2014; M-479092-01-1	Extensive survey on more than 40 pesticides carried out in 2010 and 2011 in 16 sewage treatment plants (STPs) of Ebro, Guadalquivir, Jucar and Llobregat Rivers (Spain).	The occurrence of methiocarb in wastewater in 2010 was detected in concentrations of 3.77 – 5.74 (mean 4.73) ng/L with a frequency of 20 %. In 2011 the concentration ranged from 1.26 to 105.31 (mean 14.92) ng/L with a frequency of about 31.25 %. Methiocarb was not detected in sludge samples.
[redacted].; 2013; M-479404-01-1	Combined use of liquid chromatography triple quadrupole mass spectrometry and liquid chromatography quadrupole time-of-flight mass spectrometry.	Analytical method – applied for method validation and some non target analysis of surface water from 4 rivers – no information on sampling year. Indication that presented data is a subset of results from [redacted], J.; [redacted], Y.; [redacted], A.; [redacted], C.; 2014; M-479092-01-1 therefore no further summaries are presented.
[redacted].; 2013; M-474497-01-2	The occurrence of 50 currently used pesticides and their transformation products in surface and waste waters, sediment and fish in the Guadalquivir River Basin was determined in 2010 and 2011. After selective sample extraction, pesticides were identified and quantified by liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS).	The pesticide methiocarb was not found in sediment samples from 2010 and reported as “occasionally detected” in samples from 2011. In river water samples from 2010 and 2011 methiocarb was reported as not to occur with a higher frequency and no measured residues were presented. In effluent samples from waste water treatment plants methiocarb was found in one of five samples with a concentration of 5.7 ng/L. there is an indication that this last value is a subset of results from [redacted], J.; [redacted], Y.; [redacted], A.; [redacted], C.; 2014; M-479092-01-1 therefore no further summaries are presented.

	Short method	Short evaluation
[redacted] 2014; M-492722-01-1	This study focused on the presence and distribution of pesticides in water and fish in the [redacted] River with sampling in Oct 2010, using the first extensive optimization and application of the QuEChERS method to determine pesticides in freshwater fish.	Methiocarb was neither detected in surface water nor in fish.
[redacted].; 2015; M-530612-01-1	In this monitoring study the occurrence of methiocarb in water and sediment samples of Turia and [redacted] Rivers ([redacted] Community, Eastern Spain) was assessed for a period of two consecutive years, 2010/2011 and 2012/2013.	Methiocarb was only detected at a concentration of < 0.01 ng/L in water samples in 2010 and 2013. In sediment samples it was only detected 2011 in concentration of < 0.01 ng/L.

The data presented are showing that in the few cases methiocarb is detected in the surface water of rivers, it is below < 0.01 ng/L. The data are created at only single sampling campaigns (e.g. October per year).
When water from sewage treatment plants was analysed values of 5.7 ng/L to slightly higher values were determined in [redacted] 2014; M-479092-01-1. [redacted]ver, no detailed data were presented in this study. For the supported use of methiocarb as seed treatment an entry via sewage treatment plants is highly unlikely.

On a whole this set of 5 peer reviewed articles does not provide data that influence the risk assessment in the environment for methiocarb.

Information on effect of water treatment processes on nature of residues when surface water is abstracted for drinking water

Question from RMS
Need to assess the effect of water treatment on the residue.

Answer of Bayer:
The request, complex by nature, is to be found in EC Regulation 1107/2009. [redacted]ver, it was not subject to specification at EU and Member State level, for example, in times of inclusion into Commission Regulation 283/2013 defining actual data requirements or, in Commission Regulation 2013/C95/01 defining and specifying the tests to serve as the data basis for evaluation. Beyond the general data requirements there was no specific guidance or interpretation given in the EU or national context. Even if standardized and reliable data were available it would be another step to define the complete steps in risk assessment including results of potential tests, their interpretations and to draw conclusions based on realistic scenarios that remain to be developed.

In the absence of tests, guidelines and guidance, there remain two further approaches towards the question from the RMS:

a) The PECgw concentrations for methiocarb are < 0.001 µg/L and its metabolites 0.003 µg/L at most and the PECsw concentrations for methiocarb and its metabolites are < 0.001 µg/L, thus in this no residue situation any question towards potential residues after water treatment processes is not relevant.

b) [redacted]ver, if at all of relevance, there are publications on the chlorination of methiocarb available from the public domain. Please find attached references and further down short summaries to M-495746-01-1, [redacted] C.; 2013. These publications had not been considered for the literature review as the authors investigated the breakdown of methiocarb catalysed by chlorination. This route of degradation via disinfectants was considered artificial and not of relevance for the exposure assessment of NTOs.
In the context of the specific question towards the effect of water treatment the results show that the chlorination of an aqueous solution with chlorine dioxide in aqueous solution or free chlorine or monochloramine lead in the first step to quantifiable amounts of methiocarb sulfoxide phenol (M04) or methiocarb sulfone phenol (M05), then to methiocarb sulfoxide phenol (M04) and methiocarb sulfone phenol (M05) metabolites that are known in the proposed pathways depicted in the MCA section 7 fate and behaviour in the environment for soil [redacted]; 2015; M-541464-01-1 (Figure 7.1.1-1 Proposed degradation pathway of methiocarb in soil) and in water and sediment (Figure 7.2.2.4-1 Proposed degradation pathway of methiocarb in water and sediment). Applying the conditions of the chlorination to the phenols lead to non-detectable further degradation products. Thus these publications suggest that the chlorinations of methiocarb lead to only known metabolites.

Report:	KCA 7.5/06; [redacted].; 2010; M-495746-01-1
Title:	Kinetics and mechanism for methiocarb degradation by chlorine dioxide in aqueous solution
Report No.:	M-495746-01-1
Document No.:	M-495746-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

EXECUTIVE SUMMARY

The kinetics and mechanism for methiocarb (MC) degradation by aqueous ClO_2 were investigated under simulated water treatment conditions. Experimental results indicate that the reaction between MC and ClO_2 was of second-order overall, and the rate constant rapidly increased from 0.56 to 4.5 $M^{-1/}s^{-1}$ as the solution pH increased from 6.0 to 9.1 at 23°C. The activation energy was determined to be 75 kJ/mol^{-1} in the studied temperature range of 7-35°C. Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were quantified to be the major byproducts from methiocarb degradation. Unlike the sequential formation of sulfoxide and sulfone during the oxidation of many thioethers, the two byproducts were formed simultaneously during methiocarb degradation by ClO_2. The solution pH significantly affected the type and quantity of the degradation byproducts. For example, at pH 6.5 MCX and MC Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) accumulated as the reaction proceeded and finally accounted for 71 percent and 28 percent of methiocarb degraded, resp.; while at pH 8.6 three more minor byproducts were identified. Though ClO_2 can effectively oxidize methiocarb in water, the significant increase in toxicity raises a potential risk to consumers.

MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Methiocarb
Active substance(s):	Methiocarb
Chemical state and description:	not reported
Source of test item:	[redacted] GmbH
Batch number:	not reported
Purity:	98.5%
Storage conditions:	not reported
Water solubility:	not reported

B. Study design and methods

1. Reactivity experiments

Temperature:	7 - 35°C
pH:	pH 6.53, 7.48, 8.57 and 6 – 9.1
Duration:	various 10 h or 120 minutes
Test medium:	The stock solutions of methiocarb (MC), methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were prepared individually in methanol at a concentration of about 280–300 mg L^{-1}. The mixed standards of MC, MCX and MCN were prepared in 0.1 M HCl solutions to prevent hydrolysis. Sodium chlorite was obtained from Alfa Aesar (tech. nominally 80%). The pure stock solution of ClO_2 was prepared from gaseous

	ClO_2 by slowly adding dilute H_2SO_4 to a $NaClO_2$ solution. Impurities such as chlorine were removed from the gas stream by a $NaClO_2$ scrubber and the gaseous ClO_2 was passed into ultra water in a steady stream of N_2 (APHA, 2005). The ClO_2 stock solutions (ca. 350 mg L^{-1} for kinetic study and 1350 mg L^{-1} for mechanism study) were stored in a brown bottle at 4 °C in a refrigerator. All the reaction solutions were buffered with 10 mM phosphate in the pH range of 6.0–9.1. High purity Milli Q-water was used to prepare the aqueous solutions.
Light source	Brown glass bottles
Test conduction: chlorine dioxide:	Methiocarb degradation by ClO_2 was studied under pseudo-first-order conditions with at least 10-fold excess of ClO_2 (21–63 µM). To restrain methiocarb from hydrolyzing, the aqueous reaction solution of methiocarb (100 mL) was freshly prepared by spiking 0.16 mL of its stock solution (in methanol) to reach a concentration of 2 µM. A preliminary experiment had shown that the presence of methanol (0.16% v/v) had insignificant effect on methiocarb degradation by ClO_2. A desired amount of ClO_2 stock solution (0.4–1.2 mL) was added to initiate the reaction.
Sampling:	Samples (8 mL each) were withdrawn at pre-selected time intervals. The oxidant residues were immediately quenched with the pre-added Na_2SO_3 solution. After extraction with 2 mL methyl tert-butyl ether (MTBE), the samples were analyzed with GC/MS to determine the residual concentrations of methiocarb. All experiments were conducted in duplicate, and the relative standard deviations were below 8%.
2. Analysis: Methiocarb	Methiocarb was analyzed with GC/MS (Agilent 7890 GC and 5975 MSD, USA) equipped with an HP-5 capillary column (30 m x 0.25 mm id x 0.25 µm film thickness). The column temperature was programmed as follows: started at 90 °C and held for 1 min, ramped at 30 °C min^{-1} to 180 °C, 10 °C min^{-1} to 200 °C, 40 °C min^{-1} to 280 °C and then held for 2 min. Helium gas was used as the carrier gas at a flow rate of 1 mL min^{-1}. The injection, MS quadrupole and ionization source temperatures were set at 280, 150 and 230 °C, respectively. The MS spectra were obtained in the electron ionization (EI) mode with a potential of 70 eV. The quantification and confirmation ions for methiocarb in the selective ion mode were 168 and 153, respectively.
	The concentration of ClO_2 was measured with Hach method 10126 at 530 nm on a DR5000 UV–Vis spectrophotometer. Solution pH and temperature were simultaneously measured by a Mettler Toledo Delta 320 pH meter.
methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN)	MCX and MCN were identified with LC/MS (Alliance 2695 PLC and ZQ4000 MSD, Waters, USA) by comparing their retention times and MS spectra with those of authentic standards. Thereafter, they were quantified by a photodiode array (PDA) detector in a wavelength range from 209 to 211 nm. An Atlantis C18 column (150 mm x 2.1 mm, 3 µm pore size) was used for organic separation at a constant temperature of 40 °C and an acetonitrile/water eluent flow rate of 0.2 mL min^{-1}. The eluent gradient consisted of 3 min isocratic elution with 20% acetonitrile, linearly ramped to 60% acetonitrile over 5 min and held for 4 min, then decreased to 20% acetonitrile over 3 min and held for 10 min. The MS system was operated in the positive ionization mode with an electrospray ionization source under the following conditions: capillary voltage 3.5 kV, cone voltage 20 V, source temperature 120 °C, and desolvation temperature 300 °C. Nitrogen gas was

	used as the cone and desolvating gas at 50 and 300 L h^{-1}, respectively.
Minor byproducts	were identified by GC/MS with the following procedures: (1) adjust the sample (50 mL) pH to about 3.0 with 2.0 M HCl; (2) precondition an Oasis HLB cartridge (500 mg, Waters, Milliford, MA) with 5 mL of methanol/ethyl acetate mixture (1:1 v/v) and 5 mL of ultra-pure water sequentially; (3) extract the sample with the HLB cartridge at a flow rate of approximately 1 mL min $^{-1}$; (4) elute the byproducts with 5 mL of methanol/ethyl acetate mixture (1:1 v/v); (5) blow the extract to about 1 mL under a gentle stream of N2; and (6) identify the byproducts in the final solution with GC/MS. The column temperature was programmed as follows: started at 60 °C and held for 2 min, ramped at 10 °C min^{-1} to 280 °C and then held for 2 min.

RESULTS

1. Validity criteria:

No validity criteria defined.

2. Limit of quantification:

No LoQs were defined

3. Analytical findings:

chlorine dioxide

The degradation process was extremely fast for methiocarb. After 60 minutes > 90% had degraded.

Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were identified to be the major byproducts produced from methiocarb degradation by matching their HPLC retention times and MS spectra with those of authentic standards. The methiocarb degradation associated with byproducts formation at pH values of 6.5, 7.5 and 8.6 are shown in the figure below. Results indicate that at pH 6.5, Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were simultaneously formed and accumulated in the solution unceasingly along with methiocarb degradation in the first 60 min. The concentrations of MCX and MCN increased to an apex at 60 min which accounted for 71% and 28% of methiocarb degraded, respectively. Thereafter, the concentrations of MCX and MCN remained almost constant, implying that the two byproducts were resistant to ClO_2 oxidation at this pH. The mass balance based on benzene ring, which summed up the concentrations of MC, MCX and MCN, was almost constant with only 5% discrepancy after 120 min of reaction time. At pH 7.5, MCX and MCN were still the major byproducts identified. The concentration of MCX increased to an apex at 60 min which accounted for 67% of MC degraded, and decreased very slowly afterwards. In contrast, the maximum MCN concentration appeared at 30 min which only accounted for 19% of MC degraded, and then decreased a little faster than MCX. Due to the partial degradation of MCX and MCN at pH 7.5, the mass balance was discounted by about 28% at 120 min. At pH 8.6, the MCX concentration reached the maximum at 30 min, accounting for 65% of MC degraded. MCN was not detected probably due to its increased degradation rate at a high pH. This interpretation

seemed reasonable considering the fact that the MCN yield at pH 7.5 was notably lower than that at pH 6.5. Three minor byproducts were detected with GC/MS at pH 8.6 and a high MC initial concentration (50 µM) which were identified to be 2,6-dimethylbenzoquinone (DMBQ), 2,6-dimethylhydroquinone (DMHQ), and 4-chloro-3,5-dimethylphenol (PCMX) by the National Institute of Standards and Technology library with a quality value of 92%, 93% and 90%, respectively.
(*note of notifier: no attempt was reported for the quantification of those metabolites, whereas the metabolites methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were well quantified, suggesting that the minor byproducts were only attributed by GC/MS mass spectra and comparison with the respective reference standard*)

The below figure shows the methiocarb degradation associated with byproducts formation at pH values of 6.5, 7.5 and 8.6.

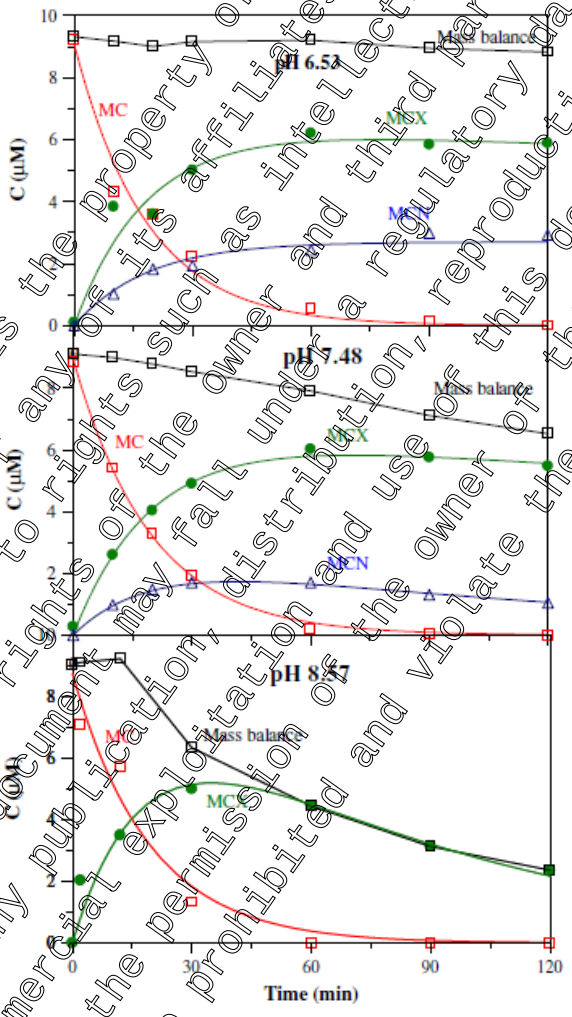


Fig. 3. Evolution of the concentrations of MC and its degradation byproducts during ClO_2 oxidation. $[MC]_o$ = 10 µM, $[ClO_2]_o$ = 1 mM, T = 25 °C. Mass balance was based on benzene ring.

RESULTS SUMMARY

The reaction between ClO_2 and methiocarb in water was of second-order overall, with first-order in methiocarb and ClO_2, respectively. The reaction rate increased fast with an increase in pH due to the promotion of OH^- on methiocarb degradation. Methiocarb sulfoxide (MCX)

and methiocarb sulfone (MCN) were two major byproducts simultaneously generated during methiocarb degradation. Under alkaline condition, (e.g., pH 8.6), three minor byproducts including DMBQ, DMHQ, and PCMX were produced. Though methiocarb can be significantly degraded by ClO_2.

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Report:	KCA 7.5/07; [redacted]; 2013; M-495842-01-1
Title:	Methiocarb degradation by free chlorine in water treatment: Kinetics and pathways.
Report No.:	M-495842-01-1
Document No.:	M-495842-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

EXECUTIVE SUMMARY

Methiocarb (MC) reacted with free chlorine at a stoichiometric ratio of 1:1 and the apparent rate constant was determined to be (1.19–2.46) × 10^8 M^{-1} s^{-1} in the pH range of 5.6–7.5 by competition kinetics. Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were identified to be the major byproducts of methiocarb degradation. MCX could be further oxidized by free chlorine to MCN under acidic and neutral conditions, or hydrolyze to methiocarb sulfoxide phenol (MCXP) under basic conditions. MCN was hardly oxidized by free chlorine but hydrolyzed to methiocarb sulfone phenol (MCNP). Once formed, both MCXP and MCNP reacted with free chlorine too fast to be detectable. Due to the formation of MCX (more toxic than MC), the toxicity of the reaction solution obviously increased after chlorination. This enhanced toxicity raises a serious concern about the safety of drinking water if source water contains MC as a micropollutant.

MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Methiocarb
Active substance(s):	Methiocarb
Chemical state and description:	not reported
Source of test item:	[redacted] GmbH
Batch number:	not reported
Purity:	98.5%
Storage conditions:	not reported
Water solubility:	not reported

2. Reference standards:

methiocarb sulfoxide (MCX)

Source:	Sigma–Aldrich (St. Louis, MO, USA).
Purity:	98.2%

methiocarb sulfone (MCN)

Source:	Sigma–Aldrich (St. Louis, MO, USA).
Purity:	94.4%

methiocarb phenol (MCP), methiocarb sulfoxide phenol (MCXP) and methiocarb sulfone phenol (MCNP)	The standard solutions of methiocarb phenol (MCP), methiocarb sulfoxide phenol (MCXP) and methiocarb sulfone phenol (MCNP) were prepared by hydrolyzing a desired volume of the stock solutions of MC, MCX and MCN respectively with NaOH

solution (1 mL, 2.0 M) for about 1 min, followed by acidifying with HCl solution (5 mL, 2.0 M) and diluting with ultrapure water to 100 mL. The completeness of hydrolysis was confirmed by the liquid chromatograph /photodiode array/mass spectrometer (LC/PDA/MS, Alliance 2695 HPLC and ZQ4000 MSD, Waters, USA) analysis.

B. Study design and methods

1. Reactivity experiments

Temperature:	25 °C
pH:	pH 6.55, 7.46, 8.50 range 6.0-9.0
Duration:	60 minutes
Test medium:	The stock solutions of methiocarb (MC) was prepared in acetone with a concentration of 250–300 mg L^{-1}. The calibration standards containing MC (0.25–10.0 lM) was prepared by mixing the stock solution and then adding 0.1 M HCl to prevent hydrolysis. The reaction solutions were buffered with 10 mM phosphate in the studied pH range of 6.0–9.0. Ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA) with a resistivity of 18.2 MX cm, was used to prepare the aqueous solutions.
Light source	Brown glass bottles
Test conduction: free chlorine:	To prevent methiocarb from hydrolysis, the reaction solution of methiocarb (10 lM, 100 mL) was freshly prepared by diluting 0.8 mL of its stock solution (in acetone) with ultrapure water containing 10 mM KH_2PO_4 (pH 4.7). After adjusting the pH to a desired value with NaOH solution (2.0 M), NaOCl solution (80 µL) was immediately spiked to initiate the reaction. A preliminary experiment had shown that the presence of acetone (0.8%, v/v) had negligible impact on methiocarb degradation by free chlorine.
	In a second test methiocarb sulfoxide phenol (MCXP) and methiocarb sulfone phenol (MCNP) were submitted to the above conditions with free chlorine.
Sampling:	Samples (5 mL each) were withdrawn at pre-selected time intervals, and the residual oxidant was immediately quenched by pre-added Na_2SO_3 solution. Thereafter, the byproducts were identified and quantified by LC/PDA/MS.

2. Analysis:

Methiocarb	In competition kinetics experiments, methiocarb and L-methionine MN (a reference compound) were quantified by high performance liquid chromatography coupled with a diode array detector (HPLC/DAD, Agilent 1200, Wilmington, USA) at 200 nm. An Atlantis C18 column (150 mm x 2.1 mm, 3 µm particle size) was used for organic separation at a constant temperature of 40 °C and an eluent flow rate of 0.2 mL min^{-1}. The eluent consisted of two mobile phases (methanol and water) with the following gradient program: started with 10% methanol for 3 min, linearly ramped to 75% methanol over 3 min and held for 8 min, then decreased to 10% methanol over 2 min and held for 9 min. The retention times of MN and MC were 3.9 and 15.6 min, respectively.
methiocarb sulfoxide (MCX) methiocarb sulfone (MCN) methiocarb phenol (MCP) methiocarb sulfoxide phenol (MCXP) methiocarb sulfone phenol (MCNP)	To identify and quantify methiocarb degradation byproducts, LC/PDA/MS was employed in combination with an Atlantis C18 column (150 mm x 2.1 mm, 3 µm particle size) at a constant temperature of 40 °C and an eluent flow rate of 0.2 mL min^{-1}. Acetonitrile and water were used as two mobile phases with the following gradient program: started with 20% acetonitrile for 3

min, linearly ramped to 60% acetonitrile over 5 min and held for 4 min, then decreased to 20% acetonitrile over 3 min and held for 10 min. The MS was operated in the positive ionization mode with an electrospray ionization source for byproducts identification under the following conditions: capillary voltage 3.5 kV, cone voltage 20 V, source temperature 120 °C, and desolvation temperature 300 °C. Nitrogen gas was used for both cone and desolvation at a flow rate of 50 and 300 L h^{-1}, respectively. The PDA was utilized to determine the concentrations of MC and its byproducts in an acquisition wavelength range of 209–211 nm.
The concentration of free chlorine was measured with a Hach DR5000 UV/Vis spectrophotometer (Hach method 10070). The concentration of TOC was determined by use of a [redacted] 5000 TOC analyser (Tekmar Dohrmann, USA). Solution pH and temperature were simultaneously measured by a Mettler Toledo Delta 320 pH meter.

RESULTS

1. Validity criteria:

No validity criteria defined.

2. Limit of quantification:

The limits of quantification, which gave a signal-to-noise ratio of 10, were determined to be about 0.03, 0.02, 0.03, 0.02, 0.01 and 0.01 µM for MC, MCN, MCNP, MCP, MCX and MCXP, respectively.

3. Analytical findings:

free chlorine

The degradation process was extremely fast for methiocarb. At all pH values, methiocarb was quickly and equivalently degraded to MCX in the first minute.

Methiocarb sulfoxide (MCX) and methiocarb sulfone (MCN) were identified to be the major byproducts produced from methiocarb degradation by free chlorine. Since MC, MCX and MCN were all subject to hydrolysis in water, their hydrolysis byproducts were analyzed by PDA (i.e., MCP, MCXP and MCNP, correspondingly).

The methiocarb degradation associated with byproducts formation at pH values of 6.55, 7.46 and 8.50 are shown in the figure below.
MC was quickly and equivalently degraded to MCX in the first minute, indicating that MCX was the sole primary byproduct from MC degradation. Afterwards, the concentration of MCX decreased, while a new byproduct (MCN) emerged whose concentration kept increasing with reaction time.
The good mass balance on benzene ring throughout the reaction course indicates that MCX and MCN were the only byproducts from MC degradation by free chlorine, and MCN could not be further oxidized by free chlorine at this pH condition.
At pH 7.46, MC was also quickly oxidized to MCX in the first minute. [redacted]ver, both MCX degradation and MCN formation slowed down as compared to those at pH 6.55, and the mass balance
on benzene ring exhibited 17% of deficiency at the end of reaction (i.e. 60 min). There were probably other byproducts undetected at this pH condition.
As pH was further increased to 8.50, MC degradation was still fast and the degradation rate

of MCX exceeded that at pH 7.46, but little MCN was formed. The mass balance on benzene ring exhibited 56% of deficiency at 60 min.
It was reported that MCX and MCN were apt to hydrolyze in water; [redacted]ver, no any hydrolysis products of MCX and MCN were detected even under a basic condition (i.e. pH 8.50) in this study. It is thus hypothesized that the hydrolysis products, once formed, could undergo rapid
reactions with free chlorine and became undetectable.
By investigating the reactions of MCXP and MCNP (i.e. the hydrolysis products of MCX and MCN,
respectively) with free chlorine, it was found that the oxidation rates of MCXP (kMCXP) and MCNP (kMCNP) by free chlorine were about two to four orders of magnitude higher than their formation
rates. It means that the hydrolysis products (MCXP and MCNP), once formed, would be immediately oxidized by free chlorine and thus became undetectable. This result well substantiates the hypothesis raised above.

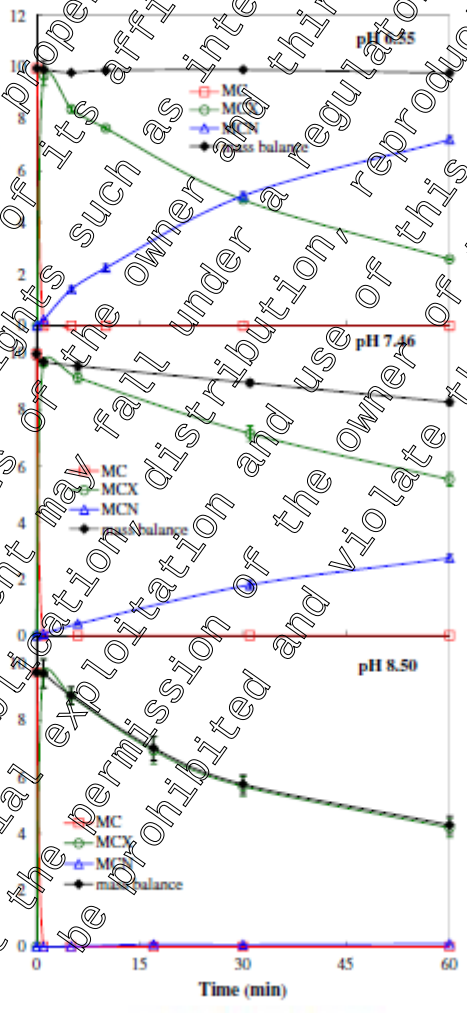
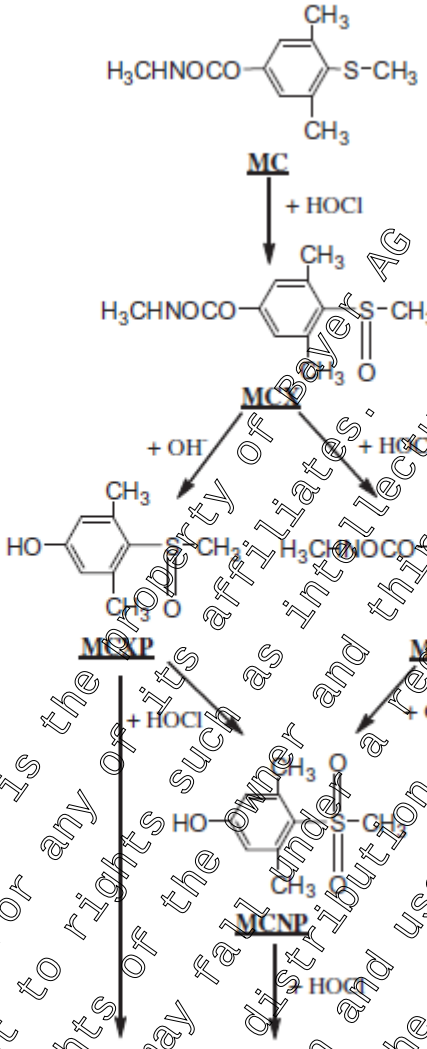


Fig. 3 The formation of byproducts along with MC degradation by free chlorine at different pH values. Experimental conditions: [MC]o = 10 µM, [NaOCl]o = 0.42 mM, 10 mM phosphate buffer, T = 25 °C. Error bars represent the standard deviation of duplicate experiments.

Proposed pathways for methiocarb degradation by free chlorine



RESULTS SUMMARY

The reaction between free chlorine and methiocarb in water very fast. Methiocarb reacted with free chlorine at an intrinsic second-order rate constant of (2.42 ± 0.09) x 10^8 $M^{-1}s^{-1}$. Upon chlorination, methiocarb was first oxidized to methiocarb sulfoxide (MCX). The continuous degradation of MCX was highly pH dependent, which yielded either methiocarb sulfone (MCN) through oxidation by free chlorine under acidic and neutral conditions or methiocarb sulfoxide phenol (MCXP) through hydrolysis under basic conditions. The oxidation of MCXP and the hydrolysis of MCN further yielded the hydrolysis product methiocarb sulfone phenol (MCNP). MCXP or MCNP once formed, will be immediately oxidized by free chlorine and thus become undetectable.

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Report:	KCA 7.5/08; [redacted].; 2013; M-496560-01-1
Title:	Degradation of methiocarb by monochloramine in water treatment: Kinetics and pathways
Report No.:	M-496560-01-1
Document No.:	M-496560-01-1
Guideline(s):	not applicable
Guideline deviation(s):	not applicable
GLP/GEP:	**no**

EXECUTIVE SUMMARY

The micropollution of drinking water sources with pesticides has become a global concern. This work investigated the degradation of methiocarb (MC), a most commonly-used carbamate pesticide, by monochloramine (NH_2Cl) under simulated water treatment conditions. Results indicate that the reaction was of first-order in MC and varied orders in NH_2Cl depending on water pH. The observed rate constant of MC degradation decreased quickly with either a decrease in the molar ratio of chlorine to ammonia (Cl_2:N) or an increase in water pH. The apparent activation energy of the reaction was determined to be 34 kJ mol^{-1}. The MC degradation pathways also exhibited a strong pH dependence: at pH 6.5, MC was first oxidized by NH_2Cl to methiocarb sulfoxide (MCX), and then hydrolyzed to methiocarb sulfoxide phenol (MCXP); while at pH 8.5, MCX, MCXP and methiocarb sulfone phenol (MCNP) were formed successively through either oxidation or hydrolysis reactions. Based on the identified byproducts and their concentrations evolution, the proposed pathways of MC degradation in the presence of NH_2Cl were further validated through kinetic model simulations.

Note of notifier: no further summary is provided as the results are very similar to [redacted] 2013, "Methiocarb degradation by free chlorine in water treatment: Kinetics and pathways."; M-495842-01-1, pp.10-16.