

ANNEX B

Metam-sodium

B.8 Environmental fate and behaviour

Revision August 2010

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.0 Introductory note [added in August 2010]

This document is based on the updated version of Vol.3 B.8 of the DAR, which was peer-reviewed in June 2008 (PRAPeR 52). Evaluations presented in addendum to B.8, dated June 2008, which were peer-reviewed and accepted by PRAPeR 52 (June 2008), have been incorporated in this document as well, for the sake of completeness. Finally, evaluations of new data that were provided in the resubmission dossier (2010) have been added and are highlighted in yellow.

B.8.1 Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1)**B.8.1.1 Route of degradation (Annex IIA 7.1.1.1)****B.8.1.1.1 Aerobic degradation in soil (Annex IIA 7.1.1.1.1)**

Vapam® Aerobic Soil Metabolism. (Burnett, T.J., 1987a)

Guideline:

Pesticide assessment Guideline, Subdivision N: 162-1

GLP:

Yes

Materials and Methods:Test substances:

¹⁴C-Metam-sodium diluted approximately 70-fold with analytical grade a.s. (WRC-9851-13-2). Radiochemical purity of 96.6% by TLC and LSC; this stock solution has a specific activity: 0.0835 mCi/mmol and contains 33.4% anhydrous metam-sodium in water.

Soil:

Table B.8.1.1.1-1: Characterisation of the test soil

Origin Soil type	Columbia River Basin Sand
Textural analysis (soil sieved to 2 mm)	Fractions (%)
1.0-2.0 mm, very coarse sand	0.3
1.0-0.5 mm, coarse sand	14.3
0.5-0.05 mm, medium fine and very fine sand	77.2
0.05-0.002 mm, silt	7.0
0-0.002 mm, clay	1.2
PH value	6.9
Organic matter (%)	0.2
Ece ¹	0.4
Cation exchange capacity (meq/100 g)	6.5
Bulk density (g/cc)	1.60

¹: Saturation extract conductivity, mmha/cm @ 25°C

Experimental design :

The 50 g soil samples containing 126 mg a.s./kg soil were incubated at 28±1°C in the dark, moisture of 75% of FC (in sealed vials). Volatile compounds were recovered several traps: cellulose thimble containing charcoal, polyurethane foam plug and in KOH solution (for CO₂).

Analytical methods :

Not clearly reported in the study

Findings:

Table B.8.1.1.1-2: Degradation and metabolism of Metam-sodium in soil (mean of 2 replicates),

Interval (days)	KOH traps	Carbon trap ³	foam plug	thimble ⁴	soil extract ¹	soil bound ²	total
	[¹⁴ C]CO ₂	MITC					
0	<0.01	<0.01	<0.01	<0.01	72.87	6.80	79.67
1	0.86	82.93	0.14	0.05	3.43	5.30	92.71
2	0.77	82.96	0.25	2.36	2.43	5.56	94.34
3	0.44	80.74	0.08	0.69	2.41	6.13	90.50
7	3.84	80.57	0.05	0.07	2.84	4.54	91.91
14	4.78	76.53	<0.01	0.23	2.24	2.49	86.27
21	6.61	78.47	<0.01	0.12	1.66	2.31	89.17
30	7.53	77.27	<0.01	0.55	1.62	2.11	89.09
60	8.66	78.59	<0.01	0.23	0.86	1.86	90.21
92	8.36	79.29	<0.01	0.16	0.27	1.62	89.68
127	8.66	79.24	<0.01	0.22	0.31	1.58	90.03

¹ aqueous soil extract: assay of the combined volume of three successive extractions² soil bound: as determined by oxidation/LSC of soil samples³ radiolabel accumulated in the carbon traps⁴ thimble: radiolabel extracted from the cellulose thimble used to hold the carbonConclusions:

This study is considered as not acceptable: analytical procedures and identification of the a.s. and metabolites in the traps and soil extracts, determination of the a.s. DT50 are not clear.

After application to the soil, metam-sodium rapidly degrades (DT50 of 23 minutes). The main metabolite is the volatile methylisothiocyanate (max 82.96%) which is trapped in charcoal. At 127 days, 8.7% AR was identified as CO₂ was 8.7% in the KOH trap.

A minor fraction is bound to the soil (6.8 % decreasing to 1.4% at the end of the study).

The degradation of [¹⁴C]-Metam-sodium and its principal degradation product [¹⁴C]-MITC in four fresh field soils under aerobic conditions. (Hall, B.E. *et al.*, 2004).

Guidelines :

Setac "Procedures for Assessing the Environmental Fate and Ecotoxicology of Pesticide (March 1995)", Dir 95/36/EC and EPA Pesticide Assessment guidelines, Subdivision N, paragraph 162-1, 1982

GLP :

yes

Material and Methods:Test substance :

[Thiocarbonyl ¹⁴C]-metam-sodium, batch no.: 3415-292, radiochemical purity: 97.3%; specific activity: 25.58 mCi/mmol, supplier: Perkin Elmer Life science

[Thiocarbonyl ¹⁴C]-MITC, batch no.: 3501-187, radiochemical purity: 98.46%; specific activity: 23.31 mCi/mmol, supplier: Perkin Elmer Life science

Soils :

Table B.8.1.1.1-3: Characteristics of the soils used to investigate the route and rate of degradation of [¹⁴C] metam-sodium

Soil (USDA Classification)	Particle Size Analysis			pH		% Organic Matter	C.E.C
	% Sand	% Silt	% Clay	Water	KCl		
Sandy Loam (Code S402)	77.90	10.21	11.89	5.4	4.7	6.97	26.2
Sandy Loam (Code S403)	71.34	15.96	12.71	5.7	5.1	1.87	11.8
Silt Loam (Code S405)	13.39	61.72	24.89	7.1	6.2	7.31	34.3
Clay Loam (Code S404)	43.51	22.81	33.68	7.7	7.1	2.89	25.8

* Lead soil

% Organic Matter = % Organic Carbon (Addendum 1) x 1.7

C.E.C = Cation Exchange Capacity

Table B.8.1.1.1-4: Characteristics of the soils used to investigate the route and rate of degradation of [¹⁴C]MITC

Soil (USDA Classification)	Particle Size Analysis			pH		% Organic Matter	C.E.C
	% Sand	% Silt	% Clay	Water	KCl		
Sandy Loam 2* (Code S480)	82.63	5.57	11.79	5.2	4.1	1.53	9.3
Sandy Loam 1 (Code S500)	77.79	12.63	9.58	4.5	3.7	12.41	16.4
Silt Loam (Code S490)	12.24	62.27	25.49	6.1	5.2	6.46	16.8
Clay Loam (Code S479)	44.59	19.95	35.45	7.6	7.0	2.38	18.8

* Lead soil

% Organic Matter = % Organic Carbon (Addendum 1) x 1.7

C.E.C = Cation Exchange Capacity

*Experimental design, Analytical methods :**Phase 1: rate of degradation of metam-sodium*

Treatment solution was applied to the surface of the soil in each incubation jar at the application rate of 310 mg metam-sodium/kg dry soil. Following application, the jars were sealed and incubated in the dark at 20 ± 2 °C and 10 ± 2 °C at 50% of MWHC.

At zero time, 10, 20, 30, 45, 60 90 and 120 minutes after application, a single sample for each soil type and temperature was subject to extraction and HPLC analysis. Chilled water was added to the soil and shaken for 2 minutes. A subsample was removed using a syringe, filtered through a glass fiber syringe filter and analysed by LSC and HPLC in order to determine the a.s level.

Phase 2: rate of degradation of MITC

Treatment solution was applied to the surface of the soil in each incubation jar at the application rate of 43 mg MITC/kg dry soil. Following application, the jars were sealed and incubated in the dark at 20 ± 2 °C and 10 ± 2 °C at 50% of MWHC. The incubation flasks were sealed with wetted heavy duty Teflon stoppers, each of which was fitted with duplicate stainless steel luer-lock needles protruding through the stopper into the headspace of the incubation flask. The luer-locks were pre-sealed with air-tight Teflon and stainless steel valves. Following sealing, the wet joint was surrounded by Parafilm layers.

Duplicate samples at day 0, 1, 7 and 21; single samples at day 0.25 (6 hours), 2, 4, 10 and 15.

3 hours prior to each scheduled sampling, flasks were connected to an aeration apparatus delivering moist CO₂-free air at a flow rate of 50 mL/min for a period of 6 hours (3 hours post interval). The valves were opened after the air flow had started and the gasses were passed through a series of traps in sequence as follows:

3 X 50 mL ethyl acetate (for MITC)

1 X 50 mL Viles' solution (1 mL diethylamine, 20 mL triethanolamine and 50 mg cupric (II) acetate in 1 liter ethanol) (for CS₂)

3 X 50 mL NaOH (0.5 M) (for CO₂)

catalytic converter (the air leaving the previous array of traps was passed over a copper (II) catalyst at 800°C to oxidize any volatile not previously trapped to CO₂)

2 X 50 mL NaOH (0.5 M) (to collect the volatiles oxidized to CO₂ in the converter)

The radioactivity of all traps was determined by LSC.

At the end of the aeration period, the soil samples were extracted with ethyl acetate and water. Following shaking the ethyl acetate phase was removed. The soil slurry was centrifuged and the resulting water layer was removed. The soil slurry was further extracted with ethyl acetate. The ethyl acetate and water fractions were analysed by LSC. Aqueous extracts were analysed by HPLC. The ethyl acetate were analysed by GC.

Two soil samples exhibiting a high level bound residue were subject to organic matter fractionation by NaOH / HCl extraction procedure in order to determine the nature of the bound residue. Determination by LSC.

Findings:

Table B.8.1.1.1-5: Percentage applied radioactivity as [¹⁴C]metam-sodium incubated at 20°C in a Sandy Loam Soil (Code S402)

Actual sampling time (minutes)	% metam-sodium remaining in soil
3	55.12
13	21.48
23	10.92
35	4.34
56	3.70
79	2.04
100	0.00
123	0.00

Table B.8.1.1.1-6: Percentage applied radioactivity as [¹⁴C]metam-sodium incubated at 20°C in a Sandy Loam Soil (Code S403)

Actual sampling time (minutes)	% metam-sodium remaining in soil (+1, for DT calculation)
3	31.71
12	6.27
23	1.00
36	1.00
52	1.00
75	1.00
96	1.00
124	1.00

Table B.8.1.1.1-7: Percentage applied radioactivity as [¹⁴C]metam-sodium incubated at 20°C in a Silt Loam Soil (Code S405)

Actual sampling time (minutes)	% metam-sodium remaining in soil
3	67.65
13	19.72
23	12.93
33	1.21
58	1.11
83	0.35
105	0.00
128	0.00

Table B.8.1.1.1-8: Percentage applied radioactivity as [^{14}C]metam-sodium incubated at 20°C in a Clay Loam Soil (Code S404)

Actual sampling time (minutes)	% metam-sodium remaining in soil
3	85.59
13	47.89
23	22.72
33	7.39
54	2.67
76	0.31
98	0.00
No sample	-

Table B.8.1.1.1-9: Percentage applied radioactivity as [^{14}C]metam-sodium incubated at 10°C in a Sandy Loam Soil (Code S402)

Actual sampling time (minutes)	% metam-sodium remaining in soil
4	49.11
13	34.92
23	9.22
34	14.07
55	5.43
77	0
97	3.89
125	0

Table B.8.1.1.1-10: Recovery and distribution of radioactivity from a Sandy Loam Soil (Code S480) incubated at 20°C following single application of [^{14}C]-MITC

Sampling Interval	Percent Applied Radioactivity Recovered										
	Soil Extract			Traps			Catalytic Converter*	Non-Extractable Residue	Connective Tubing Wash	Flask Wash	Total
	Ethyl Acetate	Water	Overlying Ethyl Acetate	Ethyl Acetate*	Vials Soln	Sodium Hydroxide*					
Zero Time	93.90	4.84	1.19	-	-	-	-	0.43	-	0.06	100.41
6 h	3.87	0.78	0.26	88.54	0.04	4.20	0.09	2.40	0.73	0.05	100.96
Day 1	4.26	1.10	0.49	75.67	0.04	14.04	0.10	4.08	0.55	0.11	100.42
Day 2	2.30	1.22	0.37	64.29	0.03	24.80	0.54	5.05	0.87	0.12	99.59
Day 4	3.64	1.52	0.44	40.79	0.06	45.02	0.10	6.92	0.10	0.10	98.69
Day 7	3.10	1.86	0.16	19.31	0.05	65.76	0.15	9.57	0.07	0.10	100.11
Day 10	0.74	1.94	0.14	7.22	0.01	78.53	0.42	9.25	0.13	0.15	98.53
Day 15	0.42	2.02	0.16	0.29	ND	85.55	0.36	9.60	ND	0.09	98.50
Day 21	0.37	1.73	0.08	0.04	-	86.25	0.21	9.88	-	0.04	98.59
Contingency	NS	NS	NS	NS	NS	94.89**	NS	NS	NS	NS	NA

NS = No sample ND = Not detected NA = Not applicable

* Combined data from individual traps

** Cumulative ca 3 weeks post Day 21

Table B.8.1.1.1-11: Recovery and distribution of radioactivity from a Sandy Loam Soil (Code S500) incubated at 20°C following single application of [¹⁴C]-MITC

Sampling Interval	Percent Applied Radioactivity Recovered										
	Soil Extract			Traps			Catalytic Converter*	Non-Extractable Residue	Connective Tubing Wash	Flask Wash	Total
	Ethyl Acetate	Water	Overlying Ethyl Acetate	Ethyl Acetate*	Viles' Soln	Sodium Hydroxide*					
Zero Time	94.21	5.55***	2.63	-	-	-	-	0.66		0.06	103.10
6 h	23.48	2.90	1.34	61.95	0.13	6.03	0.16	5.26	0.36	0.06	101.67
Day 1	18.48	2.82	1.22	49.14	0.11	19.70	0.23	9.24	0.24	0.08	101.24
Day 2	16.22	3.25	1.18	33.67	0.12	33.26	0.19	11.43	0.25	0.08	99.65
Day 4	9.08	3.03	0.59	24.29	0.06	48.25	0.30	14.75	0.15	0.08	100.60
Day 7	6.51	3.27	0.41	12.77	0.04	60.44	0.33	17.43	0.08	0.07	101.33
Day 10	3.78	3.45	0.32	8.08	0.02	66.74	0.38	17.87	0.05	0.05	100.74
Day 15	2.17	3.43	0.20	3.56	0.01	73.37	0.28	18.06	0.02	0.07	101.17
Day 21	1.20	3.60	0.14	0.95	-	74.94	0.37	17.92	0.01	0.06	99.17
Contingency	NS	NS	NS	NS	NS	80.67**	NS	NS	NS	NS	NA

NS = No sample ND = Not detected NA = Not applicable

* combined data from individual traps

** Cumulative result ca 2 weeks post Day 21

*** radioactivity in water extract identified as MITC

Table B.8.1.1.1-12: Recovery and distribution of radioactivity from a Silt Loam Soil (Code S490) incubated at 20°C following single application of [¹⁴C]-MITC

Sampling Interval	Percent Applied Radioactivity Recovered										
	Soil Extract			Traps			Catalytic Converter *	Non-Extractable Residue	Connective Tubing Wash	Flask Wash	Total
	Ethyl Acetate	Water	Overlying Ethyl Acetate	Ethyl Acetate*	Viles Soln	Sodium Hydroxide*					
Zero Time	94.59	6.14***	1.47	-	-	-	-	0.80	-	0.02	103.02
6 h	12.05	1.42	0.56	68.08	0.09	8.49	0.13	6.23	0.43	0.03	97.50
Day 1	11.83	2.30	1.08	42.00	0.11	27.21	0.12	12.03	0.23	0.04	96.94
Day 2	5.30	2.45	0.18	22.89	0.07	48.16	0.18	20.55	0.18	0.06	100.02
Day 4	1.72	2.99	0.45	2.43	0.04	66.19	0.37	20.36	0.03	0.06	94.64
Day 7	0.92	2.61	0.34	0.11	0.01	72.32	0.32	20.69	-	0.03	97.34
Day 10	0.57	2.21	0.20	0.05	0.02	74.41	0.15	20.58	ND	0.04	98.23
Day 15	0.31	1.53	0.16	0.03	0.01	77.13	0.37	18.87	ND	0.05	98.46
Day 21	0.38	1.32	0.24	0.09	0.07	77.41	0.14	17.87	-	0.03	97.53
Contingency	NS	NS	NS	NS	NS	82.89**	NS	NS	NS	NS	NA

NS = No sample ND = Not detected NA = Not applicable

* Combined data from individual traps

** Cumulative result ca 2 weeks post Day 21

*** Radioactivity in water extract identified as MITC

Table B.8.1.1.1-13: Recovery and distribution of radioactivity from a Clay Loam Soil (Code S479) incubated at 20°C following single application of [¹⁴C]-MITC

Sampling Interval	Percent Applied Radioactivity Recovered										
	Soil Extract			Traps			Catalytic Converter*	Non-Extractable Residue	Connective Tubing Wash	Flask Wash	Total
	Ethyl Acetate	Water	Overlying Ethyl Acetate	Ethyl Acetate*	Viles' Soln	Sodium Hydroxide*					
Zero Time	95.68	3.36	1.18	-	-	-	-	0.57	-	0.02	100.80
6 h	5.44	1.25	0.60	84.36	0.03	2.23	0.10	6.03	0.38	0.05	100.47
Day 1	3.74	1.28	0.95	66.85	0.03	9.76	0.34	14.15	0.51	0.06	97.66
Day 2	2.76	1.41	0.71	49.19	0.03	16.92	0.44	24.13	0.28	0.06	95.93
Day 4	5.23	2.10	0.79	22.82	0.13	27.65	0.46	34.16	0.19	0.08	93.61
Day 7	1.61	1.69	0.78	7.67	0.06	39.65	1.11	36.75	0.05	0.03	89.36
Day 10	1.64	2.07	0.57	1.00	0.07	44.27	1.14	52.61	0.01	0.04	103.42
Day 15	1.46	1.81	ND	0.15	0.03	47.45	1.23	39.30	ND	0.03	91.46
Day 21	1.22	1.44	0.46	0.05	0.01	45.96	1.41	38.38	-	0.04	88.94
Contingency	NS	NS	NS	NS	NS	62.38	NS	NS	NS	NS	NA

NS = No sample ND = Not detected NA = Not applicable

* Combined data from individual traps

** Cumulative result ca 6 weeks post Day 2

Table B.8.1.1.1-14: Recovery and distribution of radioactivity from a sandy loam soil (Code S480) incubated at a nominal temperature of 10°C Following a single application of [¹⁴C]-MITC

Sampling Interval	Percent Applied Radioactivity Recovered										
	Soil Extract			Traps			Catalytic Converter*	Non-Extractable Residue	Connective Tubing Wash	Flask Wash	Total
	Ethyl Acetate	Water	Overlying Ethyl Acetate	Ethyl Acetate*	Viles' Soln	Sodium Hydroxide*					
Zero Time	90.87	2.65	1.11	-	-	-	-	0.40	-	0.04	95.05
6 h	38.23	3.00	0.73	55.93	0.06	1.56	0.04	2.16	0.56	0.03	102.29
Day 1	18.40	1.55	0.55	71.68	0.02	4.96	0.13	2.98	0.38	1.12	101.76
Day 2	14.63	1.46	0.57	69.13	0.02	8.47	0.35	4.09	0.61	0.01	99.34
Day 4	16.99	2.58	0.59	59.15	0.03	14.49	0.30	6.13	0.51	0.19	100.98
Day 7	14.26	1.92	0.54	46.50	0.03	23.78	0.52	7.12	0.20	0.15	95.00
Day 10	12.94	2.35	0.45	33.24	0.04	28.29	0.37	9.14	0.28	0.02	87.13
Day 15	5.53	1.93	0.37	25.26	0.03	32.40	0.84	10.52	0.15	0.27	77.28
Day 21	3.43	2.07	0.17	15.42	0.02	36.40	0.09	11.30	0.09	0.16	69.15
Contingency	NS	NS	NS	NS	NS	60.87*	NS	NS	NS	NS	NA

NS = No sample ND = Not detected NA = Not applicable

* Combined data from individual traps

** Cumulative result ca 6 weeks post Day 21

Table B.8.1.1.1-15: Composition of the non extractable residues determined in 2 soil samples at study termination (at day 21) (%AR)

Soil type	Non-extractable residue	Humic acid	Fulvic acid	Humic acid
Silt loam (S 490)	17.66	8.51	3.49	1.09
Clay loam (S479)	39.03	29.76	3.32	0.15

Table B.8.1.1.1-16: Rate of degradation of ^{14}C -Metam-sodium in four soils (linear regression of the percent a.s., expressed as ln)

Soil Type	Incubation Temperature (°C)	DT ₅₀ (minutes)	DT ₉₀ (minutes)	R ²
Sandy Loam 1	20	17	57	0.87
Sandy Loam 2	20	4	13	1.00
Silt Loam	20	11	36	0.86
Clay Loam	20	9	30	0.99
Mean	20	10	34	
Sandy Loam 1	10	17*	55*	0.82
		22**	72**	0.70

* Rate of degradation calculated using data from 4 to 55 minutes.

** Rate of degradation calculated using data from 4 to 97 minutes. Seventy seven minute data point omitted as zero percent metam-sodium present.

Table B.8.1.1.1-17: Rate of degradation of ^{14}C -MITC in four soils at 20°C and one soil at 10°C (linear regression of the MITC residue, expressed as ln)

Soil Type	Incubation Temperature (°C)	DT ₅₀ (days)	DT ₉₀ (days)	R ²
Sandy Loam 2	20	2.78	9.23	0.9908
Sandy Loam 1	20	2.94	9.77	0.9917
Silt Loam	20	0.97	3.21	0.9898
Clay Loam	20	1.91	6.35	0.9995
Mean	20	2.15	7.14	
Sandy Loam 2	10	8.31	27.61	0.9449

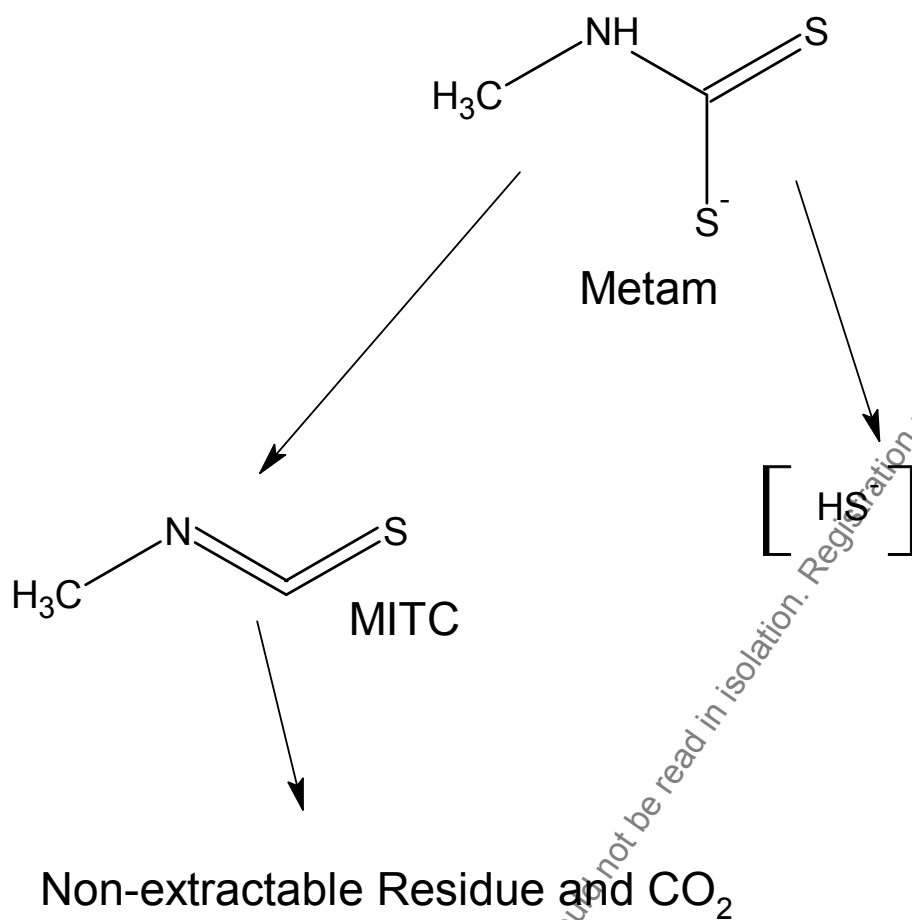
Conclusions:

The study is acceptable. This study was designed to test the degradation of metam-sodium and MITC in soils by exclusion of dissipation through volatilization. The flasks were sealed during the incubation period, with aeration only at the end of each sampling interval.

The active substance metam-sodium and its major volatile metabolite MITC are rapidly degraded at 20°C, with a mean DT₅₀ of, respectively 10 minutes and 2.15 days. At 10°C, the degradation rates are 20 minutes and 8.31 days respectively for the a.s. and MITC. No other metabolite has been formed.

In the experiments performed with MITC as test material, the mineralization reaches a maximum level 45.96-86.25% AR after incubation for 21 days at 20°C. Bound residue levels are in the range of 9.88-38.38% AR after incubation for 21 days at 20°C. Bound residue in two soil samples incubated for 21 days are containing 8.51-29.76 %AR as humin, 3.49-3.32% AR as fulvic acid and 1.09-0.15%AR as humic acid.

Figure B.8.1.1-1: Proposed degradation pathway of Metam-sodium in soil



Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.1, the notifier had to address the environmental risk assessment for major/relevant impurities. The notifier's position and the RMS conclusion had previously been reported in the addendum dated June 2008, which was peer reviewed.

The notifier submitted the following statement:

<<

It should be noted that According to Council Directive 91/414/EC and Commission Implementing Directives, environmental risk assessments of impurities in the technical material are not a dossier requirement. Therefore, addressing this issue in the dossier could not be expected from the applicant in view of the inclusion of the active substance in Annex I.

Despite this fact, the following information could be taken into account :

[...]

[As the rest of the notifier's statement contains confidential information, the reader is referred to the confidential part C (Vol.4) of the DAR, point C.1.2.2, where the relevance of impurities is discussed in detail, taking into account the argumentation provided by the applicant Taminco.]

>>

Conclusions of the RMS:

We consider as RMS that the environmental risk assessments of impurities in the technical material are not a dossier requirement (whatever the application rate of the a.s. could be) and should be considered as additional/confirmatory data. The impurities have been tested along in the ecotoxicological and toxicological studies and do not need a specific assessment.

However the impurities are small molecules with no alarming structure that can be considered as substrate for micro-organisms. As RMS we consider that no further data are required.

Conclusions of the peer review: point of clarification 4.1 addressed

Added in August 2010:

A data gap has been identified by EFSA after the meeting of experts to address the fate of DMTU in soil in order to obtain adequate input parameters for ground water modelling.

The notifier submitted the following study:

¹⁴C-N,N'-dimethylthiourea: Degradation and Metabolism in Four Soils Incubated under Aerobic Conditions. Völkel, W. (2010).

Guideline:

The study was conducted according to OECD Guideline 307 (2002), Commission Directive 95/36/EC (1995) and the SETAC (1995) guideline.

GLP:

Yes

Materials and Methods:

Test substances:

¹⁴C-N,N'-dimethylthiourea, radiochemical purity 100%. And unlabelled test item 99.4% purity.

Soils:

Table B.8.1, B.1-18: Characterisation of the test soils

Soil designation and origin	Soil I, Am Fischteich, Germany	Soil II, Grossstorkwitz, Germany	Soil III, Speyer 2.3, Germany	Soil IV, Speyer 6S, Germany
USDA Particle size distrib. [%]				
sand > 0.05 mm	13.52	42.25	60.8	29.9
silt 0.002 – 0.05 mm	65.99	41.13	29.8	36.0
clay < 0.002 mm	20.49	16.62	9.40	42.1
textural class	silt loam	loam	sandy loam	clay
Organic C [%]	2.12	2.72	0.98	1.75
pH [H ₂ O]	6.33	7.65	7.26	7.62
pH [CaCl ₂]	5.74	7.27	6.40	7.20
CaCO ₃ [%]	0.50	3.90	0.40	1.50
cation exchange capacity [mmol /100 g soil]	17.44	23.61	8.00	22.0
Soil moisture content at				
pF 1.0 (MWHC)	70.33	55.58	34.4	40.7
pF 2.0	41.02	39.01	26.5	38.0
[g water/100 g soil]				
microbial biomass				
start of incubation	45.60	43.60	21.67	39.60
end of incubation	38.73	48.16	16.39	35.42
[mg C/100 g dry weight]				

No soil had been subjected to any pesticide or organic fertilizer treatment for the past five years.

Experimental design:

The degradation of ¹⁴C-N,N'-dimethylthiourea in four soils (Am Fischteich (soil I), Grossstorkwitz (soil II), Speyer 2.3 (soil III) and Speyer 6S (soil IV)) following treatment with the test item at a rate of about 5 kg test item/ha and incubation at 20 °C, 50% MWHC for 60 days for all soils and up to 145 days for soils I and IV.

The freshly collected soils were passed through a 2 mm sieve. The test item was then applied to 100 g soil samples at a target concentration of about 0.94 to 2.77 mg a.i./kg dry soil. This target rate corresponds to the following application rate: 5 kg a.i./ha when assuming an even distribution of the test item in the top 20 cm soil layer and soil bulk densities of 0.9 to 1.3 g/cm³.

The treated soil samples were incubated at 20 ± 2 °C in the dark under continuous ventilation with moistened air. The exiting air was passed through a trapping system consisting of flasks of sodium hydroxide and ethylene glycol in series. Prior to treatment and at the end of the incubation period, the microbial biomass was determined for each soil. The results showed that the soils were viable during the study.

Analytical methods:

Duplicate samples (A and B) treated with the test item were taken immediately from each soil after treatment (day 0) and after 2, 4, 12, 24 hours and after 3, 7, 14, 35 and 60 days and, additionally for soils I and IV, after 145 days. Each sample was submitted to extraction at room temperature using acetonitrile/water (4:1; v/v) followed by Soxhlet extraction using the same solvent mixture. The individual extracts were combined and concentrated. The samples were then analyzed for the test item and degradation products by HPLC and/or TLC. Detailed structure elucidation of the metabolites has been performed using LC/MS.

Findings

Mean recoveries of radioactivity during the 60-day incubation period were 94.4 ± 1.2%, 94.8 ± 2.5%, 93.8 ± 2.1% and 95.6 ± 2.5% of the applied amount for soils Am Fischteich, Grossstorkwitz, Speyer 2.3 and Speyer 6S, respectively.

With regard to the microbial biomass, the results showed that the soils were viable during the study.

Immediately after treatment (day 0), 83.7%, 90.3%, 92.2% and 84.6% of the applied radioactivity could be extracted from soils I to IV, respectively. The total amount of extractable radioactivity decreased with time in all four soils. The decrease was fast within the first seven days and continued thereafter slower until the end of incubation. After seven days 23.4%, 21.9%, 29.4% and 16.7% of the amount applied could be extracted. By Day 60, about half of this amount (except for soil IV) was extractable i.e. 11.9%, 11.8%, 16.7% and 12.8% for soils I to IV, respectively. Samples for soils I and IV were incubated for 145 days and at that time point 10.6% and 9.5% of the amount applied was extractable.

The amount of non-extractable radioactivity was significant, reaching maximum values of 42.2%, 19.2%, 23.0% and 38.9% within 14 days, for soils Am Fischteich, Grossstorkwitz, Speyer 2.3 and Speyer 6S, respectively. At Day 60, the corresponding values amounted to 35.9%, 18.2%, 16.5% and 30.0% of the applied radioactivity. For soils I and IV, 34.8% and 32.1% remained non-extracted after 145 days of incubation.

The remaining non-extractable radioactivity from the day 14 soil samples were submitted to harsh extractions under reflux conditions. The radioactivity extracted amounted to 9.4%, 4.1%, 4.9% and 12.4% of the amount applied for soils I, II, III and IV, respectively.

Subsequent fractionation of the soil organic matter into humic acids, fulvic acids and humin fractions showed an equal distribution of the non-extractable radioactivity between mobile (fulvic acids) and the immobile fractions (humic acids and humin fraction).

The radioactivity associated with the fulvic acids was 17.7%, 5.1%, 8.6% and 15.8% AR in the four soils. The humic acids and humin fractions recovered in total 15.1%, 10.0%, 9.5% and 10.7% applied radioactivity for soils I, II, III and IV, respectively.

The mineralization of ^{14}C -N,N'-dimethylthiourea increased continuously, with $^{14}\text{CO}_2$ reaching maximum mean levels of 46.3%, 64.5%, 57.9% and 52.2% of the applied radioactivity for soils I to IV. The concentration of other volatile products was low, with maximum amounts of 0.8% of the applied radioactivity during the entire incubation period.

^{14}C -N,N'-dimethylthiourea disappeared rapidly in all four soils. At the first sampling interval, day 0, N,N'-dimethylthiourea represented 55.6%, 65.5%, 77.4% and 67.7% of the applied radioactivity for soils I to IV, respectively. After 12 hours of incubation, it was 7.1%, 25.3%, 24.4% and 8.5% of the applied radioactivity in the four soils. After 24 hours, N,N'-dimethylthiourea further decreased to 3.0%, 6.2%, 8.8% and 0.9% for soils I, II, III and IV, respectively. At later intervals no N,N'-dimethylthiourea was detected anymore.

Table B.8.1.1.1-19: Balance of the applied radioactivity in the Am Fischteich soil (I) treated with $^{14}\text{C-N,N}'$ -dimethylthiourea. Values in percent of applied radioactivity.

N,N-dimethylthiourea Am Fischteich (% AR)	Sample	INCUBATION TIME IN DAYS									
		0	0.17	0.50	1	3	7	14	35	60	145
Extractables*	A	78.7	64.2	51.4	45.8	31.7	16.6	10.3	6.2	5.5	6.1
	B	79.8	63.8	52.1	46.6	32.3	16.8	10.8	5.7	5.1	6.0
Soxhlet**	A	4.7	4.9	5.4	7.7	7.3	6.3	5.3	6.7	6.1	4.7
	B	4.2	3.8	6.1	7.7	7.7	7.2	6.4	5.8	5.7	4.2
Total Extractables	A	83.4	69.1	56.8	53.5	39.0	22.9	15.6	12.8	12.0	10.8
	B	83.9	67.6	58.2	54.3	40.1	23.9	17.2	11.5	11.8	10.3
	Mean	83.7	68.3	57.5	53.9	39.5	23.4	16.4	12.2	11.9	10.6
Non-extractables	A	10.2	25.2	34.6	36.8	38.8	38.9	42.7	41.3	35.8	34.6
	B	10.1	27.6	32.7	38.1	38.8	36.6	41.7	41.8	35.9	35.0
	Mean	10.1	26.4	33.7	37.4	38.8	37.7	42.2	41.6	35.9	34.8
¹⁴ CO ₂	A	np.	0.2	1.5	4.0	17.4	31.6	36.6	41.2	46.4	50.1
	B	np.	0.2	1.3	3.3	17.3	31.5	36.5	42.8	46.1	49.1
	Mean	n.p.	0.2	1.4	3.7	17.3	31.6	36.5	42.0	46.3	49.6
Other volatiles in EG	A	np.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	np.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TOTAL	A	93.6	94.5	92.9	94.2	95.2	93.4	94.9	95.4	94.3	95.5
	B	94.0	95.4	92.2	95.8	96.2	92.1	95.0	96.1	93.9	94.4
MEAN ± SD				94.4	±	1.2					

* Extracted with acetonitrile/water (1:1; v/v), three times

** Soxhlet extraction with acetonitrile/water (4:1; v/v) for four hours

n.p.: Not performed

SD: Standard deviation

Table B.8.1.1-20: Balance of the applied radioactivity in the Grossstorkwitz soil (II) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N'-dimethylthiourea Grossstorkwitz (% AR)	Sample	INCUBATION TIME IN DAYS								
		0	0.17	0.50	1	3	7	14	35	60
Extractables*	A	86.5	79.5	72.0	63.8	42.1	11.3	9.8	7.3	5.2
	B	86.7	82.5	68.7	63.0	42.4	12.4	9.7	6.9	5.4
Soxhlet**	A	3.8	5.1	7.7	10.5	10.8	9.6	7.8	7.5	6.7
	B	3.5	5.5	9.1	10.2	11.9	10.4	9.3	7.5	6.3
Total Extractables	A	90.3	84.6	79.7	74.4	52.9	20.9	17.6	14.5	11.9
	B	90.3	88.0	77.8	73.3	54.4	22.9	19.0	13.8	11.8
	Mean	90.3	86.3	78.7	73.8	53.6	21.9	18.3	14.2	11.8
Non-extractables	A	5.2	8.3	15.2	15.3	18.7	18.5	19.4	18.6	18.1
	B	4.7	7.3	11.8	15.2	17.3	17.7	19.0	17.5	18.4
	Mean	5.0	7.8	13.5	15.3	18.0	18.1	19.2	18.1	18.2
$^{14}\text{CO}_2$	A	n.p.	0.1	0.5	2.6	14.4	57.9	63.8	64.8	64.2
	B	n.p.	<0.1	0.7	2.7	16.7	53.3	55.6	63.7	64.8
	Mean	n.p.	0.0	0.6	2.6	15.6	55.6	59.7	64.3	64.5
Other volatiles in EG	A	n.p.	<0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1
	B	n.p.	<0.1	0.1	0.2	<0.1	0.1	<0.1	<0.1	<0.1
	Mean	n.p.	<0.1	0.1	0.1	<0.1	0.1	0.1	<0.1	<0.1
TOTAL	A	95.5	92.9	95.4	92.4	86.1	97.4	100.8	98.0	94.2
	B	95.0	95.4	90.4	91.3	84.1	94.0	93.7	95.1	94.9
MEAN $\pm$ SD				94.8	$\pm$	2.5				

* Extracted with Acetonitrile/water (1:1; v/v), three times

** Soxhlet extraction with Acetonitrile/water (4:1; v/v) for four hours

¹ Incomplete mass balance due to loss of $^{14}\text{CO}_2$, not used for the calculation of the mean value

n.p.: Not performed

SD: Standard deviation

Table B.8.1.1-21: Balance of the applied radioactivity in the Speyer 2.3 soil (III) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N-dimethylthiourea Speyer 2.3 (% AR)	Sample	INCUBATION TIME IN DAYS								
		0	0.17	0.50	1	3	7	14	35	60
Extractables*	A	90.8	77.1	68.9	63.9	47.8	19.4	17.9	12.7	9.8
	B	89.2	77.6	70.0	64.1	49.2	20.7	16.8	12.3	10.6
Soxhlet**	A	2.1	4.6	7.6	8.9	8.9	8.7	7.4	8.8	6.7
	B	2.1	4.7	6.9	7.6	9.6	10.0	7.8	12.2	6.4
Total Extractables	A	92.9	81.8	76.5	72.8	56.7	28.0	25.3	21.6	16.5
	B	91.4	82.2	76.9	71.7	58.8	30.7	24.6	20.0	16.9
	Mean	92.2	82.0	76.7	72.3	57.7	29.4	24.9	20.8	16.7
Non-extractables	A	3.6	9.5	14.7	15.9	18.0	21.7	23.7	18.7	16.8
	B	3.5	9.6	15.4	16.2	16.9	19.3	23.3	19.2	16.2
	Mean	3.6	9.6	15.0	16.0	17.4	20.5	23.0	19.0	16.5
$^{14}\text{CO}_2$	A	n.p.	0.1	0.9	2.5	19.2	46.1	48.7	56.5	58.4
	B	n.p.	0.1	0.9	2.7	18.3	45.2	46.5	55.8	57.4
	Mean	n.p.	0.1	0.9	2.6	18.7	45.6	47.6	56.2	57.9
Other volatiles in EG	A	n.p.	0.8	0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
	B	n.p.	0.8	0.1	<0.1	<0.1	0.3	0.1	<0.1	<0.1
	Mean	n.p.	0.8	0.1	<0.1	<0.1	0.2	0.1	<0.1	<0.1
TOTAL	A	96.6	92.2	92.1	91.2	93.8	96.0	96.8	96.8	91.7
	B	94.9	92.8	93.3	90.5	91.9	95.5	94.5	95.1	90.6
MEAN $\pm$ SD				93.8	$\pm$	2.1				

* Extracted with Acetonitrile/water (1:1; v/v), three times

** Soxhlet extraction with Acetonitrile/water (4:1; v/v) for four hours

n.p.: Not performed

SD: Standard deviation

Table B.8.1.1-22: Balance of the applied radioactivity in the Speyer 6S soil (IV) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N-dimethylthiourea Speyer 6S (% AR)	Sample	INCUBATION TIME IN DAYS									
		0	0.17	0.50	1	3	7	14	35	60	145
Extractables*	A	80.8	60.8	49.7	43.0	26.5	8.2	5.7	4.7	4.6	3.7
	B	80.6	62.8	51.9	41.4	25.2	8.0	5.7	4.7	4.4	3.9
Soxhlet**	A	4.1	6.2	10.8	13.0	9.5	8.6	5.9	7.8	7.9	5.7
	B	3.8	7.0	10.7	12.0	12.4	8.5	7.0	8.5	8.7	5.6
Total Extractables	A	84.8	66.2	60.6	55.9	36.0	16.8	11.6	12.5	12.5	9.4
	B	84.4	69.8	62.6	53.4	37.6	16.5	12.8	13.2	13.1	9.5
	Mean	84.6	68.0	61.6	54.7	36.8	16.7	12.2	12.9	12.8	9.5
Non-extractables	A	8.3	27.1	32.0	37.1	40.1	36.2	40.4	34.4	29.6	32.2
	B	6.5	25.1	37.5	38.5	36.3	36.0	37.4	35.9	30.4	32.0
	Mean	7.4	26.1	34.8	37.8	38.2	36.1	38.9	35.2	30.0	32.1
$^{14}\text{CO}_2$	A	n.p.	0.1	0.8	3.3	18.6	43.5	47.7	49.2	51.1	52.7
	B	n.p.	0.1	0.6	3.8	18.3	45.4	46.7	49.1	53.3	53.2
	Mean	n.p.	0.1	0.7	3.6	18.5	44.4	47.2	49.2	52.2	52.9
Other volatiles in EG	A	n.p.	0.6	0.1	0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1
	B	n.p.	0.5	0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1
	Mean	n.p.	0.6	0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
TOTAL	A	93.2	94.0	93.4	96.5	94.7	96.6	99.8	96.1	93.2	94.3
	B	90.9	95.5	100.7	95.8	92.1	98.0	96.9	98.3	96.8	94.7
MEAN $\pm$ SD				95.6	$\pm$	2.5					

* Extracted with Acetonitrile/water (1:1; v/v), three times

** Soxhlet extraction with Acetonitrile/water (4:1; v/v) for four hours

n.p.: Not performed

SD: Standard deviation

Table B.8.1.1.1-23: Pattern of degradation and formation of metabolites in the Am Fischteich soil (I) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N-dimethylthiourea Am Fischteich (% AR)	Sample	INCUBATION TIME IN DAYS									
		0	0.17	0.50	1	3	7	14	35	60	145
Parent	A	55.0	23.9	6.5	3.0	*	*	*	*	*	*
	B	56.1	23.2	7.6	3.1	*	*	*	*	*	*
	Mean	55.6	23.6	7.1	3.0	*	*	*	*	*	*
M1	A	23.1	31.1	35.9	33.5	13.5	10.0	7.3	2.4	1.0	0.7
	B	24.6	31.8	33.9	32.3	11.9	9.7	6.7	2.4	1.2	0.6
	Mean	23.9	31.4	34.9	32.9	12.7	9.8	7.0	2.4	1.1	0.6
M2	A	1.3	1.0	0.9	0.3	2.2	1.1	0.3	*	*	*
	B	1.2	0.1	1.7	0.3	2.5	1.2	0.3	*	*	*
	Mean	1.2	0.5	1.3	0.3	2.3	1.1	0.3	*	*	*
M3	A	2.6	4.8	8.0	1.5	2.1	3.5	3.4	5.6	6.6	7.6
	B	0.8	7.7	9.9	1.8	5.7	3.8	4.0	6.0	7.0	7.0
	Mean	1.7	6.2	9.0	1.7	3.9	3.6	4.0	5.8	6.8	7.3
M4	A	0.8	5.9	2.7	9.8	17.5	6.2	3.1	2.1	1.4	1.1
	B	0.6	2.7	1.9	11.0	13.3	6.1	3.8	1.4	1.3	0.9
	Mean	0.7	4.3	2.3	10.4	15.4	6.2	3.5	1.8	1.4	1.0
M5	A	*	1.6	1.2	2.8	2.0	2.2	1.2	2.4	2.7	1.2
	B	*	1.1	1.8	2.0	2.6	1.1	1.5	1.5	2.0	1.5
	Mean	*	1.3	1.5	2.4	2.3	1.1	1.4	2.0	2.4	1.4
M6	A	*	0.4	0.8	1.7	1.3	0.6	*	*	*	*
	B	*	0.4	0.9	2.3	2.0	0.5	*	*	*	*
	Mean	*	0.4	0.8	2.0	1.0	0.6	*	*	*	*
M7	A	0.2	0.4	0.6	0.5	*	*	*	*	*	*
	B	0.5	0.6	0.4	0.5	*	*	*	*	*	*
	Mean	0.4	0.5	0.5	0.5	*	*	*	*	*	*
M8	A	*	*	*	*	*	*	*	*	*	*
	B	*	*	*	*	*	*	*	*	*	*
	Mean	*	*	*	*	*	*	*	*	*	*
M9	A	0.4	0.1	<LOQ	0.3	0.5	0.4	0.4	0.2	0.3	0.2
	B	0.1	0.1	<LOQ	0.3	1.3	1.6	0.4	0.2	0.3	0.2
	Mean	0.2	0.1	<LOQ	0.3	0.9	1.0	0.4	0.2	0.3	0.2
Non-extractables	A	10.2	25.2	34.6	36.8	38.8	38.9	42.7	41.3	35.8	34.6
	B	10.1	27.6	32.7	38.1	38.8	36.6	41.7	41.8	35.9	35.0
$^{14}\text{CO}_2$	A	np.	0.2	1.5	4.0	17.4	31.6	36.6	41.2	46.4	50.1
	B	np.	0.2	1.3	3.3	17.3	31.5	36.1	42.8	46.1	49.1
TOTAL	A	93.6	94.5	92.9	94.2	95.2	93.4	94.9	95.4	94.3	95.5
	B	94.0	95.4	92.2	95.8	96.2	92.1	95.0	96.1	93.9	94.4

* Not detected or below limit of detection

LOQ: Limit of quantification

n.p.: Not performed

Table B.8.1.1.1-24: Pattern of degradation and formation of metabolites in the Grossstorkwitz soil (II) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N'-dimethylthiourea Grossstorkwitz (% AR)	Sample	INCUBATION TIME IN DAYS								
		0	0.17	0.50	1	3	7	14	35	60
Parent	A	64.5	52.1	27.7	5.9	*	*	*	*	*
	B	66.5	54.3	23.0	6.5	*	*	*	*	*
	Mean	65.5	53.2	25.3	6.2	*	*	*	*	*
M1	A	19.0	21.9	36.5	47.9	34.6	2.6	1.5	2.2	0.9
	B	18.7	22.8	40.5	47.1	32.8	2.9	1.6	2.0	0.8
	Mean	18.9	22.3	38.5	47.5	33.7	2.7	1.6	2.1	0.9
M2	A	1.0	1.3	0.8	0.5	*	0.6	*	*	*
	B	1.3	0.8	0.7	0.3	*	0.6	*	*	*
	Mean	1.1	1.0	0.8	0.4	*	0.6	*	*	*
M3	A	2.9	2.0	3.4	1.2	4.8	6.5	4.8	3.9	3.9
	B	1.6	2.3	2.1	1.0	5.8	5.8	5.0	3.1	3.8
	Mean	2.3	2.2	2.8	1.1	5.3	6.2	4.9	3.5	3.9
M4	A	2.0	4.4	7.0	11.8	9.5	6.7	7.4	6.4	3.0
	B	1.2	4.9	6.8	11.5	10.2	7.8	8.2	5.9	3.4
	Mean	1.6	4.6	6.9	11.7	9.8	7.8	7.8	6.2	3.2
M5	A	0.8	2.5	2.7	4.6	3.3	3.9	3.5	3.1	3.9
	B	0.9	2.6	3.7	4.6	4.8	4.3	3.8	3.7	3.5
	Mean	0.8	2.5	3.2	4.6	4.1	4.1	3.7	3.4	3.7
M6	A	*	*	0.3	2.3	*	*	*	*	*
	B	<LOQ	0.2	0.7	2.0	*	*	*	*	*
	Mean	*	0.1	0.5	2.1	*	*	*	*	*
M7	A	*	0.2	0.8	*	*	*	*	*	*
	B	*	0.1	*	*	*	*	*	*	*
	Mean	*	0.1	0.4	*	*	*	*	*	*
M9	A	0.2	<LOQ	0.3	0.3	0.8	0.5	0.4	0.3	0.2
	B	<LOQ	0.1	0.3	0.2	0.8	0.5	0.4	0.2	0.2
	Mean	0.1	<LOQ	0.3	0.3	0.8	0.5	0.4	0.2	0.2
M10	A	*	0.3	*	*	*	*	*	*	*
	B	*	0.1	*	*	*	*	*	*	*
	Mean	*	0.2	*	*	*	*	*	*	*
Non-extractables	A	5.2	8.3	15.2	15.3	18.7	18.5	19.4	18.6	18.1
	B	4.7	7.1	11.8	15.2	17.3	17.7	19.0	17.5	18.4
$^{14}\text{CO}_2$	A	n.p.	0.1	0.5	2.6	14.4	57.9	63.8	64.8	64.2
	B	n.p.	<LOQ	0.7	2.7	16.7	53.3	55.6	63.7	64.8
TOTAL	A	95.5	92.9	95.3	92.3	86.0	97.3	100.7	97.9	94.2
	B	95.6	95.4	90.3	91.2	88.4	93.9	93.6	95.0	94.9

* Not detected or below limit of detection

LOQ: Limit of quantification

n.p.: Not performed

Table B.8.1.1.1-25: Pattern of degradation and formation of metabolites in the Speyer 2.3 soil (III) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N-dimethylthiourea Speyer 2.3 (% AR)	Sample	INCUBATION TIME IN DAYS								
		0	0.17	0.5	1	3	7	14	35	60
Parent	A	78.8	49.2	26.8	8.5	*	*	*	*	*
	B	76.0	50.7	21.9	9.1	*	*	*	*	*
	Mean	77.4	49.9	24.4	8.8	*	*	*	*	*
M1	A	13.3	22.2	35.3	39.6	30.6	4.7	1.2	1.1	0.3
	B	13.0	21.1	37.3	40.8	32.0	4.8	2.2	1.1	1.0
	Mean	13.1	21.7	36.3	40.2	31.3	4.7	1.7	1.2	0.6
M2	A	0.4	*	*	0.3	*	*	*	*	*
	B	*	*	0.8	0.2	2.1	*	*	*	*
	Mean	0.2	*	0.4	0.3	1.0	*	*	*	*
M3	A	0.1	2.1	1.7	1.8	3.1	8.4	2.6	9.4	7.5
	B	1.1	2.4	1.6	1.4	10.1	9.1	10.0	8.4	9.7
	Mean	0.6	2.3	1.6	1.6	6.6	8.7	11.3	8.9	8.6
M4	A	0.1	4.7	9.6	15.4	17.2	7.3	3.9	5.5	5.0
	B	0.9	3.8	12.0	15.1	10.3	8.4	7.7	6.6	3.0
	Mean	0.5	4.2	10.8	15.3	13.7	8.4	5.8	6.1	4.0
M5	A	0.1	2.3	1.5	2.8	2.0	2.4	3.0	3.1	2.3
	B	0.3	3.7	2.6	2.9	2.7	3.5	3.6	2.6	2.2
	Mean	0.2	3.0	2.0	2.8	2.4	3.0	3.3	2.9	2.3
M6	A	*	0.1	0.7	2.9	*	*	*	*	0.8
	B	*	0.3	0.7	2.0	*	*	*	*	*
	Mean	*	0.2	0.7	2.4	*	*	*	*	0.4
M7	A	*	1.0	0.9	0.5	*	*	*	0.6	*
	B	*	0.2	*	*	*	*	*	*	*
	Mean	*	0.6	0.5	0.3	*	*	*	0.3	*
M8	A	*	*	*	0.7	*	*	*	*	*
	B	*	*	*	*	*	*	*	*	*
	Mean	*	*	*	0.3	*	*	*	*	*
M9	A	0.1	<LOQ	<LOQ	<LOQ	3.9	5.0	4.6	1.7	0.5
	B	<LOQ	<LOQ	<LOQ	0.2	1.6	4.0	1.1	1.2	1.0
	Mean	<LOQ	<LOQ	<LOQ	0.1	2.7	4.5	2.9	1.5	0.8
M10	A	*	*	*	0.3	*	*	*	*	*
	B	*	*	*	*	*	*	*	*	*
	Mean	*	*	*	0.1	*	*	*	*	*
Non-extractables	A	3.6	9.5	14.7	15.9	18.0	21.7	22.7	18.7	16.8
	B	3.5	9.6	15.4	16.2	16.9	19.3	23.3	19.2	16.2
$^{14}\text{CO}_2$	A	n.p.	0.1	0.9	2.5	19.2	46.1	48.7	56.5	58.4
	B	n.p.	0.1	0.9	2.7	18.3	45.2	46.5	55.8	57.4
TOTAL	A	98.6	91.4	92.0	91.2	93.9	95.9	96.7	96.8	91.6
	B	94.9	92.0	93.2	90.5	93.9	95.2	94.4	95.1	90.6

* Not detected or below limit of detection

LOQ: Limit of quantification

n.p.: Not performed

Table B.8.1.1.1-26: Pattern of degradation and formation of metabolites in the Speyer 6S soil (IV) treated with ^{14}C -N,N'-dimethylthiourea. Values in percent of applied radioactivity.

N,N-dimethylthiourea Speyer 6S (% AR)	Sample	INCUBATION TIME IN DAYS										
		0	0.17	0.5	1	3	7	14	35	60	145	
Parent	A	68.7	33.4	8.6	0.6	*	*	*	*	*	*	
	B	66.7	36.3	8.4	1.1	*	*	*	*	*	*	
	Mean	67.7	34.8	8.5	0.9	*	*	*	*	*	*	
M1	A	13.4	24.2	38.1	38.4	18.8	4.6	3.3	2.5	1.2	0.4	
	B	14.2	23.8	38.7	34.4	19.6	5.5	2.7	2.1	1.3	0.4	
	Mean	13.8	24.0	38.4	36.4	19.2	5.0	3.0	2.3	1.2	0.4	
M2	A	0.1	1.5	1.0	*	1.2	0.6	*	*	*	*	
	B	0.3	1.4	0.6	0.6	1.1	*	*	*	*	*	
	Mean	0.2	1.4	0.8	0.3	1.2	0.3	*	*	*	*	
M3	A	1.5	4.0	4.0	7.9	4.5	4.7	4.6	5.1	5.1	4.8	
	B	1.2	1.8	8.5	8.8	6.2	3.7	5.3	5.4	5.5	5.5	
	Mean	1.4	2.9	6.2	8.3	5.4	4.2	5.0	5.2	5.3	5.1	
M4	A	0.2	1.3	4.4	1.9	8.9	4.2	2.1	2.1	3.4	1.8	
	B	0.8	4.2	1.3	1.4	5.8	4.7	1.1	3.2	3.1	1.7	
	Mean	0.5	2.7	2.9	1.7	7.4	4.4	1.8	2.6	3.3	1.7	
M5	A	0.1	1.2	2.3	2.2	2.2	2.3	0.9	2.0	1.6	2.0	
	B	0.4	1.7	2.1	2.3	3.3	1.4	1.4	1.6	2.1	1.4	
	Mean	0.3	1.5	2.2	2.3	2.7	1.9	1.1	1.8	1.8	1.7	
M6	A	*	*	0.7	2.7	*	*	*	*	*	*	
	B	*	*	1.9	3.2	*	*	*	*	*	*	
	Mean	*	*	1.3	3.0	*	*	*	*	*	*	
M7	A	0.3	0.4	1.3	1.7	*	*	*	0.5	0.7	0.1	
	B	0.2	0.4	0.9	0.4	0.5	0.8	*	0.7	0.7	0.3	
	Mean	0.3	0.4	1.1	1.0	0.7	0.4	*	0.6	0.7	0.2	
M8	A	*	*	*	*	*	*	*	*	*	*	
	B	*	*	*	0.6	*	*	*	*	*	*	
	Mean	*	*	*	0.3	*	*	*	*	*	*	
M9	A	0.2	0.1	0.2	0.5	0.4	0.4	0.3	0.3	0.4	0.5	
	B	<LOQ	0.2	0.3	0.7	0.3	0.3	0.3	0.3	0.4	0.3	
	Mean	0.1	0.2	0.3	0.6	0.3	0.3	0.3	0.3	0.4	0.4	
M10	A	0.3	*	*	*	*	*	*	*	*	*	
	B	0.4	*	*	*	*	*	*	*	*	*	
	Mean	0.4	*	*	*	*	*	*	*	*	*	
Non-extractables	A	8.3	27.1	32.0	37.1	40.1	36.2	40.4	34.4	29.6	32.2	
	B	6.5	25.1	37.5	38.5	36.3	36.0	37.4	35.9	30.4	32.0	
¹⁴ CO ₂	A	np.	0.1	0.8	3.3	18.6	43.5	47.7	49.2	51.1	52.7	
	B	np.	0.1	0.6	3.8	18.3	45.4	46.7	49.1	53.3	53.2	
TOTAL	A	93.2	93.4	93.4	96.4	94.7	96.5	99.7	96.1	93.2	94.3	
	B	90.9	94.9	100.7	95.8	92.1	97.9	96.9	98.3	96.8	94.6	

* Not detected or below limit of detection

LOQ: Limit of quantification

n.p.: Not performed

Proposed metabolic pathway of ^{14}C -N,N'-dimethylthiourea in soil incubated under aerobic conditions.

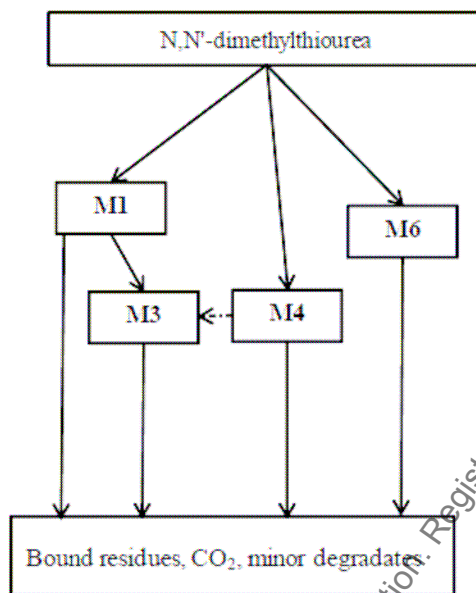


Table B.8.1.1.1-27: N,N'-dimethylthiourea (P) and degradation products

Degradation Product Code (see HPLC)	Elemental Formula	Molecular Mass [Da]	Chemical Structure
M6	$\text{C}_3\text{H}_8\text{N}_2\text{O}_2\text{S}$	136	
M1 ($\equiv$ R2)	$\text{C}_3\text{H}_8\text{N}_2\text{O}$	88	
M3	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}$	156	
P ($\equiv$ R1)	$\text{C}_3\text{H}_8\text{N}_2\text{S}$	104	
M4	$\text{C}_6\text{H}_{14}\text{N}_4\text{S}$	174	

Table B.8.1.1.1-28: DT₅₀, DT₉₀ values for DMTU

Soil	Alternative denomination	N,N'-dimethylthiourea	
		DT ₅₀ (d)	DT ₉₀ (d)
Am Fischteich	I	0.15	0.49
Grossstorkwitz	II	0.35	1.18
Speyer 2.3	III	0.30	0.99
Speyer 6S	IV	0.17	0.57

Conclusion:

The geomean DT₅₀ of DMTU (impurity of the technical substance that has a maximum content of 3.5 g/L in metam-sodium) in soils is 0.23 days.

Determination of modelling endpoints for DMTU from laboratory degradation studies using ModelMaker 4.0, according to FOCUS Kinetics (McMillan C. (2010a))

Guideline:

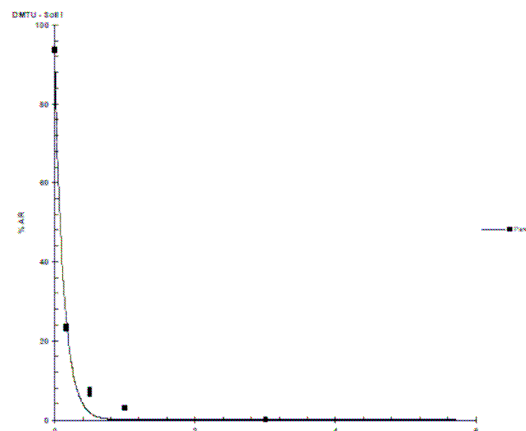
FOCUSkinetics guidance document (FOCUS, 2006).

Findings and conclusions:

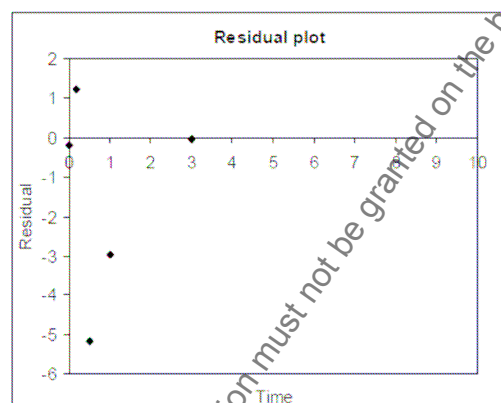
A rate of degradation in soil study (under laboratory conditions), has been conducted with DMTU in 4 soils. It was possible to derive modelling endpoints (DT₅₀) for this compound in all four soils using single first-order (SFO) kinetics. The selected model adequately described the decline of DMTU in soil.

Appendix 4 – Plots of residues and residuals with time

SI



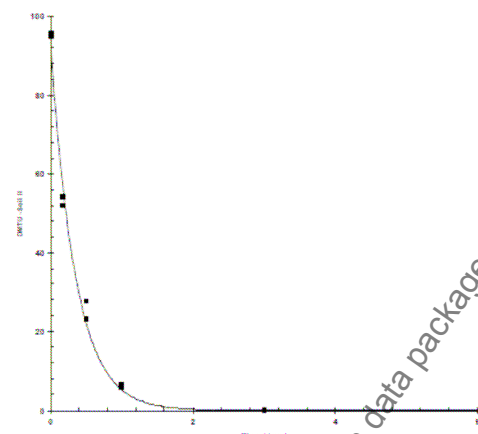
(a)



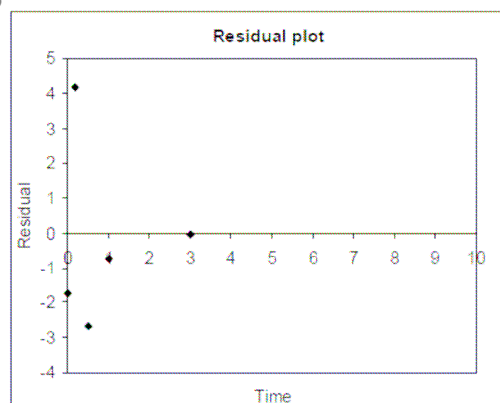
(b)

Figure 1 - Visual assessment of goodness of fit of SFO model to DMTU in SI:
(a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

SII



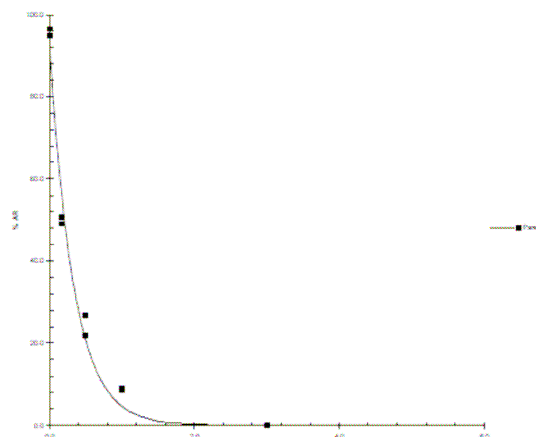
(a)



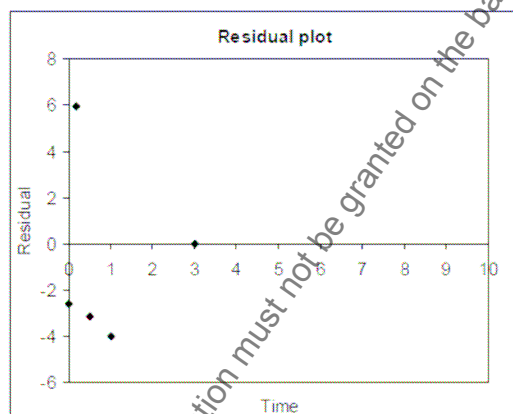
(b)

Figure 2 - Visual assessment of goodness of fit of SFO model to DMTU in SII:
(a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

SIII



(a)

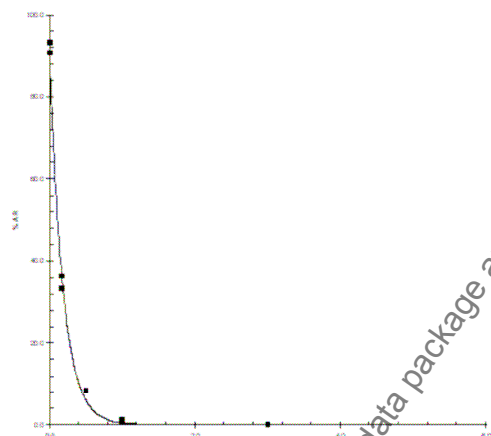


(b)

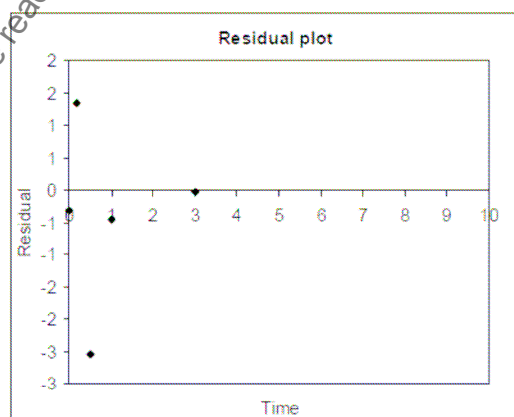
Figure 3 - Visual assessment of goodness of fit of SFO model to DMTU in SIII:

(a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

SIV



(a)



(b)

Figure 4 - Visual assessment of goodness of fit of SFO model to DMTU in SIV:

(a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

Table B.8.1.1.1-29: Modelling DT₅₀ and DT₉₀ values derived for DMTU (normalised to pF2.0)

Soil	Kinetic Model	χ^2 error	DT ₅₀ (days)	DT ₉₀ (days)	Moisture correction factor	Modelling DT ₅₀ (days)	Modelling DT ₉₀ (days)
I	SFO	8.5	0.089	0.295	0.898	0.080	0.265
II	SFO	5.2	0.241	0.801	0.789	0.190	0.632
III	SFO	8.2	0.231	0.769	0.739	0.171	0.568
IV	SFO	3.8	0.127	0.422	0.646	0.082	0.273
					Geometric mean:	0.121	0.401

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.1, the RMS had to assess and summarize in an addendum information available on metabolite MITC including Phys-Chem properties relevant for the environmental risk assessment. Valid studies to be included in the list of references relied on. The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

Table 2: Physical and chemical properties of the metabolite MITC (methylisothiocyanate)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
B.2.1.5 Vapour pressure (IIA 2.3.1)	OECD 104 EEC A4 (Gas saturation method) GLP	Methylisothiocyanate (MITC), 99.4% pure (Batch AO17701301): 1739 Pa (20°C) (interpolated from measurements at 15°C and 25°C) <i>Note:</i> In first instance, dynamic method was chosen, but this method was not applicable to test item MITC due to decomposition at elevated temperatures.	Acceptable MITC is considered to be a highly volatile substance.	Lindemann, 2003 (RCC 850435)
B.2.1.6 Volatility – Henry's law constant (IIA 2.3.2)	Calculation GLP not relevant (calculation)	MITC: $H = 14.2 \text{ Pa.m}^3/\text{mol}$ (20°C) values used for calculation: water solubility at 20°C: 8.94 g/L (see point B.2.1.14) vapour pressure at 20°C: 1739 Pa (see point B.2.1.5)	Acceptable MITC is considered to be moderately volatile from water.	Taminco, 2004b
B.2.1.7 Physical state, colour (IIA 2.4.1)	Visual inspection	MITC, 97.0% pure (Lot No. 66905-026): Colourless crystalline solid	Acceptable	Flack, 1997 (FCC 153/962827)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References																										
B.2.1.9 Spectra of the active substance (IIA 2.5.1)	OECD 101 GLP	MITC, 97.0% pure (Lot No. 66905-026): Following spectra were provided: UV/VIS (scanned range: 190-500 nm) IR (KBr; sample scanned over range 4500-500cm⁻¹) ¹H-NMR (CDCl₃; 400 MHz) MS (EI, 70 eV) The different spectra were found to be in agreement with the chemical structure of MITC. UV/VIS absorption characteristics : <table><tr><td></td><td>λ_{max} (nm)</td><td>ϵ (L.mol⁻¹.cm⁻¹)</td></tr><tr><td rowspan="3">Neutral (distilled water)</td><td>235</td><td>635</td></tr><tr><td>283</td><td>65</td></tr><tr><td>321</td><td>17</td></tr><tr><td rowspan="3">Alkaline (0.1 M NaOH)</td><td>276</td><td>46</td></tr><tr><td>320</td><td>5</td></tr><tr><td>at λ 290 nm</td><td>Not reported, but > 10 based on spectrum</td></tr><tr><td rowspan="4">Acidic (0.1M HCl)</td><td>235</td><td>635</td></tr><tr><td>283</td><td>23</td></tr><tr><td>324</td><td>6</td></tr><tr><td>at λ 290 nm</td><td>Not reported, but > 10 based on spectrum</td></tr></table> The absorption in the wavelength range 200-300 nm was shown to be significantly different / higher in alkaline medium, compared to that observed under neutral and acidic conditions.		λ_{max} (nm)	ϵ (L.mol ⁻¹ .cm ⁻¹)	Neutral (distilled water)	235	635	283	65	321	17	Alkaline (0.1 M NaOH)	276	46	320	5	at λ 290 nm	Not reported, but > 10 based on spectrum	Acidic (0.1M HCl)	235	635	283	23	324	6	at λ 290 nm	Not reported, but > 10 based on spectrum	The submitted UV, IR, NMR and MS spectra for MITC are considered acceptable	Flack, 1997 (FCC 153/962827)
	λ_{max} (nm)	ϵ (L.mol ⁻¹ .cm ⁻¹)																												
Neutral (distilled water)	235	635																												
	283	65																												
	321	17																												
Alkaline (0.1 M NaOH)	276	46																												
	320	5																												
	at λ 290 nm	Not reported, but > 10 based on spectrum																												
Acidic (0.1M HCl)	235	635																												
	283	23																												
	324	6																												
	at λ 290 nm	Not reported, but > 10 based on spectrum																												

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
B.2.1.11 Solubility in water (IIA 2.6)	EEC A6 (Flask method; analysis of MITC conc. by HPLC-UV) GLP	MITC, 97.0% pure (Lot No. 66905-026): 8,94 g/L at 20°C (pH 7.5)	Acceptable; MITC is readily soluble in water.	Flack, 1997 (FCC 153/962827)
B.2.1.13 Partition coefficient n-octanol/water (IIA 2.8)	EEC A8 (Shake-flask method) GLP	MITC, 97.0% pure (Lot No. 66905-026): log P _{ow} at 20°C: 1.05 (pH 7.5)	Acceptable; MITC has a log P _{ow} of 1.05 and hence, bioaccumulation of MITC in the environment is not expected.	Flack, 1997 (FCC 153/962827)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References																
B.2.1.14 Hydrolysis rate at pH 4, 7 and 9 under sterile conditions in the absence of light (IIA 2.9.1)	OECD 111 GLP	[¹⁴C]-Methyl Isothiocyanate (CH₃N=[¹⁴C]=S) (Batch No. 3501-187); radiochemical purity = 98.46%; 30 days incubation at 15°C, 25°C and 50°C; pH 4, 7 and 9 buffer solutions; Test conc. < 0.01 M <i>Estimated half-lives DT₅₀ (days) (assuming first order kinetics):</i> <table><tr><td></td><td>15°C</td><td>25°C</td><td>50°C</td></tr><tr><td>pH 4</td><td>(a)</td><td>≈ 40</td><td>2*</td></tr><tr><td>pH 7</td><td>(a)</td><td>50</td><td>2*</td></tr><tr><td>pH 9</td><td>22</td><td>11</td><td>< 1 day (b)</td></tr></table> *possibly underestimation because of poor resolution of MITC from degradation products in severely degraded samples → DT₅₀ calculated based on decline of MITC in first 7 days of incubation (a) No significant degradation observed → No DT50 calculated (b) Rapid degradation, but kinetics not linear → No DT50 calculated Degradation was found to be more extensive at higher temperatures and higher pH (concomitant with higher hydroxyl ion concentration).		15°C	25°C	50°C	pH 4	(a)	≈ 40	2*	pH 7	(a)	50	2*	pH 9	22	11	< 1 day (b)	Acceptable MITC is shown to degrade significantly by hydrolysis at every pH and temperature (with the exception of pH 4 and 7 at 15°C). Estimations of half-lives were given and degradation pathways for MITC at pH 4, 7 and 9, respectively, were proposed in the study report. Degradation of MITC was found to be more extensive at higher temperatures and at higher pH (concomitant with higher hydroxyl ion concentration). Major degradation products were identified as dimethylurea (DMU), dimethyl thiourea (DMTU) and methyldithiocarbamic acid (MDTCA, i.e. metam) Besides, there were indications that volatile degradates were formed at pH 4 (and pH 7).	Kidd <i>et al.</i> , 2005 (Inveresk Report No. 24450)
	15°C	25°C	50°C																	
pH 4	(a)	≈ 40	2*																	
pH 7	(a)	50	2*																	
pH 9	22	11	< 1 day (b)																	

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
		<i>Major degradation products ($\geq 10\%$ of applied radioactivity AR):</i> Dimethylurea, dimethyl thiourea and methyldithiocarbamic acid (MDTCA) <i>Product identification:</i> By match of HPLC retention times with those of reference compounds. Confirmation by mass spectrometry. <i>Mass balance:</i> At pH 4: clear decrease of overall recovery of AR at higher temperature (down to 41% at 50°C), indicating that MITC was degrading to volatile degradates. At pH 7: decrease down to 79% at 50°C. At pH 9: mean recoveries in range 100-118% and no decrease, indicating that degradation of MITC at pH 9 gives rise to non-volatile components.		

Conclusions of the peer review: open point fulfilled; the phys-chem data of MITC will be included in the LoEP.

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.2, RMS had to provide an addendum with the following additional information from aerobic degradation in soil study Hall, B.E. et al 2004:

- to provide in an addendum gravimetric water content at MWHC and at field capacity of the soils investigated
- to provide at least recovery, and LOQ of the extraction and analytical method employed in an addendum; ideally other details as temperature, pH and volume of water should be provided as well
- clarify that in both radioactivity in soil ethyl acetate extract and in the ethyl acetate trap were added together to determine the rate of degradation of MITC and that the identity of MICT was only checked in the first sample of the ethyl acetate trap.

The Notifier's position and the RMS conclusion, which were reported in the addendum dated June 2008, are reported hereunder as the conclusion of the peer review.

Extract from the addendum dated June 2008 :**Soil moisture**Table B.8.1.1.1-3: Characteristics of the soils used to investigate the route and rate of degradation of [¹⁴C] metam-sodium

Soil (USDA Classification)	Particle Size Analysis			pH		% Organic Matter	C.E.C	WHC (at 0.33 bar)
	% Sand	% Silt	% Clay	Water	KCl			
Sandy Loam (Code S402)	77.90	10.21	11.89	5.4	4.7	6.97	26.2	28.8
Sandy Loam (Code S403)	71.34	15.96	12.71	5.7	5.1	1.87	11.8	19.9
Silt Loam (Code S405)	13.39	61.72	24.89	7.1	6.2	7.31	34.3	26.6
Clay Loam (Code S404)	43.51	22.81	33.68	7.7	7.1	2.89	25.8	38.9

* Lead soil

% Organic Matter = % Organic Carbon (Addendum 1) x 1.7

C.E.C = Cation Exchange Capacity

Table B.8.1.1.1-4: Characteristics of the soils used to investigate the route and rate of degradation of [¹⁴C]MITC

Soil (USDA Classification)	Particle Size Analysis			pH		% Organic Matter	C.E.C	WHC (at 0.33 bar)	MWHC
	% Sand	% Silt	% Clay	Water	KCl				
Sandy Loam 2* (Code S480)	82.63	5.57	10.79	5.2	4.1	1.53	9.3	18.7	46.7
Sandy Loam 1 (Code S500)	77.79	12.63	9.58	4.5	3.7	12.41	16.4	29.5	84.8
Silt Loam (Code S490)	12.24	62.27	25.49	6.1	5.2	6.46	16.8	42.5	91.0
Clay Loam (Code S479)	44.59	19.95	35.45	7.6	7.0	2.38	18.8	26.0	57.7

* Lead soil

% Organic Matter = % Organic Carbon (Addendum 1) x 1.7

C.E.C = Cation Exchange Capacity

LOQ etc.

The assay was radiolabelled therefore LOQs as such were not determined. From Report section 4.2.2 (Phase 1) we know that metam sodium was detectable at the 1% applied radioactivity level. From Table 24 (Phase 2) we know that unknowns in the water fraction were detected at less than 1%AR. We only profiled at the 5% level (regulatory cut-off for identification).

Regarding extraction efficiency, this is indicated in the mass balance data for Phase 2. In some cases non-extractable residues were high but we did try other extractants to reduce these (report 3.7.7.2.2). Regarding extraction methods,

these are in the report (volumes etc). We did not fix the pH for extraction. Where chilled extractant was used, this was placed on ice but the temperature was not recorded.

MITC in traps and extracts

As stated in the report the traps were combined when calculating the %MITC used in DT calculations. MITC was the only component detected in the first EA trap there it seems reasonable to assume that radioactivity in subsequent EA traps was also MITC. It would be strange for another metabolite to pass through the first trap and be collected in the second identical trap.

Conclusions of the peer review: open point 4.2 fulfilled

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.3, MSs experts to discuss in a meeting of experts the acceptability and the end points to be derived from the aerobic degradation in soil study Hall, B.E et al. 2004.

Among the aspects to be discussed are the following:

- if the study may be considered an appropriate route study considering that identity of compounds in the ethyl acetate trap is only analyzed for the first sampling point

-effect of mode of application of the substances tested on the study results

-validity of the analytical method employed

-if half life in sandy loam 2 soil may be considered reliable taking into consideration that only 3 data points are available.

-if degradation may actually be considered microbially driven or due to hydrolysis and potential effect of pH

- effect of using linear regression instead of non linear regression to derive the half lives

-use of single samples for metam experiments and for MITC at 0.25 (6 hours), 2, 4, 10 and 15 DAT.

The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

Extract from the addendum dated June 2008 :

Ethylacetate trap:

See also open point 4.2

The identity of compounds has been determined by GC in the first ethyl acetate trap (in the sequence of 3 ethyl acetate traps used at each timepoint) at each sampling point from t0 to study termination.

Mode of application: surface application

Validity of Analytical Method employed

All methods used radiodetection for accuracy and selectivity; both methods used afforded adequate resolution of components

- Metam sodium (Phase 1): Direct analysis of aqueous extracts by radio-HPLC.

- MITC (Phase 2): GC is the preferred method for analysing MITC, we did this in conjunction with radiodetection.

This methods would also have detected other volatile degradation products of radiolabelled MITC.

- HPLC was also used in Phase 2 to detect radiolabelled entities which partitioned into the aqueous extract phase.

Half-life in sandy loam 2

The EFSA point is valid since the number of time points available is low, however from the data it is clear that the half life is short and less than 10 minutes. It would not be unreasonable to discount this data set, but even if this was done, the risk assessment would not be affected.

Microbial vs Hydrolysis

Historically soil studies have been acceptable to regulatory authorities when conducted at moisture levels of between 40 and 60% MWHC (variety of guidelines); we used 50% as an average. Therefore the incubation conditions were conducive to microbial degradation. Reference to the MITC hydrolysis results

1) the degradation half lives are significantly shorter than the hydrolytic half lives and

2) the degradation half lives do not show a pH trend which is in keeping with the hydrolysis study data

It can be concluded that the effect of the presence of the soil is having a far more significant effect on the degradation half life than would be expected from pH alone.

Linear regression vs SFO Kinetics

DT50 values are calculated by using linear regression of $\ln$ values. According to FOCUS kinetics non-linear regression using SFO should be used in the first instance. However in this case the end results by both calculations methods are the same. For all regressions (Phases 1 and 2), the R values are very good / acceptable and indicative of the goodness of fit of the regression line. Looking at the plots there is only one case where an SFO model might be better, this is Soil S402 in Phase 1.

Use of single vs replicate samples

Single samples were taken at each time point to derive the DT50 of metam. Considering the rapid degradation of the compound (mean DT50 of 10 minutes), this deviation has no impact on the final risk assessment

In order to derive the DT50 of MITC (mean DT50 of 2.15 days), duplicate samples were taken at day 0, 1, 7 and 21 while single samples were taken at day 0.25 (6 hours), 2, 4, 10 and 15. This deviation would have an impact on the error level but not on the endpoint derivation. As RMS we have considered that the deviation was minor.

Conclusions of the peer review on open point 4.3: a new data gap has been proposed.

Added in August 2010

A data gap was identified by the meeting of experts to address the range of half-lives available for metam and MITC and whether they are applicable to metam EU risk assessment. The notifier should address the different variables that might impact on the degradation in soil, such as method of application dose rate and soil adaptation.”

An Evaluation of the Fate in Soil of MITC under Aerobic Conditions. (Terry, 2010a)

MITC (methyl isothiocyanate) is the metabolite of metam-sodium (sodium N-methyldithiocarbamate), a liquid formulation used to control organisms preplant in a number of crops. Metam-sodium degrades in soil to give MITC, which is a gaseous soil fumigant (vapour pressure 1739 Pa at 20°C) and the active ingredient. The information available for MITC arising from dazomet was found to be of little relevance to MITC arising from metam-sodium.

Regulatory studies

Two regulatory soil degradation studies are available which investigate the fate in soil of metam-sodium or MITC. One of these (Hall, 2004) was a well designed study specifically modified to investigate the degradation of MITC taking into account its very high volatility. This study concluded that metam-sodium very rapidly transformed to give MITC, and that MITC rapidly degraded (DT50 0.97 to 2.94 days) to carbon dioxide and unextractable soil bound residues. See point B.8.1.1.1. (above)

Published literature

In addition to these regulatory studies, there have been numerous investigations into the fate of MITC in soil and volatile loss from soil published in the literature. Unfortunately, the reported investigations were not conducted to modern guidelines, were not carried out to Good Laboratory Practice and did not use radiolabelled materials. In addition, the number of sampling points was small (typically three or four) and the actual residue data was not reported (either graphs or tables of rate constants/DT50 values only were reported).

Table B.8.1.1.1-5: Summary of selected literature for metam-sodium and MITC

Reference	Title	Summary
(1) Boesten J.J.T.I. Van der Pas L.J.T., Smelt J.H. and Leistra M. (1991) Netherlands Journal of Agricultural Science, 39, 179-190.	Transformation of methyl isocyanate and 1,3-dichloropropene in water-saturated sandy subsoils.	Water-saturated sandy subsoils (collected from 2 – 4 m below the surface) from 4 sites in the Netherlands incubated in sealed vessels with MITC at 10°C, in the laboratory, for up to 205 days. No GLP, non-radiolabelled, no tabulated residue data given. In 3 subsoils degradation very fast (<10% remaining after 30 days); in 1 subsoil DT ₅₀ about 35 days. Little quantitative relevance for regulatory risk assessment.
(2) Frick A., Zebarth B.J. and Szeto S.Y. (1998) Journal of Environmental Quality, 27, 1158-1169.	Behaviour of the soil fumigant methyl isothiocyanate in repacked soil columns.	4 soils, from British Columbia (Canada), packed into PVC columns. 30 cm of soil, 1.35 g/cm ³ , leached with Ca(NO ₃) ₂ ; air headspace flow-through system; non-radiolabelled MITC injected into column as a liquid; charcoal volatility traps employed. Leaching loss, volatilization loss, and soil-extractable MITC simultaneously measured, at 21°C. Percent degradation inferred indirectly. In one soil different leaching regimes applied to the columns. Conditions leading to leaching suppressed volatilization fluxes. Gas phase diffusion very important in determining fate, as gas phase diffusion coefficient 1000-10000 bigger than liquid diffusion coefficient. Site specific characteristics (bulk soil density, water content) strongly influence outcome. Soil DT ₅₀ values cannot be calculated from the data. Useful qualitative data, but no quantitative data for use in regulatory risk assessment.
(3) Gan J., Papiernik S.K., Yates S.R. and Jury W.A. (1999) Journal of Environmental Quality, 28, 1436-1441.	Temperature and moisture effects on fumigant degradation in soil.	Degradation in soil (2 Californian and one Minnesotan soil) for MITC investigated across a range of soil temperatures (20 – 50°C), and one soil moisture (12%). 10 g of soil in 21 mL headspace, sealed vials. Sterile soil samples included. Soil moisture investigation (soil moisture contents 1.6 – 16%) carried out with 2 soils and at one temperature (30°C). MITC rate of degradation increased by a factor of 4.8 to 10.6 times from 20 to 50°C. Microbial degradation was the predominant degradation pathway for MITC (rather than chemical). MITC degradation decreased as soil moisture content increased. Only 4 timepoints; only graphical data presented. Useful qualitative data, but no quantitative data for use in regulatory risk assessment.
(4) Leistra M. (1973) Proceedings 7th British Insecticide and Fungicide Conference, 90-95	Computations on soil fumigation with metam-sodium.	A set of equations were presented which simulate the conversion of metam-sodium to MITC by considering vapour diffusion and leaching simultaneously. No relevance for regulatory risk assessment.
(5) Leistra M. (1974) Netherlands Journal Plant Pathology, 80, 61-71.	Predictions on effectivity and after-effects of metam-sodium by simulating soil fumigations.	Simulations were conducted to give 2D predictions of the distribution of MITC with soil depth, in various soils with different application methods, at different temperatures. The dissipation of MITC from the soil, over time, was also simulated.

		Adequate nematode control with peaty soils was predicted to be difficult to achieve (because of adsorption and dilution), and was predicted to be possible only under drier conditions. Injection as a line was predicted to give less favourable dose patterns than injection as a plane. The main conclusion was that temperature is very important in determining the waiting period required following treatment until planting could be undertaken, with higher temperatures being more favourable. No relevance for regulatory risk assessment.
(6) Leistra M. and Boesten J.J.T.I. (1989) Agriculture, Ecosystems and Environment, 26, 369-389.	Pesticide contamination of groundwater in Western Europe.	MITC not mentioned.
(7) Leistra M. and Crum S.J.H. (1990) Water, Air, and Soil Pollution, 50, 109-121.	Emission of methyl isothiocyanate to the air after application of metam-sodium to greenhouse soil.	The residues in a greenhouse soil treated with metam-sodium were determined 8 days after treatment. Various soil properties and soil moisture values were also measured, as was the permeability of LDPE (used as a soil cover following treatment) to MITC. Simulations for the dissipation of MITC from the greenhouse soil were carried out for various scenarios. Prediction fits to measured residues were not reported. No relevance for regulatory risk assessment.
(8) Smelt J.H., Crum S.J.H. and Teunissen W. (1989) Journal Environmental Science and Health, B24(5), 437-455.	Accelerated transformation of the fumigant methyl isothiocyanate in soil after repeated application of metam-sodium.	Non-GLP investigations were carried out to explore if enhanced degradation of MITC explained the efficacy failure encountered for some fields (problem fields) in the Netherlands. A selection of field soils and greenhouse soils were collected; some having been treated many times with metam-sodium and some never treated, in addition to soil from the problem fields. Incubations with non-radiolabelled-MITC were carried out in the laboratory, with 50 g of soil in 300 or 600 mL stoppered flasks, at 15°C; flasks were analysed after incubation up to 45 days (depending on rate of MITC degradation). Degradation of metam-sodium to MITC was also measured in a smaller number of soils. Metam-sodium was found to degrade very fast in all soils tested. Measured MITC degradation rates were found to be 0.5 to 50 days. Degradation in three humic sand soils was particularly slow. In some of the soils a pronounced 'lag' phase was evident; characterized as an accelerating degradation. Generally, the transformation in previously treated soils was faster, to much faster, than in never treated soils. Tables of residues with time were not reported (only log graphs). No relevance for regulatory risk assessment.
(9) Leistra M. and Smelt J.H. (1974) Agro-Ecosystems, 1, 169-176.	Optimum soil conditions for fumigation with metam-sodium.	Aim, for the use of a fumigant, is to how to achieve satisfactory control with the lowest dose and shortest period of after-effects. Calculations were carried out to simulate the use of metam-sodium when the soil moisture and temperature were varied.

		The simulations indicated that under wet conditions (pF 1.5) diffusion rates for MITC are too low such that MITC would degrade too rapidly to allow sufficiently high concentrations to build up in a spatially sufficient manner for efficacy. Overall, conditions promoting a higher vapour phase mobility (e.g. drier conditions, pF2 – 2.5) are preferred with respect to efficacy. More favourable efficacy was predicted at lower temperatures. However, lower temperatures led to a higher persistence of MITC which would lead to more pronounced after-effects in the field. Quantitatively these analyses are of no relevance to regulatory risk assessment. However, qualitatively, they indicate that a lower soil moisture content (and higher temperatures) are preferable for efficacy of treatment, and these conditions would generally lead to less leaching potential, faster degradation, and more volatile loss of MITC.
(10) Leistra M., Smelt J.H. and Nollen H.M. (1974) Pesticide Science, 5, 409-417.	Concentration-time relationships for methyl isothiocyanate in soil after injection of metam-sodium.	Two field experiments with metam-sodium (in a humic sandy soil near Bergen, and a loamy sand soil near Espel) were carried out and detailed information collected so that results of computations and concentration measurements could be compared. On two occasions (3 or 4, 11 or 12 days) soil samples were taken at 6 or 7 depths and MITC extracted. Soil composition, density, pH, soil moisture at sampling, soil moisture tensions at 5 and 15 cm, rainfall, soil temperatures at 15 cm, were measured. No attempt was made to relate the experimental findings to the simulated concentrations. The field investigations highlighted the importance of complicating factors (such as dried-out top layers and temporary downward transport following rain events). Under wet soil conditions much of the MITC may decompose near the injection depth before the spreading required for satisfactory efficacy can take place. At lower soil temperatures MITC decomposes more slowly, so adverse after-effects may be prolonged, particularly as low temperatures are usually combined with wet conditions. Quantitatively these analyses are of no relevance to regulatory risk assessment.
(11) Ma Q.L., Papiernik S.K., Becker J.O. and Yates S.R. (2001) Journal Environmental Quality, 30, 1278-1286.	Degradation of soil fumigants as affected by initial concentration and temperature.	Soil fumigation using shank injection creates high fumigant concentration gradients in soil from the injection point to the soil surface. A temperature gradient also exists along the soil profile. The degradation of non-radiolabelled MITC was investigated in 10 g aliquots of one soil (Arlington sandy loam) at 4 temperatures (20, 30, 35 and 40°C) and 4 initial concentrations (3.31, 24.35, 56.01 and 142.70 mg/kg) under sealed vial conditions, in the laboratory. Investigations with sterilized soil samples were also carried out at two initial concentrations. Generally, the rate of degradation decreased as concentration increased (by a factor of 9 at 20°C). Degradation in sterile soil was 10 times slower than that in non-sterile soil, for the lower initial concentration, but only 1.8 times slower for the higher initial concentration. There was evidence of adaptation at the higher concentration as the degradation rate increased over time. Rate constants increased as temperature increased. The average Arrhenius equation activation energy (Ea) for MITC was 46.21 KJ/mol. Tables of residues with time not reported; only rate constants. Non-GLP.

		Quantitatively these analyses are of no relevance to regulatory risk assessment, but qualitatively the analyses demonstrate that degradation rates are possibly more rapid away from the highest concentrations of MITC at the injection points.
(12) Smelt J.H. and Leistra M. (1974) Pesticide Science, 5, 401-407	Conversion of metham-sodium to methyl isothiocyanate and basic data on the behaviour of methyl isothiocyanate in soil.	Investigations were carried out to collect data on the rate and extent of the conversion of metam-sodium to MITC, on the distribution of MITC between the different phases in soil, and on the rate of decomposition of MITC in soil. The following were determined: partition of MITC between air and water (Kw/g), adsorption of MITC to three soils, conversion of metam-sodium to MITC (in 3 soils, at 12 and 20°C), decomposition of MITC in soil (3 soils, at 4, 13 and 21°C, sampling at only 3 time points). For most of these investigations quantities of MITC were measured in the vapour phases and concentrations in the other phases of the test systems back calculated using the Kw/g for MITC. MITC was extracted from soil samples for the 'decomposition of MITC in soil' investigation. Conversion of metam-sodium to MITC in soil was very rapid (complete conversion took only a few hours). MITC degraded more rapidly at higher temperature. Rate constants were derived, but soil residue data was not reported. None of these non-GLP investigations were conducted according to modern guidelines, and non-radiolabelled MITC was used. For the MITC degradation in soil investigations only 3 timepoints were available. Quantitatively these analyses are of no relevance to regulatory risk assessment.
(13) Suett D.L., Fournier J-C., Papadopoulou-Mourkidou E. Pussemier L. and Smelt J. (1996) Soil Biology and Biochemistry, 28, 1741-1748.	Accelerated degradation: The European dimension.	Summary of the deliberations of two European workshops held to discuss the issue of accelerated degradation of soil-applied pesticides. The issue was identified as being of most relevance to soil applied pesticides used in relatively minor crops. Prior exposure of the soil microbial population to a particular pesticide can lead to adaptation and subsequent enhanced degradation of the pesticide, resulting in decreased efficacy. For MITC, it is reported that a rapid bioassay has been developed to detect enhanced degradation, and that limiting usage to no more than 1 in 5 years also addresses the issue. No significance to regulatory risk assessment.
(14) Van den Berg F. (1993) Atmospheric Environment, 27A, 63-71.	Measured and computed concentrations of methyl isothiocyanate in the air around fumigated fields.	Concentrations of MITC in the air around 2 fields (in the north eastern part of the Netherlands) were measured 4 to 5 times over a 7 – 9 day period, 1.5 m above the surface, following injection of metam-sodium in September/October (average soil temperatures in plough layers 11/12°C in first few weeks following applications). Fields were rolled as part of the treatment. The measured concentrations were compared to calculations made with Gaussian plume model. Emission rates of MITC from the fields, for use in the plume model, were calculated using a different model (they were not directly measured); and are reported as being the result of "a simplified description of fumigant behaviour in soil.....should be considered as first estimates." The cumulative loss of MITC during the first 3 weeks was calculated to be approximately 10% for both fields. During the first few days after injection the computed concentrations of MITC in air around the

		second field were lower than those measured, whereas no great differences were found for the first field. In the subsequent period, the calculated concentrations for both fields tended to be higher than those measured. The authors concluded that a better description of concentration patterns of fumigants in air requires more detailed measurements on input parameters of the dispersion model. Quantitatively these analyses are of no relevance to regulatory risk assessment.
(15) Van den Berg F., Smelt J.H., Boesten J.J.T.I. and Teunissen W. (1999) Journal Environmental Quality, 28, 918-928.	Volatilization of methyl isothiocyanate from soil after application of metam-sodium with two techniques.	To describe the fate of fumigants in the soil, the PESTLA model was extended to include the diffusion of pesticides through the gas phase and subsequent volatilization at the soil surface. Twice in 1989 (October and November), plots in a field located in the north east of the Netherlands, were treated with metam-sodium using two different techniques (blade injection, and injection immediately followed by rotavating of the topsoil). Between 0.25 and 9 days after treatment, soil samples were taken 3 or 4 times (down to 30 cm) and MITC residues determined in 5 cm depth increments. An attempt was also made to measure MITC emission rates from the soil surface. The MITC Enthalpy of Volatilisation was calculated to be 74 KJ/mol, Enthalpy of Dissolution assumed to be 40 KJ/mol, Coefficient of gas diffusion $0.73 \text{ m}^2/\text{d}$, Coefficient of liquid diffusion $0.4 \times 10^{-4} \text{ m}^2/\text{d}$. Following application by blade injector, at 1 day after both applications, the contents measured in the 10 – 15 cm layer were higher than the calculated values. After a week the measured contents were lower than the calculated values. Overall, less MITC remained in the soil profile than the model predicted (34 vs 46%, and 46 vs 58%). This was speculated to be due to a higher actual rate of degradation than used in the modeling, and/or higher volatilization rates. Similar factors could explain the differences between modeled and actual residues for the second application technique. Comparison of calculated volatile loss against measured flux indicated that the modeling significantly underestimated loss, particularly for the first few days following application. The authors concluded that a better description of fumigant behaviour in soil could be obtained by improving the description of the water flow in the soil, understanding the variation of the rate of degradation with concentration of MITC better, and accounting for 'local' heterogeneity such as large voids in the topsoil created by the application equipment/technique used. Air concentrations of MITC are greatly affected by the prevailing soil and weather conditions. Under cooler and wetter conditions, lower volatilization rates from soil can be expected. Some of the values given in the publication (e.g. Enthalpy of Volatilisation) could be used in regulatory modeling, but overall it is clear that this version of PESTLA (which developed into FOCUS PEARL) does not predict volatile loss very accurately.
(16) Van den Berg F., Wolters A., Jarvis N., Klein M., Boesten J.J.T.I., Leistra M., Linneman V., Smelt J.H. and Vereecken H., EU-FP5 R&D	Improvements of concepts for pesticide volatilization from bare soil in PEARL, PELMO, and MACRO Models.	This paper reports attempts to improve the way volatility processes are implemented in the main regulatory efate models (PEARL, PELMO and MACRO). At present, this emission pathway has not been described adequately in those models used to calculate PEC's needed for EU risk assessments. Datasets for volatilization under field conditions were collected and process studies in the laboratory carried out.

project: "Effective approaches for predicting environmental concentrations of pesticides: APECOP"		For the process studies, a chamber was built such that treated soil (at different soil moistures) could be subjected to a controlled air flow (moisture and temperature controlled) and volatile losses captured for analysis. Test pesticides were sprayed onto the soil surface (no fumigants were used in the studies). It was clear that the models, even when improved as described in the paper, have significant limitations with respect to predicting volatile loss. The authors recommend altering the models so that they can process hourly meteorological data, and that further improvements are required to take atmospheric stability into account.
(17) Verhagen C., Lebbink G. and Bloem J. (1996) Soil Biology and Biochemistry, 12, 1753-1756.	Enhanced biodegradation of the nematicides 1,3-dichloropropene and methyl isothiocyanate in a variety of soils.	Enhanced biodegradation of MITC was investigated in 10 Dutch soils under field conditions. Soils were treated 6 times in a year to induce enhanced degradation. No further treatments were undertaken for the next 3 years, but soil samples were incubated with MITC under laboratory conditions and degradation investigated during this period. Enhanced degradation of MITC was achieved following the intensive treatment of soil. After three years of no treatments, the rate of degradation of MITC had returned to control levels. In soils with pH>7 degradation was likely to be too rapid for efficacy, even without enhanced degradation. Non-radiolabelled MITC was used, non-GLP, non-guideline study. Only graphs of DT₅₀ values given. No significance to regulatory risk assessment
(18) Wales P.C. (2002) California Environmental Protection Agency, Sacramento, California, USA	Evaluation of methyl isothiocyanate as a toxic air contaminant; Part A – Environmental Fate.	A large data review, with respect to the fate and behaviour of MITC is reported. Most of the references listed above are included. Several other studies relevant to the wider fate of MITC (i.e. in water and air) are also included. With respect to the fate in soil, the primary MITC transport and transformational pathways were stated to be volatilization and hydrolysis. Persistence in soil depends upon soil temperature, soil type, pH, moisture content and application method. Overall, there is some evidence that MITC degrades fastest in soils with higher pH values and loams, and slowest in humic sands.

As such, it is not possible either to vouch for the reliability of the experimental data or to further analyse the data. The consequence of this is that it is not possible for the information contained in the papers to be used quantitatively as part of the regulatory risk assessment process. However, it is possible to derive qualitative information from these sources with relevance to the factors important for the degradation in soil of MITC and the volatile loss of MITC from soil.

Metam-sodium degrades very rapidly in soil, to MITC. MITC in turn degrades rapidly, via microbial processes, and continues to degrade relatively rapidly in sub-soils. MITC degradation is more rapid with increasing temperature and decreasing soil moisture content. It degrades more slowly at higher concentrations. There is evidence of enhanced degradation where a plot has been treated very frequently, and of increasing degradation rate with time (especially at higher concentrations), with rates returning to control levels after three years of no treatment. Method of application effects degradation rates in so far as it determines the concentration gradient of MITC over time. Where the application method leads to a more homogeneous dispersion (as required for good efficacy) then degradation will be more rapid.

Conditions that promote volatile loss from the soil will increase dissipation of MITC from the soil, but not degradation of MITC. Good MITC mobility in the gas phase is required for optimal efficacy, and will also lead to enhanced volatile loss from the soil. In addition, lower soil moisture content and higher temperatures are preferable for efficacy of treatment, which would generally also lead to faster degradation, less leaching potential and more volatile loss of MITC.

Overall, the most reliable rate of degradation data for use in regulatory FOCUS modeling was reported in Hall (2004). It is also clear that the current regulatory simulation models available to predict concentrations in soil, water and air do not describe the key processes driving the dissipation of MITC well (especially volatile loss) and would return overly conservative Predicted Environmental Predictions (PECs).

Conclusions of the RMS:

The additional field studies reported in the open literature are not adequate to derive regulatory endpoints.

The lab study of Hall (2004) is the most suitable study to determine DT50 for PEC assessment.

The current regulatory simulation models available to predict concentrations in soil, water and air do not describe the key processes driving the dissipation of MITC well (especially volatile loss) and would return overly conservative Predicted Environmental Concentrations (PECs).

Determination of modelling endpoints for MITC from laboratory degradation studies using ModelMaker 4.0, according to FOCUS Kinetics. (McMillan C., 2010b)

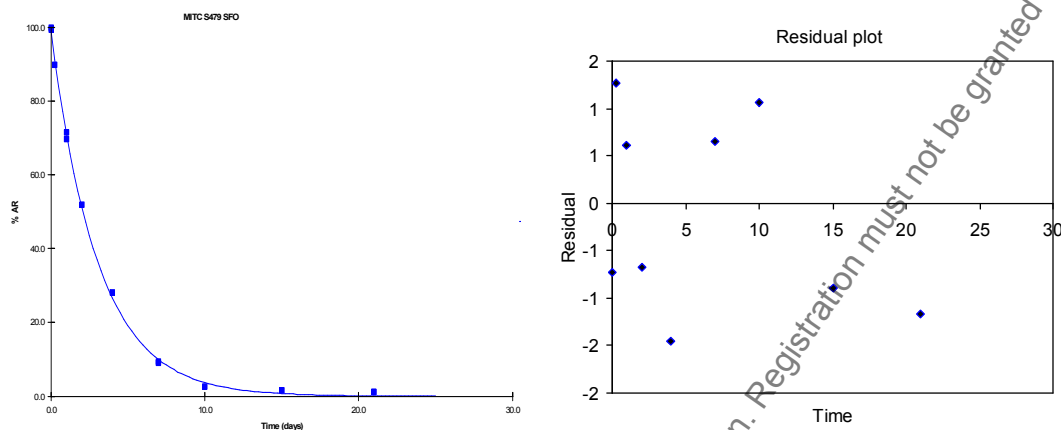
Guideline:

FOCUS kinetics guidance document (FOCUS, 2006).

Findings:

Appendix 4 – Plots of residues and residuals with time

S479

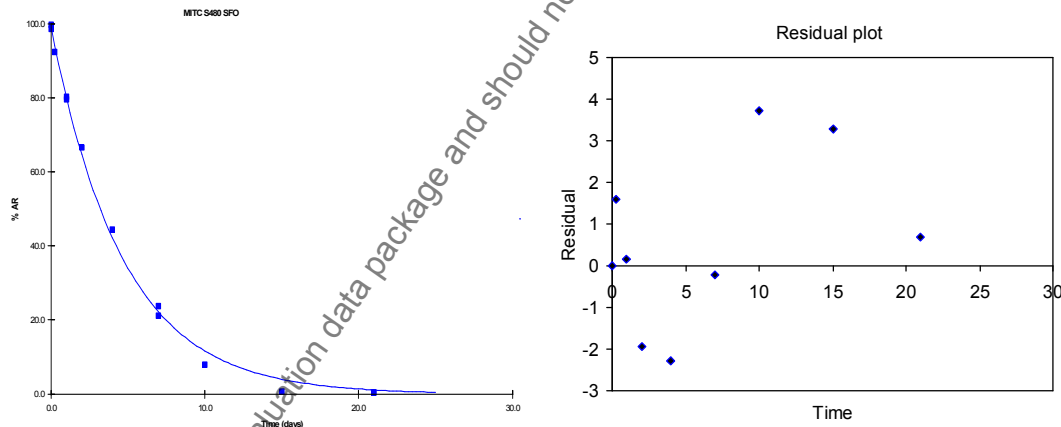


(a)

(b)

Figure 1 - Visual assessment of goodness of fit of SFO model to MITC in S479: (a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

S480



(a)

(b)

Figure 2 - Visual assessment of goodness of fit of SFO model to MITC in S480: (a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

S490

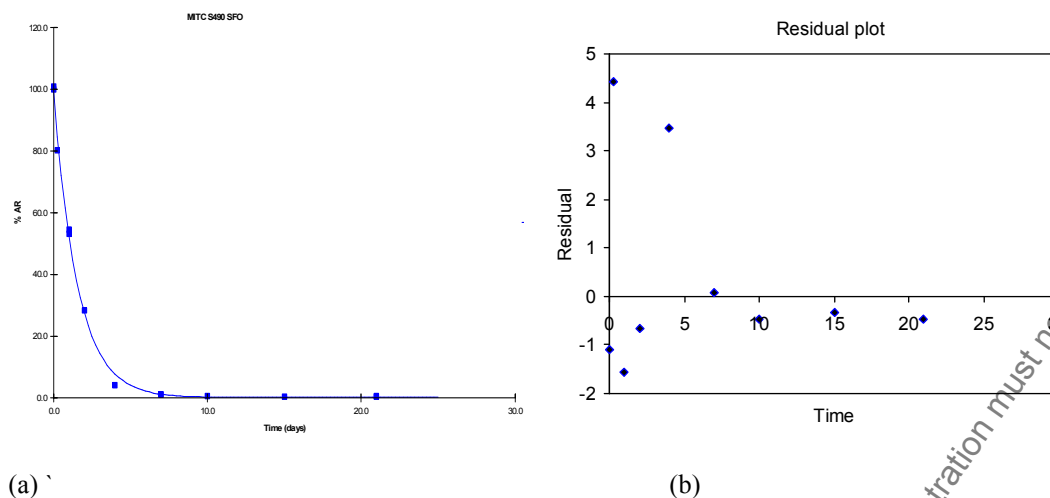


Figure 3 - Visual assessment of goodness of fit of SFO model to MITC in S490: (a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

S500

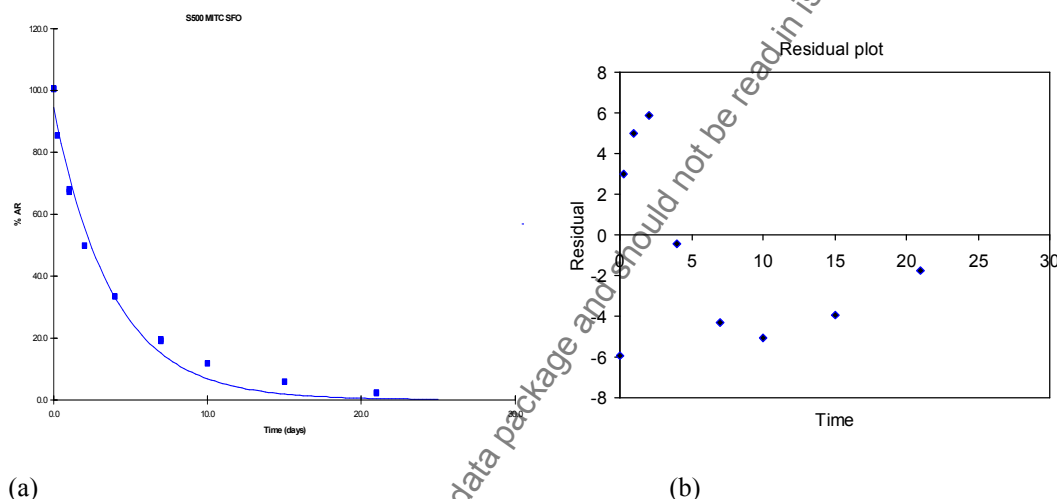


Figure 4 - Visual assessment of goodness of fit of SFO model to MITC in S500: (a) % applied radioactivity and fitted model versus time; (b) plot of the residuals

A rate of degradation in soil study (under laboratory conditions), has been conducted with MITC in 4 soils. It was possible to derive modelling endpoints (DT_{50}) for this compound in all four soils using single first-order (SFO) kinetics. The selected model adequately described the decline of MITC in soil.

Table B.8.1.1.1-6: Modelling DT_{50} and DT_{90} values derived for MITC (normalised to pF2.0 – moisture correction factor of 1 for the 4 soils)

Soil	Kinetic Model	χ^2 error	Modelling DT_{50} (days)	Modelling DT_{90} (days)
S479	SFO	2.0	2.12	7.03
S480	SFO	3.5	3.24	10.78
S490	SFO	5.4	1.08	3.60
S500	SFO	8.3	2.64	8.76
		Geometric mean	2.10	6.99

B.8.1.1.2 Anaerobic degradation in soil (Annex IIA 7.1.1.1.2)

Considering the supported uses of metam-sodium (Application into the soil by direct injection or through drip-irrigation system), it is not expected that metam-sodium or its volatile metabolite MITC would be exposed to anaerobic conditions. The efficacy of the compound is depending on volatilization of MITC in the soil pores under aerobic conditions.

As RMS, we consider that anaerobic soil degradation study is not required.

However one study has been submitted

Vapam® Anaerobic Soil Metabolism. (Burnett, T.J., 1987b)

Guideline:

Pesticide assessment Guideline, Subdivision N: 162-1

GLP:

Yes

Materials and Methods:Test substances:

¹⁴C-Metam-sodium diluted approximately 70-fold with analytical grade a.s. (WRC-9851-13-2). Radiochemical purity of 96.6% by TLC and LSC; this stock solution has a specific activity: 0.0835 mCi/μmol and contains 33.4% anhydrous metam-sodium in water.

Soil:

No detailed information on the sandy soil from the Columbia River Basin (soil batch different from the batch used in Burnett, T.J., 1987a)

Experimental design :

“¹⁴C]-Metam-sodium was applied to a sandy soil from the Columbia River Basin at a rate of 131 ppm. The flasks were incubated for one half life (= 23 min, based on Burnett, 1987a) in sealed flasks under aerobic conditions. After this period, 100 ml of water was added, and flasks were connected to a nitrogen source. The flasks were maintained at 28°C in the dark. Duplicate samples were taken after 1, 29 and 60 days.”

Analytical methods :

Not clearly reported in the study

Findings and Conclusions:

This study is considered as not acceptable: no indication on the establishment of anaerobic conditions. The analytical procedures and identification of the a.s./ metabolites in the traps and soil extracts as well as the determination of the a.s. DT50 are not clear.

B.8.1.1.3 Soil photolysis (Annex IIA 7.1.1.1.2)

As metam-sodium is incorporated in the soil with special equipment, it is basically not exposed to sunlight. Therefore it is not subject to photolysis. The volatile degradation product MITC dissipates from the soil and is therefore subject to the sunlight in the air phase.

As RMS, we consider that soil photolysis study is not required.

However, two study reports were submitted.

Photodegradation of Vapam on soil (Burnett, T.J., 1985)

Findings and Conclusions:

This study is considered as not acceptable: The analytical procedures and identification of the a.s./ metabolites in the traps and soil extracts as well as the determination of the a.s. DT50 are not clear. Very low mass balance (12-20% after 100-125 minutes); no recovery of volatile compounds.

Photolysis of Metam-Sodium on Soil (Haag W.R., Irwin K. and Mill T., 1989)

Findings and Conclusions:

This study is considered as not acceptable: The analytical procedures and identification of the a.s./ metabolites in the traps and soil extracts as well as the determination of the a.s. DT50 are not clear. No mass balance; test performed with non-radiolabelled a.s.

B.8.1.2 Rate of degradation (Annex IIA 7.1.1.2.1; Annex IIIA 9.1.1.1.1)**B.8.1.2.1 Aerobic degradation**

See B.8.1.1.1

B.8.1.2.2 Anaerobic degradation

See B.8.1.1.2

B.8.1.3 Field studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)**B.8.1.3.1 Soil dissipation testing**

The DT₅₀ lab determined at 20°C for both Metam-sodium and MITC is less than 60 days. However, several field studies were conducted, investigating the fate of MITC in the soil.

The field studies do not reflect the supported uses in Europe. The application was made by overhead-sprinkler system. The formulation was injected in the sprinkler irrigation pipeline while water was applied to the plot.

Incorporation of the a.s. in soil was achieved by post-application spray irrigation in some experiments.

The method of application for the supported uses of metam-sodium in Europe is as follows:

- injection of the undiluted formulation in the soil, followed by incorporation by rotavation and soil surface sealing with a roller (carrots, lamb's lettuce, potato, tomato)
- injection of the undiluted formulation in the soil (grape replanting)
- drip irrigation under a plastic film on the planting row (strawberry)
- drip irrigation on the planting row in glasshouse (cucumber, eggplant, pepper, tomato)

As the active substance has not been incorporated deeply into the soil by rotavation in the field experiments, it can be expected that the volatilisation at soil surface is very important. Consequently, the dissipation rate of MITC is highly overestimated (Field dissipation of MITC in the range 0.54-3 days with a mean of 1.57 days). These results are not considered in the final risk assessment.

Vapam: field dissipation study for terrestrial uses, Leland, Mississippi, 1989. Residue data to support registrations of products containing Metam-sodium as an active ingredient. (Iwata Y., 1989a)

Guideline:

EPA §164-1

GLP:

yes

Material and methods:Test substance:

VAPAM, water soluble liquid containing 381 g a.s./l (32.7% w/w)

Experimental design:

VAPAM was injected in the sprinkler irrigation pipeline while water was applied by spraying to the surface of a bare fallow loam/silt loam soil at a rate equivalent to 356 kg a.s./ha in Leland, Mississippi on 20 April 1989, and incorporated by spray irrigation.

“Samples of soil were collected at one week immediate pre-application and 11 weeks post-application intervals, varying from the immediate post-application to 5 months after application. Samples were analysed for residues of methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU).”

Meteorological data, detailed soil properties are available.

Findings:

The individual data can be found in the appendix.

“The zero-time residue was 18 ppm of MITC in the upper six inches (15.2 cm) of soil. MITC dissipated with a nominal half-life of 26 hours (1.08 days) under normal agricultural conditions. Thirteen days after application, no residues were present in any of the soil samples.

Except for one minor exception (0.03 ppm in one 6- to 9 inch soil sample), metam-sodium was present only in the 0- to 6-inch soil depth.

Dimethylurea residues were present up to 0.23 ppm in the 0- to 6-inch soil depth. The maximum residue was found 4 days after application; residues then dissipated with a half-life of 4 days. No DMU residues were found 30 days post application in any soil samples. There was no movement of DMU below the 0- to 6-inch soil depth.”

Conclusion:

The application technique in this field study does not reflect the supported uses in Europe. The results are not considered in the final risk assessment.

Vapam: field dissipation study for terrestrial uses, Visalia, California, 1989. Residue data to support registrations of products containing Metam-sodium as an active ingredient. (Iwata Y., 1989b)

Guideline:

EPA §164-1

GLP:

yes

Material and methods:Test substance:

VAPAM, water soluble liquid containing 381 g a.s./l (32.7% w/w)

Experimental design:

VAPAM was injected in the sprinkler irrigation pipeline while water was applied by spraying to the surface of a bare fallow loam/silt loam soil at a rate equivalent to 356 kg a.s./ha at Visalia, California, on 13 April 1989.

“Samples of soil were collected at one immediate pre-application and 11 post-application intervals, varying from the immediate post-application to 3 months after application. Samples were analysed for residues of methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU).”

Meteorological data, detailed soil properties are available.

Findings:

The individual data can be found in the appendix.

“The zero-time residue was 42 ppm of MITC in the upper six inches (15.2 cm) of soil. MITC dissipated with a nominal half-life of 13 hours (0.54 days) under normal agricultural conditions. Residues were undetectable, i.e. less than 0.02ppm, seven days after application. Residues were never detected below the upper six inches of soil.

Dimethylurea residues varied between 0.24 and 0.51 ppm during the initial four days post-application. Residues then dissipated with a half-life of about 7 days. Residues were non-detectable, i.e. below 0.02 ppm, 32 days after application. Residues were never found below the upper 6 inches of soil. “

Conclusion:

The application technique in this field study does not reflect the supported uses in Europe. The results are not considered in the final risk assessment.

Metam-Sodium groundwater data call-in: California field dissipation study. (Anonymous, 1986a)

Guideline:

not specified

GLP:

no

Material and methods:Test substance:

VAPAM, water soluble liquid containing 381 g a.s./l (32.7% w/w)

Experimental design:

VAPAM was injected in the sprinkler irrigation pipeline while water was applied by spraying to the surface of bare soil at a rate equivalent to 356 kg a.s./ha at Parlier California (3 fields) on 18 April 1986.

Soil samples were collected at different intervals between 0 and 49 days after application, at different depths, and analyzed (method based upon conversion to MITC). Soil characteristics: field I: clay loam/loam, field II and III: sandy loam. pH: 7.00-8.24, organic matter 0.16-0.87%. Application in April, soil temperature between 15 and 21°C.

Meteorological data not available; soil properties are available.

Findings:

The individual data can be found in the appendix.

The initial residue in the 0-15 cm soil layer was 81.00 mg/kg MITC.

“As residues declined at the soil surface, residues at deeper depths approached non-detectable levels (1 to 4 days after application). Residue levels approached non-detectable levels at the 0 to 0.5 foot depth 13 days after application; residues were not detectable 21 days after application.

The half-life of MITC under the conditions of the study was found to be 1.2 days.”

Conclusion:

The application technique in this field study does not reflect the supported uses in Europe. The results are not considered in the final risk assessment.

Metam-Sodium groundwater data call-in: Washington field dissipation studies. (Anonymous, 1986b)

Guideline:

Not specified

GLP:

no

Material and methods:Test substance:

VAPAM, water soluble liquid containing 381 g a.s./l (32.7% w/w)

Experimental design:

In a first study, VAPAM was injected in the sprinkler irrigation pipeline while water was applied by spraying to the surface of a bare sandy loam soil at a rate equivalent to 178 kg a.s./ha on 28-29 March 1985 at four different plots (E, E2, T, T2) in Moses Lake, Washington. (two different fields)

Soil samples were taken at 0-3 inch, 3-6 inch and 6-12 inch.

In a second study, VAPAM was applied on 15 October 1985, at two plots (A, B) at a rate equivalent to 356 kg a.s./ha and one to 178 kg a.s./ha (C). Samples were taken from the following increments (in feet): 0 to 0.5, 0.5 to 1, 1 to 2, 2 to 3, 3 to 4 and 4 to 5. (1 field)

Meteorological data, soil properties are available.

Findings:

The individual data can be found in the appendix.

'First study: The half-lives were calculated to be 0.9 days (site E), 0.9 days (site E2), 1.3 days (site T) and 1.4 days (site T2). MITC was detected at all three sampling depths, therefore additional studies were performed (= second study is in the same report).

In the second study, soil half-life values are summarized as follows:

site A - 0 to 0.5 foot = 2.4 days, 0 to 1 foot = 3.4 days, 0 to 2 feet = 3.6 days; site B - 0 to 0.5 foot = 2.0 days, 0 to 1 foot = 3.7 days, 0 to 2 feet = 4.1 days; and site C - 0 to 0.5 foot = 2.6 days, 0 to 1 foot = 3.2 days, 0 to 2 feet = 3.2 days.

It was concluded that the half-life of MITC ranges from 2.0 to 4.0 days, depending upon soil depth considered."

Conclusion:

The application technique in this field study does not reflect the supported uses in Europe. The results are not considered in the final risk assessment.

Vapam® Field dissipation study (McKay, J.C., 1987)

Guideline:

Not specified

GLP:

no

Material and methods:Test substance:

VAPAM, water soluble liquid containing 381 g a.s./l (32.7% w/w)

Experimental design:

VAPAM was injected in the sprinkler irrigation pipeline while water was applied by spraying to the surface of a bare clay soil at a rate equivalent to 343 kg a.s./ha and incorporated by spray irrigation. The application was performed on 16 October 1986 at 2 replicate plots in Saskatoon, Saskatchewan, Canada.

Samples of soil were collected from the application site at post-application intervals of 0 and 12 hours, and 1, 2, 3, 8 and 15 days. The samples were analyzed for MITC. The soil temperature did not exceed 6.5°C at any time during the study and was 0°C at the termination of the study.

Meteorological data, soil properties are available. Pesticide treatment history is not available.

Findings:

The individual data can be found in the appendix.

The initial residue in the 0-15 cm soil layer was 13.38 mg/kg MITC.

"The half-life calculated for MITC residues in soil was 3 days following Metam-sodium application.

Residues of MITC at soil depths below 15 centimeters were much lower than corresponding residues in the upper 15 centimeters throughout the study."

Conclusion:

The application technique in this field study does not reflect the supported uses in Europe. The results are not considered in the final risk assessment.

The field dissipation were determined by the notifier by linear first order kinetics after log transformation of the data.

Table B.8.3.1.1-1: DT50 values of MITC determined in field dissipation studies

Report	Location	Application date	dose rate (kg metam a.i. /ha)	1 st order DT ₅₀ (day)
1	Leland, Mississippi	20 April 1989	356	1.08

2	Visalia, California	13 April 1989	356	0.54
3	Parlier, California	18 April 1986	356	1.2
4	Site E, Washington	28 March 1985	178	0.9
4	Site E2, Washington	29 March 1985	178	0.9
4	Site T, Washington	28 March 1985	178	1.3
4	Site T2, Washington	29 March 1985	178	1.4
4	Site A, Washington	15 October 1985	356	2.4
4	Site B, Washington	15 October 1985	356	2.0
4	Site C, Washington	15 October 1985	178	2.6
5	Saskatchewan, Canada	16 Oct 1986	345	3
			Mean value	1.57

B.8.1.3.2 Soil residue testing - soil accumulation testing

Soil residue studies : Not required – The DT₅₀lab is less than one third of the period between application and harvest. In fact Metam-sodium and MITC have disappeared already before planting of the crop. Therefore absorption by the succeeding crop is not possible.

Soil accumulation studies: Not required. – The DT₉₀ of metam-sodium and MITC are less than one year and repeated applications in the same year are not intended.

B.8.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and 7.1.3; Annex IIIA 9.1.2)

B.8.2.1 Adsorption and desorption of the active substance and relevant metabolites (Annex IIA 7.1.2)

Stability of Metam-sodium in Soil / Water mixtures. (Dohn, D.R., 1988).

Guideline:

US EPA Guidelines §163-1: Leaching and Adsorption/Desorption

GLP:

no

Experimental design:

The feasibility of conducting batch equilibrium studies on Metam-sodium was evaluated by shaking solutions of 9.93 ppm Metam-sodium in 0.01 M CaCl₂ with Manteca sandy loam or with Biggs clay. The decomposition of Metam-sodium after 1 hr of shaking was determined by measuring its breakdown product, methylisothiocyanate by gas chromatography with nitrogen / phosphorus detection.

Findings:

“No MITC was detected in any of the blank samples, while added MITC was quantitatively recovered from all spiked samples. Very little decomposition of Metam-sodium (2.2 and 2.0% as measured by MITC formation) occurred in the absence of soil. However, Metam-sodium completely decomposed in the presence of Manteca sandy loam (97.8 and 95.6%) and extensively decomposed in the presence of Biggs clay (77.2 and 80.6%).

The conditions of this experiment (temperature of 21°C and a short equilibrium time of 1 hour) were chosen to minimize Metam-sodium decomposition. Despite these favorable parameters, the exposure of Metam-sodium to the experimental conditions used to determine Freundlich adsorption constants resulted in rapid and extensive decomposition of the parent chemical to MITC.

Conclusion:

This preliminary study is acceptable. It confirms that metam-sodium is rapidly degraded to MITC. It is therefore not feasible to perform a satisfactory measurement of the Freundlich adsorption constants of Metam-sodium by the batch equilibrium method.

Adsorption of Metam-sodium on Ditch-Bottom Sludge (Vonk, J.W.; van den Hoven, A.M.; van Osenbruggen, W.A., 1985).

Conclusions:

The adsorption coefficient of metam-sodium has been determined in 2 river sediments under anaerobic conditions. This study is not useful for the final assessment.

Due to the short half-life of Metam-sodium in soils, the standard column leaching study has been replaced with the determination of soil adsorption coefficient by HPLC method as described in OECD Draft Guideline 121 (August 1999).

Metam Sodium: soil adsorption by HPLC (Betteley, J., 2002).

Guideline:

OECD 121 (draft), August 1999 - Determination of soil adsorption coefficient.

GLP:

Yes

Material and Methods:

Test substance:

Non-radiolabeled Metam-sodium, purity 99.2%, Batch N° V799R.

Experimental design:

Metam-sodium was introduced onto a HPLC column in a 10 µl injection containing 507.90 ng (test 1, pH 4), 508.80 ng (test 2, pH4), 501.55 ng (test 1, pH 9) and 530.30 ng (test 2, pH 9).

The capacity factor (k) was determined based on the retention time of Metam-sodium and sodium nitrate (inert substance). In order to correlate k with its Koc, six reference compounds (acetanilide, atrazine, triadimenol, naphthalene, pyrazophos and DDT) with log Koc values between 1.25 and 5.63 were selected and injected.

Findings:

Metam-sodium was eluted from the column more quickly than acetanilide (the reference standard with the lowest literature value for log Koc).

Therefore, the soil adsorption coefficient of Metam-sodium has been determined as: $K_{oc} < 17.8$ at pH 4 and 9

The result indicates that the test substance is likely to have very high mobility in soils.

The pH's of 4 and 9 were chosen as the two limits of pH likely to be found in the environment as this material is known to have a dissociation constant. However in each case the material was found to be very mobile in soil. An intermediate value of pH (neutral) would not be expected to give another result for the Koc if the two extremes give the same result.

The values from the dissociation constant study support these findings (values were 2.99 and 11.06) and hence no change would be expected over the range pH 4 to 9.

Conclusion:

The study is acceptable. The Koc of metam-sodium is < 17.8 mL/g at pH 4 and 9

However, based on the rapid degradation of Metam-sodium to MITC, the relevance of its mobility is minor.

Methyl isothiocyanate: Adsorption in soil (Komatsu K. 1990)

Guidelines:

OECD 106

GLP:

No

Material and Methods:

Test substance:

Methyl isothiocyanate (MITC), chemical purity: not reported

Soils:

B.8.2.1-4: Characteristics of the soils

Soil designation	Hokkaido Tokachi	Fukushima	Okayama	Miyazaki
Textural class	clay loam	clay loam	sandy clay loam	sand

Soil designation	Hokkaido Tokachi	Fukushima	Okayama	Miyazaki
Particle size distribution [%]				
Sand	57.1	53.4	60.5	87.1
Silt	21.5	22.8	17.5	5.7
Clay	21.4	23.8	22.0	7.2
Organic C [%]	2.56	1.08	0.69	1.50
pH [H ₂ O]	6.2	7.6	6.7	7.2
pH [KCl]	5.8	6.7	5.5	6.3
Cation exchange capacity [meq/100 g]	11.7	13.5	8.7	7.0

Experimental design:

Solutions of test item were added to pre-equilibrated mixtures of soil and 0.01 M CaCl₂ solution and allowed to adsorb while being stirred. A solution soil ratio of 5:1 was used: 5 g dry soil/ 25 ml 0.01 M CaCl₂. Dose solutions of the test article were 0.03564, 0.1782, 0.891, and 4.455 mg/L; the equilibration time was 8 hours; the test temperature was 25±1°C.

Analytical methods :

The samples were centrifugated. Gas phase was sampled and analyzed by GC-NPD. Aliquot of the supernatant was extracted by ethyl-acetate and analysed by GC-NPD. The solid phase was extracted by ethyl-acetate by reflux. The extracts were separated, filtered and analyzed by GC-NPD.

Findings :

The mass balance (stability of the test substance) has been determined by summing up the amount MITC in the gas, aqueous and solid phases. The average mass balance was 91.5%, 92.5%, 93.0% and 94.5% respectively for the soils tested. The ratio of test chemical existing in each phase were: aqueous phase: 89.8-95.8%; solid phase: 3.5-9.5%, gas phase 0.7-0.8%. Consequently the concentration in the gas phase had no effect on the adsorption equilibrium.

Table B.8.2.1-5: Adsorption and desorption of MITC in 4 soils

Soil	pH (H ₂ O)	Organic Carbon content (OC %)	K _F (ml/g)	Correlation coefficient	1/n	K _{FOC} (ml/g)
Hokkaido Tokachi	6.2	2.56	0.68	0.97803	1.12	27
Fukushima	7.6	1.08	0.48	0.98383	1.09	44
Okayama	6.7	0.69	0.32	0.98324	1.04	46
Miyazaki	7.2	1.50	0.40	0.98967	1.02	27

Conclusions:

Study acceptable. Mean K_{oc} of MITC is 36 ml/g, mean 1/n is 1.07

Added in August 2010

"The meeting of experts proposed a data gap for a new soil adsorption / desorption study conducted with consideration of the volatility and the low adsorption properties of MITC (eg. with shorter equilibration times, soil solution ratios of 1:1, high organic carbon soils)."

A new study was carried out in compliance with the recommendations of the meeting of experts. This study is co-owned with KST and already presented in the resubmission dossier of Dazomet.

Determination of the Adsorption/Desorption of Methyl isothiocyanate (MITC) (Herrchen, 2009c)**Guidelines:**

OECD 106 – direct method (deviation: none)

GLP:

Yes

Material and Methods :**Test substance:**

Unlabelled MITC, chemical purity: 99.9%

¹⁴C-radiolabelled MITC (specific radioactivity = 6.94 mCi/mM = 3.51 MBq/mg, radiochemical purity ≥97.7%)

Soils :

B.8.2.1-9: Characteristics of the soils used to investigate adsorption of MITC

Soil	Refesol 01-A	Refesol 03-G	Refesol 04-A	Refesol 05-G	Refesol 06-A
Textural class (USDA scheme)	loamy sand	clay loam	loamy sand	loam	clay
Particle size distribution [%]					
0.05 - 2 mm (sand)	71	32	82	37	22
0.002 - 0.05 mm (silt)	23	38	10	41	34
< 0.002 mm (clay)	6	30	8	22	44
Organic matter [%]	1.76	6.95	4.90	5.67	4.72
Organic C [%]	1.02	4.03	2.84	3.29	2.74
pH (0.01 M CaCl ₂)	5.55	7.25	5.41	4.78	6.86
Eff. cation exchange capacity [meq/100g]	3.7	12.6	8.9	10.0	24.5

Experimental design:

The soils were air dried and sieved to 2 mm mesh before they were used in the study. As in preliminary tests the test item was found to be unstable in an unsterile CaCl₂/soil system the entire experiment was performed under sterile conditions. All soils were sterilised by gamma irradiation and stored in the dark at 4 °C. Five different concentrations (0.5, 1.0, 5.0, 25 and 50 µg MITC/ml) of the mixture of ¹⁴C-radiolabelled test item and unlabelled test item in 0.01 M CaCl₂ solution were used. Portions of the test solutions were mixed with soil and allowed to equilibrate while shaking at a temperature of 20 °C. A soil-to-solution ratio of 1:1 (20 g air-dried soil and 20 ml solution) was selected for all tests due to the expected low adsorption properties of MITC. From the adsorption kinetics an agitation time until equilibrium (16 h) was determined for the adsorption isotherms. After equilibration, the samples were centrifuged (2000 rounds per min, 10 min, tightly closed caps) and the supernatant was decanted. The remaining soil was extracted twice (2 x 40 ml water + methanol (80:20, v/v)).

The adsorption was determined by quantification of MITC in the adsorption solutions (LOQ of 5 ng/ml) and in the soil extracts (LOQ of 0.01 mg/kg) by Head-space-GC-MS using Ethyl isothiocyanate (EITC) as internal standard. All samples were analysed in triplicate. The GC-MS methods were validated before the definitive test. In further pre-tests, sorption of MITC to glass surfaces (max. 0.6%) as well as volatilisation losses were checked and found to be negligible.

In addition to the chemical analyses of MITC using GC/MS, aqueous samples, soil extracts as well as selected samples of extracted soils were subjected to radiocounting of the added ¹⁴C-MITC in order to establish a mass balance (direct method). The total radioactivity of the aqueous samples and the soil extracts was determined by Liquid Scintillation Counting (LSC). The non-extractable radioactivity of selected soil samples was determined by combustion followed by LSC. The mass balance for the adsorption kinetics within 16 h ranged from 92.7 to 101.2% except for one soil (Refesol 03-G) with 84.6 %.

Findings :

The results demonstrated that the Freundlich isotherm (correlation coefficients R^2 of 0.947 to 0.998) was applicable to adsorption phenomena of MITC. Based on the results of the adsorption experiments, Freundlich adsorption coefficients (K_F) in the range from 0.21 to 0.43 ml/g were obtained resulting in organic carbon normalized adsorption coefficients (K_{FOC}) in the range from 9.0 to 20.2 ml/g with an average K_{FOC} of 13.5 ml/g. The Freundlich exponents ($1/n$) were in the range from 0.755 to 0.905 with a mean of 0.830. There is no evidence for a pH dependence of the adsorption. The adsorption data are given in Table B.8.2.1-10.

Table B.8.2.1-10: Adsorption data for 14C-MITC on different soils

Soil	pH	C _{org} (%)	K _F (ml/g)	1/n	K _{FOC} (ml/g)
Refesol 01-A	5.55	1.02	0.21	0.845	20.2
Refesol 03-G	7.25	4.03	0.42	0.819	10.5
Refesol 04-A	5.41	2.84	0.43	0.825	15.3
Refesol 05-G	4.78	3.29	0.42	0.905	12.7
Refesol 06-A	6.86	2.74	0.25	0.755	9.0
Mean	-	-	-	0.830	13.5

Conclusions:

The measured adsorption data for MITC indicate that MITC is weakly sorbed to soil with an average K_{FOC} of 13.5 mL/g and an average $1/n$ of 0.83. The Study is acceptable.

Added in August 2010

"A data gap has been identified by EFSA after the meeting of experts to address the fate of DMTU in soil in order to obtain adequate input parameters for ground water modelling."

14C-N,N'-dimethylthiourea: adsorption/desorption on soil. (Völkel, W., 2009)

Guideline:

OECD 106 (2000)

GLP:

yes

Material and Methods:**Test substance:**

Unlabelled N,N' -dimethylthiourea, chemical purity: 99%

¹⁴C-radiolabelled N,N' -dimethylthiourea (specific radioactivity = 4.94 MBq/mg, radiochemical purity 100%)

Soils:

B.8.2.1-11: Characteristics of the soils used to investigate adsorption of DMTU

	Soil				
	I	II	III	IV	V
Site location	Attenschwiller	Speyer 6S	Speyer 2.2	Witterswil	Speyer 2.3
Country	France	Germany	Germany	Switzerland	Germany
pH (0.01 M CaCl ₂)	7.46	7.20	5.40	7.36	6.40
OC (%)	0.95	1.75	2.16	3.93	0.98
Clay content (%)	16.6	42.1	6.4	40.5	9.4
Texture (USDA)	Silt loam	Clay	Loamy sand	Silty clay	Sandy loam

Experimental design:

An initial preliminary/screening test was performed in order to investigate the adsorption behaviour of 14C-N,N'-dimethylthiourea. For this purpose, soils I and III, a test concentration of 0.20 mg/L and three soil (dry weight) to aqueous phase ratios: 1/25 (1 g/25 mL), 1/5 (5 g/25 mL) and 1/1 (10 g/10 mL) were used. The aqueous phase consisted of 0.01 M CaCl₂ solution. The soil/solution samples were incubated in sealed Teflon centrifuge tubes on a shaker to

keep the soil as a suspension in solution, at 20 °C in the dark. After 24 hours of agitation, aliquots of the aqueous phase were measured by Liquid Scintillation Counting (LSC). Considering these results a soil-to-solution ratio of 1:1 was selected for the subsequent screening test.

A first screening test (screening test 1) was performed at a test concentration of 0.19 mg/L and a soil-to-solution ratio of 1:1. The radioactivity adsorbed was measured after 2, 5, 24 and 48 hours of adsorption. Additionally, the supernatants were analysed by HPLC after 48 hours. These analyses revealed that the test item almost completely degraded within 48 hours. In the control samples without soil N,N'-dimethylthiourea remained stable.

A non-GLP test was performed with samples of sterilized and non-sterilized soil I to follow the degradation kinetics revealing that there was no significant difference in the degradation of the test item. Probably, degradation was due to catalytic processes.

The screening test was repeated, using an adsorption time of two hours and a desorption time of two hours to avoid complete degradation in any of the soils until the end of desorption time. After 2 hours of adsorption, 8%, 11%, 15%, 14% and 9% of the applied amount was absorbed at the ratios 1:1 for soils I to III and V and at the ratio 1:1.5 for soil IV. For soil IV a higher ratio had to be selected since at the ratio of 1:1 all water was adsorbed.

For the determination of the Freundlich adsorption/desorption isotherm to determine the influence of the concentration on the extent of adsorption/desorption, the advanced test was performed using four soils, five initial test item concentrations (0.518, 0.131, 0.052, 0.013 and 0.005 mg/L) and a soil-to-solution ratio of 1/1 (1/1.5 for soil IV) and a maximum agitation time of 2 hours.

After 2 hours of shaking, duplicate tubes were sampled and the supernatants and acetonitrile/water soil extracts measured by LSC and analyzed by HPLC. Freundlich desorption isotherms were determined on the soils used in the adsorption isotherms experiment (five concentrations). After the adsorption step, the soil-solution mixture was centrifuged and the aqueous phase was removed. The volume of solution was replaced by an equal volume of 0.01 M CaCl₂ without test item. The new mixture was agitated for further 2 hours. Thereafter, duplicate tubes were sampled and analyzed as for the adsorption step.

Findings:

All of the applied radioactivity was recovered in the control samples thereby confirming no loss of the test item through adsorption to the test vessel wall.

Degradation of the test item was observed in all soils during the adsorption phase. Therefore, the radioactivity measured in the supernatant solutions was corrected by the amount of N,N'-dimethylthiourea as analyzed by HPLC. The amount adsorbed to the soils was considered completely as N,N'-dimethylthiourea, since almost no radioactivity could be extracted from the soils and analyzed. Once adsorbed to the soil the test item was strongly bound. Evaluated under these presumptions the calculated distribution values showed a significant correlation with the organic carbon content of the soils.

Table B.8.2.1-12: Adsorption data for DMTU on different soils

	Soil
--	------

Parameter	II	III	IV	V	Mean
K _F [mL/g]	0.175	0.152	0.290	0.100	-
K _{FOC} [mL/g]	10	7	7	10	9
K _{FOM} [mL/g]	6	4	4	6	5
l/n [mL/g]	0.75	0.73	0.82	0.75	0.76
r ² [mL/g]	0.9937	0.9971	0.9915	0.9992	0.9954
K _{des3 F} [mL/g]	0.458	0.421	0.752	0.242	-
K _{des3 FOC} [mL/g]	26	20	19	25	22
K _{des3 FOM} [mL/g]	15	11	11	14	13
l/n [mL/g]	0.78	0.77	0.82	0.76	0.78
r ² [mL/g]	0.9773	0.9937	0.997	0.9954	-

Note: The values were corrected for degradation of the test item

Conclusion:

The measured adsorption data for DMTU ((impurity of the technical substance that has a maximum content of 3.5 g/L in metam-sodium) indicate that the substance is weakly sorbed to soil with an average K_{FOC} of 22 mL/g and an average l/n of 0.76. The Study is acceptable.

B.8.2.2 Column leaching studies with the active substance and relevant metabolites (Annex IIA 7.1.3.1; Annex IIIA 9.1.2.1)

Not required. Adsorption/desorption study is available for the active substance.

B.8.2.3 Column leaching studies with the active substance and relevant metabolites (Annex IIA 7.1.3.1; Annex IIIA 9.1.2.1)

Not required. Adsorption/desorption study is available for the major metabolite MITC.

B.8.2.4 Lysimeter and field leaching studies (Annex IIA 7.1.3.3; Annex IIIA 9.1.2.2)

Not required. The estimated PEC_{gw} for the active substance and metabolites were well below the 0.1 µg/l EU trigger value for a majority of FOCUS scenarios.

Basamid Granular – A halogen-free soil disinfectant (Fritsch H.J., et al., 1995)

Published review of information on the chemical properties, the toxicology and ecotoxicology, fate and behaviour of dazomet. This publication also contains brief information on the lysimeter study that has been performed with dazomet. This study is fully evaluated in the DAR of dazomet. In leachates samples of all lysimeters, the major metabolite MITC was found at level <0.1 µg/L.

B.8.3 Predicted environmental concentration in soil (PECs) Annex IIIA 9.1.3)

“Metam-sodium is a soil fumigant which is active against nematodes, soil-borne diseases, weed seeds and seedlings and soil pests. Metam-sodium is acting by decomposition to Methylisothiocyanate (MITC) and is used as a soluble concentrate (SL) containing 510 g/L (42.1 % w/w) Metam-sodium. Application of Metam-sodium is carried out by a soil-injection technique using tractor mounted equipment as well as by a drip irrigation technique the latter of which does not require the presence of an operator except for coupling the drum to the drip irrigation installation. In addition, Metam-sodium is also applied for soil fumigation in greenhouses. Metam-sodium is an aqueous solution and will be applied at a rate of up to 1200 L/ha corresponding to 612 kg Metam-sodium/ha and the product will be marketed in 60, 200 and 1,000 L containers or drums, respectively.”

The method of application for the supported uses of metam-sodium in Europe is as follows:

- injection of the undiluted formulation in the soil followed by incorporation by rotavation and soil surface sealing with a roller (carrots, lamb's lettuce, potato, tomato)
- injection of the undiluted formulation in the soil (grape replanting)
- drip irrigation under a plastic film on the planting row (strawberry)
- drip irrigation on the planting row in glasshouse (cucumber, eggplant, pepper, tomato)

B.8.3-1: Overview of the supported uses

Crop	Field or greenhouse	Application rate of metam-sodium		Incorporation depth (cm)
Carrot	F	800 L/ha	408 kg a.s./ha	25 cm
Lamb's lettuce	F	600 L/ha	306 kg a.s./ha	15 cm
Potato	F	300 L/ha	153 kg a.s./ha	25 cm
Strawberry	F	1200 L/ha	612 kg a.s./ha	Drip irrigation under plastic
Tomato	F	1200 L/ha	612 kg a.s./ha	15 cm
Grape	F	2400 L/ha	1020 kg a.s./ha	40 cm
Cucumber	G	900 L/ha	459 kg a.s./ha	Drip irrigation on the planting row
Eggplant, pepper, tomato	G	1200 L/ha	612 kg a.s./ha	Drip irrigation on the planting row

The PEC calculations were performed for the worst case use in field tomato (higher dose rate, superficial incorporation).

Parent

Method of calculation

Application data

DT₅₀ (metam-sodium): 0.0118 days (17 minutes)Kinetics: 1st order

representative worst case from laboratory study.

Crop: field tomato

Depth of soil layer: 15 cm

Soil bulk density: 1.5 g/cm³

% plant interception: 0%

Number of applications: 1

Interval (d): -

Application rate(s): 612 kg as/ha

PEC_(s)
(mg/kg)Initial
Short term 24h

Single application	Single application	Multiple application	Multiple application
Actual	Time weighted average	Actual	Time weighted average
272	-	-	-
<0.0001	4.630	-	-

	2d	<0.0001	2.315		
	4d	<0.0001	1.158		
Long term	7d	<0.0001	0.661	-	-
	28d	<0.0001	0.165		
	50d	<0.0001	0.092		
	100d	<0.0001	0.046		

MITC

Method of calculation

Application data

Molecular weight relative to the parent: 0.566
 73.11/129.17
 DT₅₀ (d): 2.94 days
 Kinetics: first order kinetics
 Field or Lab: representative worst case from lab study.

Crop: field tomato
 0 % plant interception:
 15 cm soil incorporation
 Number of applications: 1
 Interval (d): -
 Application rate assumed: 346 kg MITC/ha (assumed
 MITC is formed at a maximum of 100 % of the applied
 dose)

PEC_(s)
(mg/kg)

	Single application Actual	Single application Time weighted average	Multiple application Actual	Multiple application Time weighted average
Initial	153.778	-	-	-
Short term	121.479	136.995	-	-
	95.965	122.608		
	59.887	99.561		
Long term	29.523	75.290	-	-
	0.209	23.263		
	0.001	13.045		
	<0.0001	6.523		

B.8.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2)

B.8.4.1 Hydrolysis rate of relevant metabolites, degradation and reaction products (Annex IIA 7.2.1.1)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
B.2.1.14 Hydrolysis rate at pH 4, 7 and 9 under sterile conditions in the absence of light (IIA 2.9.1)	EEC C7 GLP	Metam-sodium 99.9% pure (Batch No. MNA SAP01): conc. 1 g/L (0.01M); analysis by HPLC Incubation at 50°C: pH 7: approx. 10% hydrolysis after 2.4 h and 60% hydrolysis after 5 days pH 9: approx. 10% hydrolysis after 2.4 h and 40% hydrolysis after 5 days ⇒ DT₅₀ of metam-sodium at 25°C can be estimated as between 1 day and 1 year for pH 7 and pH 9. Incubation at 25°C: pH 4: approx. 54% hydrolysis after 2.4 h and 95% hydrolysis after 23 hours ⇒ DT₅₀ of metam-sodium at pH 4 is less than 1 day at 25°C.	Not acceptable as stand-alone document, but acceptable as preliminary test. On the basis of the test results, it can only be concluded that metam-sodium is very rapidly hydrolysing at pH 4 (>50% hydrolysis after 2.4 hrs at 25°C). Furthermore, the test results suggest that metam-sodium is fairly hydrolysing at pH 7 and pH 9, but precise DT₅₀ values are not provided. Moreover, the study is not fully in accordance with EEC C7 (e.g. for pH 7 and 9 only a preliminary test at 50°C was performed; no degradation curve provided, no half-life calculation).	Betteley, 1997 (FCC 152/963829)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
	US-EPA Subdivision N Series 161-1 GLP	Aqueous solution containing 30% w/w [methyl ¹⁴C]-metam-sodium (Lot no. WRC 9471-45-01); radiochemical purity = 78% (major radioimpurities: 12% DMTU and 2% DMU (1,3-dimethylurea)); At 25°C in pH 5, 7 and 9 buffer; Initial concentrations of metam-sodium in buffered aqueous solutions were in range 57 – 65 mg/L; ⇒ Metam-sodium degrades rapidly in water at 25°C Estimated half-lives (assuming pseudo-first order kinetics): pH 5: DT₅₀ = 1.9 days pH 7: DT₅₀ = 2.2 days pH 9: DT₅₀ = 4.5 days <i>Major degradation products (≥ 10% of applied radioactivity AR):</i> - <u>MITC (methylisothiocyanate)</u>: 60% of AR at end of study at pH 7 (5d); 20% of AR at end of studies at pH 5 (1.8 d) and at pH 9 (5.4 d); - <u>MCDT (sodium methylcarbamodithioperoxo)thioate</u>: 16% of AR at end of study at pH 9 (5.4 d) $\text{H}_3\text{C}-\text{NH}-\text{C}(=\text{S})-\text{S}-\text{S}^- \text{ } ^+\text{Na}$ This compound is detected only at pH 9, because probably formed by reaction of metam-sodium with elementar sulphur [S], which is only significantly formed in basic medium by oxidation of HS⁻.	Acceptable Metam-sodium is readily hydrolysed. Moreover, hydrolysis appears to be accelerated with decreasing pH. At low pH (pH 5), MITC and methylamine are the main degradation products. At higher pH (pH 7 and 9), mainly MITC and MCDT are formed.	Ericson, 1990 (RR 90-110B)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References																
		<i>Minor degradation products:</i> Methylamine (particularly at pH 5); 1 unidentified compound (representing ± 5% of AR at start of study and not increasing appreciably). <i>Product identification:</i> By match of HPLC retention times and TLC R_f values with those of reference compounds. Confirmation by mass spectrometry. <i>Mass balance:</i> Average recoveries of radioactivity were 95, 94 and 101% at pH 5, 7 and 9, respectively.																		
	No guideline referenced GLP	Metam-sodium, 99,2% pure (Batch No. V799R): 200 mg/L solution, at pH5: measurement of concentration after 24 hours: at 10°C: 23.5% metam-sodium remained at 20°C: 15.2% metam-sodium remained at 30°C: 0% metam-sodium remained	Not acceptable Very limited information provided in the report; no raw data	Betteley, 2002a (UCB809/013754)																
	OECD 111 GLP	[¹⁴C]-Methyl Isothiocyanate (CH₃N=[¹⁴C]=S) (Batch No. 3501-187), radiochemical purity = 98.46%; 30 days incubation at 15°C, 25°C and 50°C; pH 4, 7 and 9 buffer solutions; Test conc. < 0.01 M <i>Estimated half-lives DT₅₀ (days) (assuming first order kinetics):</i> <table><tr><td></td><td>15°C</td><td>25°C</td><td>50°C</td></tr><tr><td>PH 4</td><td>(a)</td><td>≈ 40</td><td>2*</td></tr><tr><td>PH 7</td><td>(a)</td><td>50</td><td>2*</td></tr><tr><td>PH 9</td><td>22</td><td>11</td><td>< 1 day (b)</td></tr></table>		15°C	25°C	50°C	PH 4	(a)	≈ 40	2*	PH 7	(a)	50	2*	PH 9	22	11	< 1 day (b)	Acceptable as supplementary information MITC is shown to degrade significantly by hydrolysis at every pH and temperature (with the exception of pH 4 and 7 at 15°C). Estimations of half-lives were given and degradation pathways for MITC at pH 4, 7 and 9, respectively, were proposed in the study report. Degradation of MITC was	Kidd et al., 2005 (Inveresk Report No. 24450)
	15°C	25°C	50°C																	
PH 4	(a)	≈ 40	2*																	
PH 7	(a)	50	2*																	
PH 9	22	11	< 1 day (b)																	

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
		*possibly underestimation because of poor resolution of MITC from degradants in severely degraded samples → DT₅₀ calculated based on decline of MITC in first 7 days of incubation (c) No significant degradation observed → No DT₅₀ calculated (d) Rapid degradation, but kinetics not linear → No DT₅₀ calculated Degradation was found to be more extensive at higher temperatures and higher pH (concomitant with higher hydroxyl ion concentration).	found to be more extensive at higher temperatures and at higher pH (concomitant with higher hydroxyl ion concentration). Major degradation products were identified as dimethylurea (DMU), dimethyl thiourea (DMTU) and methyldithiocarbamic acid (MDTCA, i.e. metam) Besides, there were indications that volatile degradates were formed at pH 4 (and pH 7).	
		Major degradation products (≥ 10% of applied radioactivity AR): Dimethylurea, dimethyl thiourea and methyldithiocarbamic acid (MDTCA) Product identification: By match of HPLC retention times with those of reference compounds. Confirmation by mass spectrometry. Mass balance: At pH 4: clear decrease of overall recovery of AR at higher temperature (down to 41% at 50°C), indicating that MITC was degrading to volatile degradates. At pH 7: decrease down to 79% at 50°C. At pH 9: mean recoveries in range 100-118% and no decrease, indicating that degradation of MITC at pH 9 gives rise to non-volatile components.		

B.8.4.2 Direct phototransformation of relevant metabolites, degradation and reactions products in water (Annex IIA 7.2.1.2)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
B.2.1.15 Direct phototransformation in purified water using artificial light under sterile conditions (IIA 2.9.2)	No guideline referenced GLP	Metam-sodium 99.9% pure (Batch No. MNA SAP01): Irradiation for 5 hours, pH 7 buffer solution: Metam-sodium: 0.24183 h^{-1} Actinometer: 0.15791 h^{-1} Estimated photochemical half-life in the environment (latitude 52°N) = 3 days Due to potential hydrolytic behaviour of metam-sodium over an extended time period at pH 7, the photolysis measurements were not carried out directly on the test substance, but instead, the experiment was conducted on an actinometer adjusted to yield a similar rate of photolysis as the test substance.	Not acceptable Insufficient information provided in the study report, e.g. mass balance, identity of breakdown products, rate constant for dark controls	Betteley, 1997 (FCC 152/963829)
	No guideline referenced Not GLP (publication)	Metam-sodium dihydrate 98% pure Crescent Chemical Half-life: 2.9 - 8.4 min (equivalent to 44 min of midsummer sunlight at latitude 40°N in 10 cm deep water)	Study is not conducted according to GLP (publication) and therefore, it is not relied upon.	Draper en Wakeham, 1993
	US-EPA Subdivision N Series 161-2 GLP-compliance stated (no GLP certificate, but study before 1993)	[methyl ^{14}C]-metam-sodium (WRC 9902-15-1), radiochemical purity > 95% Irradiation for up to 25 min; at 25°C ; Initial concentration of metam-sodium in aqueous pH 7 buffered solutions was 53 mg/L: Irradiated: $k_{\text{overall}} = 0.064 \text{ min}^{-1}$; Dark control: $k_{\text{dark}} = 0.006 \text{ min}^{-1}$ $\Rightarrow k_{\text{photolysis}} = 0.058 \text{ min}^{-1}$	Acceptable In pH 7 buffered solution metam-sodium is very rapidly degraded by photolysis into N-methylthioformamide, MITC, methylamine and MCDT.	Spurgeon, 1990 (RR 90-091B)

Study	Guidelines/Methods and GLP	Findings	Evaluation and conclusion	References
		⇒ Photochemical half-life: $DT_{50} = 12$ min (equivalent to 27.8 min of natural summer sunlight at latitude 38° N) <i>Major degradation products ($\geq 10\%$ of applied radioactivity AR):</i> - <u>N-methylthioformamide (syn- and anti- rotamer):</u> 22% of AR after 25 min $\text{H}_3\text{C}-\text{NH}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{H}$ - <u>MCDT (sodium methylcarbamo(dithioperoxo)thioate):</u> 14% of AR after 25 min - <u>MITC (methylisothiocyanate):</u> 16% of AR after 25 min - <u>Methylamine:</u> 18% of AR after 25 min (zero-time sample contained 14% methylamine) <i>Product identification:</i> HPLC with UV-DAD or radioactive flow detector; Identity confirmation by GC-MS and ^1H-NMR spectroscopy. <i>Material balance:</i> Average recovery of radioactivity for the photolysed and dark control samples was 94%.		

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.4.3 Ready biodegradability of the active substance (Annex IIA 7.2.1.3.1)

Biodegradation of metam sodium in an aerobic water/sediment system. (Hanstveit A.O., 2003)

Guideline:

OECD 301C 'Ready Biodegradability; Modified MITI Test'

GLP:

yes

Experimental design:

"Test substance: Metam-sodium 510 g/l aqueous solution. Reference substance: sodium acetate, anhydrous. A blank control, 3 concentrations of the test substance: 5, 10 and 15 mg/l corresponding to a ThOD of 10.6, 21.1 and 31.6 mg O₂/l, an inoculum activity control containing sodium acetate at 100 mg/l and a toxicity control containing test substance at 10 and 15 mg/l in addition to sodium acetate at 100 mg/l were prepared with ditch water enriched with nutrients and sediment inoculum. Incubation temperature 20°C. The O₂ concentration was measured continuously with a Sapromat system during the test with duration of 33 days."

Findings:

The following elements are supporting the non-acceptability of the study:

The (artificial medium + sewage treatment plant inoculum) has been replaced by a sample of ditch water and sediment.

At 5 mg a.s./L, the oxygen consumption is equivalent to 19600-77200% of the ThOD.

At 10 mg a.s./L (2 replicates), the oxygen consumption is equivalent to 95-145% of the ThOD.

At 15 mg/l the oxygen consumption was less than in the control indicating that at this concentration, Metam-sodium is toxic to the sediment inoculum.

In the activity control (sodium acetate), the oxygen consumption is equivalent to 108-134% of the ThOD

In the toxicity control at 15 mg/L (2 replicates), the oxygen consumption is equivalent to 72-337% of the ThOD at day 33.

Conclusion:

The study is not acceptable.

B.8.4.4 Water/sediment study (Annex IIA 7.2.1.3.2)

Potassium N-methyldithiocarbamate (PNMDC): Aerobic Aquatic Metabolism of PNMDC (Cohen, S.P.,1993)

Guidelines :

US EPA Guidelines, § 162-4: Aerobic aquatic metabolism study

GLP :

Yes

Material and Methods :Test substance

[Thiocarbonyl ¹⁴C]-metam-potassium, batch no.: 102H9203, radiochemical purity: 92.6%, 96.8% after further purification; specific activity: 14.0 mCi/mmol, supplier: Sigma Chemical Company

Sediments, waters :

Table B.8.4.4-1: Characteristics of the Allegheny River sediment and water

Sediment	Percent organic matter	4.3
	Particle size distribution	
	% sand	66.0
	% silt	24.0
	% clay	10.0
	Textural class	Sandy loam
	pH	6.7
	Cation exchange capacity (Meq/ 100 g)	5.3
Water	Bulk density (g/cm ³)	1.08
	Dissolved oxygen (mg/L)	7.2
	pH	7.4
	Conductivity (mmhos/cm)	0.19
	Hardness (mg/L)	94.2
	Total organic carbon	< 2 g/L

Experimental design :

Metam-potassium was applied at a concentration of 26 mg a.s./L to vessels containing 3.5 g sediment and 8.75 g water (equivalent to a ratio of water to sediment of 5:2 by weight). Each mixture was then vortexed for 30 seconds to homogeneously distribute the test substance. The test vessels were incubated in the dark at a temperature of 25 ± 1 °C. Aeration was achieved by continuous bubbling of humidified air. Percent dissolved oxygen (in the range 71.3-78.9%) and aerobic microbial activity (bacteria and actinomycetes levels stable during 2 days) were monitored during the whole experiment. Duplicate samples were taken at different intervals up to 480 minutes after application.

The test concentration (26 mg a.s./L) is based on assays in w/s systems at various concentrations at which the viability of aerobic microbial population was observed. Decrease of the microbial populations was observed at concentrations above 50 ppm.

For incubation greater than 4 hours, activated charcoal traps were used to capture the volatiles. No NaOH traps present.

Analytical methods :

At each sampling interval, the aqueous and sediment phases were separated and analyzed separately.

The sediment was washed with distilled water and extracted with 3 times with toluene.

The charcoal traps were extracted with carbon disulfide. Each aqueous phase, water wash, toluene and carbon disulfide extract was analyzed by LSC and HPLC, and confirmation by TLC. The extracted sediment and charcoal was combusted to determine levels of bound radioactivity. Bound residue were fractionated in a series of extraction steps (NaOH, HCL) to determine humins, humic and fulvic acids.

Identification of compounds by HPLC co-chromatography with reference substances (a.s., 1,3-dimethylurea (DMU), 1,3-dimethylthiourea (DMTU), methylisocyanate (MITC)); unknown N° 7 was identified as 1,1'-dimethylthiuramdisulfide, (DMTD).

Unknown 4, 5 and 6 were tentatively identified by means of derivatisation steps, GC/MS identification.

Findings :

Table B.8.4.4-2: Recovery of radioactivity in % AR after application of [^{14}C]-metam-potassium to one water/sediment system and incubation under aerobic conditions in water and in sediment, at 25°C

Elapsed time (min)	Aqueous phase	Sediment extract	Sediment bound	Volatile phase	Material balance
4.5	52.6	16.2	31.2	N/D	100.0
7	54.4	16.3	33.0	N/D	103.7
12	50.5	22.7	29.1	N/D	102.3
57	52.2	17.3	30.5	N/D	100.0
122	55.8	19.4	24.0	N/D	99.2
240	18.3	13.4	18.0	43.1	92.8
480	8.5	4.8	14.4	63.6	91.2

N/D = not done

The figures in the table Table B.8.4.4-3 are the sums of metabolites found in the aqueous phase, the sediment extract and the volatile phase.

Table B.8.4.4-3: Distribution of metabolites in % AR after application of [^{14}C]-metam-potassium to one water/sediment system and incubation under aerobic conditions at 25°C

Elapsed time (min.)	DMU RT=3.3	DMTU RT=4.0	MITC RT=6.2	Unk#4 RT=7.0	a.s. = PNMD C RT=13.5	Unk#6 RT=15.0	DMTD RT=28.0	Unk#5 RT=41.0	Total extractable
W/S	0.0	0.8	0.0	1.3	97.9	0.0	0.0	0.0	100.0
4.5	0.2	0.9	31.1	0.0	9.3	3.6	19.7	4.2	68.8
7	0.1	0.6	36.1	0.0	6.6	3.4	21.5	2.6	70.9
12	0.0	0.8	42.5	0.0	4.3	2.4	21.2	2.0	73.2
57	0.0	0.8	46.3	0.0	1.2	2.6	18.5	0.3	69.7
122	0.0	0.8	42.8	0.0	0.0	2.7	29.0	0.0	75.3
240	0.0	0.8	58.7	0.5	0.9	0.5	13.6	0.0	75.0
480	0.0	0.8	74.4	0.0	1.5	0.2	0.0	0.0	76.9

W/S = working stock dilution of Metam-K diluted to 26 ppm and analyzed immediately prior to application.

Table B.8.4.4-4: 1st order half-life of Metam-potassium in water/sediment system under aerobic conditions

	Test conditions	DT ₅₀	DT ₉₀	R ²	kinetics
Metam-potassium	Non-sterile aerobic	19.72 minutes	65.51 minutes	0.945578	Linear 1 st order regression
MITC	Non-sterile aerobic	158.75 minutes	527.37 minutes	0.90642	Non-linear 1 st order regression

Conclusions :

In non-sterile aerobic water/aerobic sediment system at 25°C in the dark, Metam-K metabolized with an estimated half-life of 19.72 minutes. It has been considered that the type of salt has no influence on the metabolism in water/sediment systems.

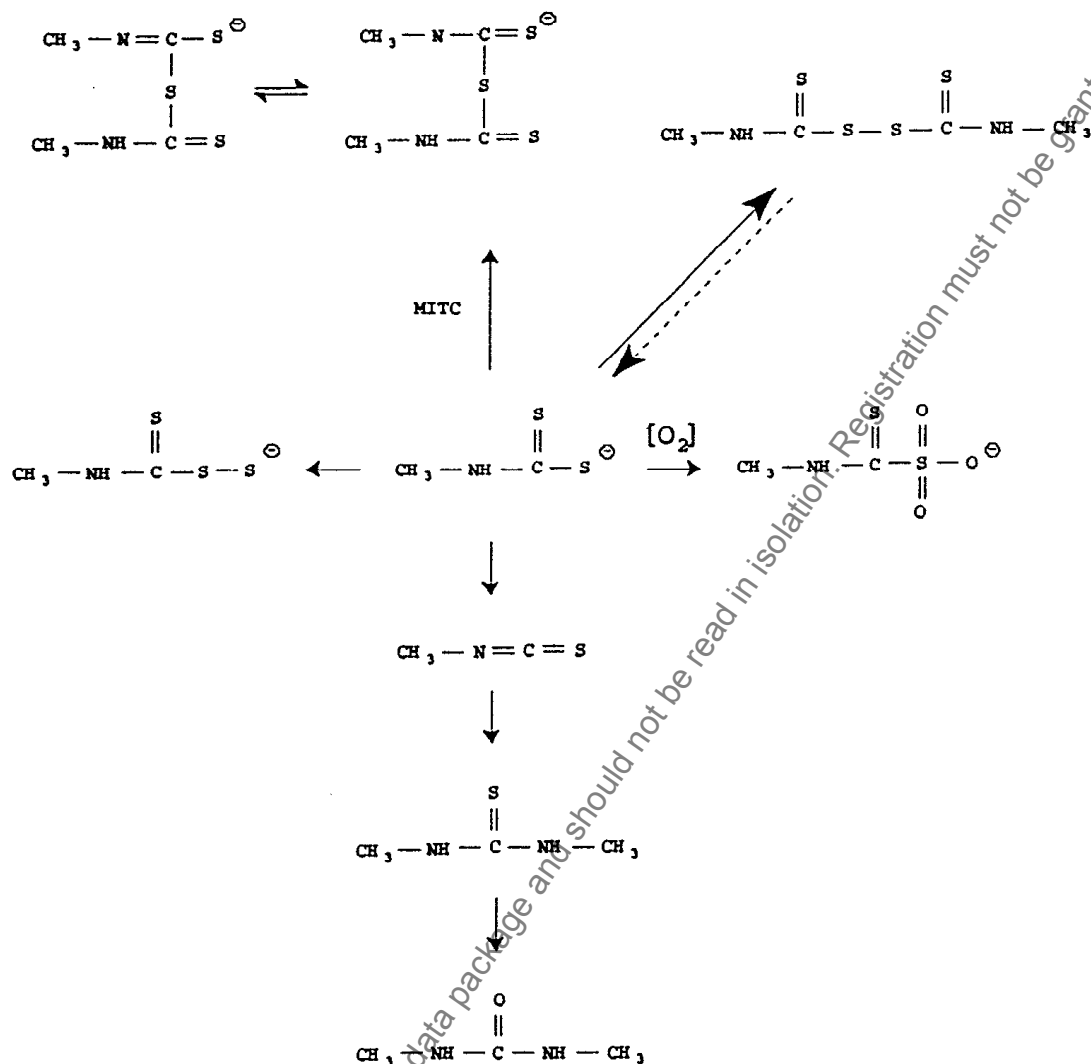
The major metabolite observed was MITC, which represented 74.4 % of the initial radioactivity at the 480 minutes sampling point. The fate of MITC in the aerobic water/sediment system was re-evaluated to obtain first order dissipation of DT₅₀ values for MITC. These values include the volatilization of MITC from the system into the loss term. The half life of MITC in the system was found to be 158.75 min (2.6 hours).

No CO₂ determination has been performed (No NaOH trap present).

A second metabolite, identified as 1,3-Dimethylthiuramdisulfide (DMTD), reached a maximum of 29.0% of the initial radioactivity at 122 minutes, then declined to 13.6% at time 240 minutes and was not detected at 480 minutes.

The bound residue level decreased from a maximum level of 33%AR after 7 minutes to 14.4 %AR after 480 minutes (8 hours).

Figure B.8.4.4-1: Proposed degradation pathway of Metam-sodium in aerobic water/sediment systems



Potassium N-methyldithiocarbamate (PNMDC): Anaerobic Aquatic Metabolism of PNMDC (Cohen, S.P., 1992)

Potassium N-methyldithiocarbamate (PNMDC): Supplemental Report: Anaerobic Aquatic Metabolism of PNMDC – Isolation and Identification of Metabolites (Cohen, S.P., 1993b)

Guidelines :

US EPA Guidelines, § 162-3: Anaerobic aquatic metabolism study

GLP :

Yes

Material and Methods :

Test substance

[Thiocarbonyl ^{14}C]-metam-potassium, batch no.: 111H9205, radiochemical purity: 85%, 94.66% after further purification; specific activity: 16.7 mCi/mmol, supplier: Sigma Chemical Company

Sediments, waters :

Table B.8.4.4-5: Characteristics of the Allegheny River sediment and water

Sediment	Percent organic matter	4.3
	Particle size distribution	
	% sand	66.0
	% silt	24.0
	% clay	10.0
	Textural class	Sandy loam
	PH	6.7
	Cation exchange capacity (Meq/ 100 g)	5.5
Water	Bulk density (g/cm ³)	1.08
	Dissolved oxygen (mg/L)	7.2
	PH	7.4
	Conductivity (mmhos/cm)	0.19
	Hardness (mg/L)	94.2
	Total organic carbon	< 2 g/L

Experimental design :

The anaerobic aquatic metabolism was studied according to the same protocol in sterile and non-sterile systems.

Sediment/water vessels were pre-incubated at 25 °C under nitrogen in order to establish anaerobic conditions. Metam-potassium was applied at a concentration of 26 mg a.s./L to vessels containing 3.5 g sediment and 9.0 g water (equivalent to a ratio of water to sediment of 5:2 by weight). Each mixture was purged with N₂ and then vortexed for 30 seconds to homogeneously distribute the test substance. The test vessels were incubated in the dark at a temperature of 25 ± 1 °C. For sampling intervals > 10 hours, test systems were incubated under continuous nitrogen flow. The redox potential was measured at each sampling interval to confirm anaerobic conditions in the whole system. The anaerobic microbial activity was monitored during the whole experiment (no decrease of the activity in the non-sterile samples; sterility maintained in the sterile samples).

Duplicate samples were taken at different intervals up to 72 hours after application.

Activated charcoal traps were used to capture the volatiles. No NaOH traps present.

Analytical methods :

At each sampling interval, the aqueous and sediment phases were separated and analyzed separately.

The sediment was washed with distilled water and extracted with 3 times with toluene.

The charcoal traps were extracted with carbon disulfide. Each aqueous phase, water wash, toluene and carbon disulfide extract was analyzed by LSC and HPLC, and confirmation by TLC. The extracted sediment and charcoal was combusted to determine levels of bound radioactivity. Bound residue were fractionated in a series of extraction steps (NaOH, HCL) to determine humins, humic and fulvic acids.

Identification of compounds by HPLC co-chromatography with reference substances (a.s., 1,3-dimethylurea (DMU), 1,3-dimethylthiourea (DMTU), methylisocyanate (MITC)). Unknown 2,3, 4, 5 and 6 were tentatively identified by means of derivatisation steps, GC/MS identification.

Table B.8.4.4-6: Recovery of radioactivity in % AR after application of [^{14}C]-metam-potassium to one water/sediment system (mean of 2 replicates) and incubation under non-sterile anaerobic conditions at 25°C

time (hours)	Water phase	Sediment extract	Sediment bound	Volatile phase	Material balance
0	95.4	5.9	4.8	N/A	106.1
2	86.5	5.0	4.0	7.0	102.4
4	72.4	5.9	5.9	9.9	94.2
6	66.8	6.0	6.1	11.4	90.2
8	67.5	7.4	8.7	9.9	93.5
10	59.7	7.0	10.1	15.7	92.5
24	21.6	4.8	14.8	61.5	102.7
48	6.7	3.0	16.5	67.6	93.8
72	3.2	1.5	13.3	79.4	97.2

N/A = not applicable

Table B.8.4.4-7: Recovery of radioactivity in % AR after application of [^{14}C]-metam-potassium to one water/sediment system (mean of 2 replicates) and incubation under sterile anaerobic conditions at 25°C

time (hours)	Water phase	Sediment extract	Sediment bound	Volatile phase	Material balance
0	74.2	10.1	13.1	N/A	97.6
2	71.1	9.0	9.8	5.6	95.5
8	49.0	14.6	21.9	19.9	105.4
24	16.0	8.8	19.6	48.2	92.6
72	7.2	4.5	21.2	58.2	91.1

N/A = not applicable

The distribution of parent and metabolites is shown in Table B.8.4.4-8 (non-sterile) and Table B.8.4.4-9 (sterile) below. The figures presented in this table are the sums of parent and metabolites found in the aqueous phase, the sediment extract and the volatile phase.

Table B.8.4.4-8: Distribution of metabolites in % AR after application of [^{14}C]-metam-potassium to one water/sediment system (mean of 2 replicates) and incubation under non-sterile anaerobic conditions at 25°C

Sampling time (hours)	DMU RT=3.3	Unk #2 RT=4.0	Unk #3 RT=4.9	MITC RT=6.0	Unk#4 RT=6.5	Unk#5 RT=10.0	a.s. = PNMD C RT=12.5	Unk#6 RT=14.0	Total Bound	Total Percent
WS	0.3	1.2	0.0	1.1	0.9	0.7	95.1	0.8	N/A	100.1
0	0.5	0.9	0.0	34.3	0.9	4.0	57.1	3.8	4.8	106.1
2	0.5	1.2	1.3	41.2	0.0	3.7	49.0	1.7	4.0	102.4
4	0.9	0.9	0.0	63.2	0.0	0.0	20.0	3.3	5.9	94.1
6	0.4	1.0	0.0	59.7	0.0	0.0	12.1	2.1	6.1	90.2
8	0.3	1.3	0.0	72.5	0.0	0.0	10.7	0.0	8.7	93.4
10	0.3	0.7	0.0	73.8	1.5	0.0	4.6	1.7	10.1	92.5
24	0.1	0.0	0.0	86.8	0.0	0.0	0.5	0.7	14.8	102.9
48	0.0	0.0	0.0	77.3	0.0	0.0	0.0	0.0	16.5	93.5

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72	0.0	0.0	0.0	84.0	0.0	0.0	0.0	0.0	13.3	97.3
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N/A = not applicable

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

Table B.8.4.4-9: Distribution of metabolites in % AR after application of [¹⁴C]-metam-potassium to one water/sediment system (mean of 2 replicates) and incubation under sterile anaerobic conditions at 25°C

Sampling time (hours)	DMU RT=3.3	Unk #2 RT=4.0	Unk #3 RT=4.9	MITC RT=6.0	Unk#4 RT=6.5	Unk#5 RT=10.0	a.s. = PNMD C RT=12.5	Unk#6 RT=14.0	Total Bound	Total Percent
WS	0.3	1.2	0.0	1.1	0.9	0.7	95.1	0.8	N/A	100.1
0	0.7	1.0	0.0	58.4	0.0	0.0	17.7	6.5	13.1	97.3
2	0.7	1.2	0.0	52.8	0.0	0.0	26.3	4.8	9.8	95.5
8	0.9	2.4	0.6	76.9	0.0	0.7	1.2	1.0	21.9	105.4
24	1.1	2.0	0.0	67.1	0.0	2.3	0.7	0.0	19.6	92.8
72	1.0	1.4	0.0	65.0	0.0	2.2	0.5	0.0	21.2	91.3

N/A = not applicable

Table B.8.4.4-10: 1st order half-life of Metam-potassium in water/sediment system under anaerobic conditions (linear regression analysis)

	Test conditions	DT ₅₀	DT ₉₀	R ²	kinetics
Metam-potassium	Sterile anaerobic	1.59 hour	5.28 hours	0.9278	Linear 1 st order regression
Metam-potassium	Non-sterile anaerobic	2.87 hours	9.53 hours	0.9761	Linear 1 st order regression
MITC	Sterile anaerobic	10.60 hours	35.22 hours	0.97351	Non-linear 1 st order regression
MITC	Non-sterile anaerobic	13.44 hours	44.65 hours	0.99479	Non-linear 1 st order regression

Conclusions:

The anaerobic aquatic metabolism was studied according to the same protocol in sterile and non-sterile systems. Metam-potassium degraded with an estimated half-life of 2.87 and 1.59 hours, respectively under non-sterile and sterile conditions.

The major metabolite observed was MITC, which represented 84.0% (non-sterile) and 65.0% (sterile) of the initial radioactivity by the end of the study. The fate of MITC in the anaerobic water/sediment systems was re-evaluated to obtain first order dissipation of DT₅₀ values for MITC. These values include the volatilization of MITC from the system into the loss term. The half life of MITC in anaerobic non-sterile system was found to be 13.44 hours. In the sterile system, it was 10.60 hours.

Minor metabolites were formed during the course of this study at max level of 4.0% AR and decreased up to 0%AR after 3 days (under non-sterile anaerobic conditions).

The bound residue level reached a maximum level of 16.5% AR after 2 days (under non-sterile anaerobic conditions).

No CO₂ determination has been performed (No NaOH trap present).

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.2, the applicant had to address the effect of temperature on the dissipation of MITC from water by volatilization. The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

"The study is compliant with the US EPA guideline under which it was undertaken (25°C) and also compliant with the current requirements according to OECD 308, which state "at a constant temperature in the range 10 to 30°C"

At lower temperatures (15, 20°C, the volatilisation would be expected to be slightly lower but, given the amount of volatilisation occurring at 25°C (64% in 8hr) it is not considered that these lower temperatures would significantly effect the losses by volatilisation

The calculated dissipation DT₅₀ for MITC from this study (Cohen, 1993) was 2.6hr, whereas the dissipation DT₅₀ used in the PEC_{sw} calculations (Jarvis, 2007b) was 8.9 hr. Hence any theoretical effect of temperature on volatilisation in the risk assessment is addressed by this protective value.”

Conclusion of the RMS:

We agree with the notifier. According to the OECD guideline, the test may be performed between 10 and 30°C with 20°C as recommended value.

We consider that it is not necessary to perform a new study at another temperature.

Conclusion of the peer review: a new data gap has been identified

Added in August 2010:

“A data gap was identified by the meeting of experts to address the effect of temperature on the dissipation of MITC from water by volatilization.”

Estimation of volatilisation of methyl isothiocyanate (MITC) from sediment/water systems at 12°C, and consequences for chronic aquatic ecotoxicology risk. (Mason P. & Terry A., 2010)

Introduction

A study investigating the fate of Potassium N-Methyldithiocarbamate (metam-potassium) in a sediment/water system (Cohen, 1993) reported 63.6% of applied radioactivity was measured in the volatile phase by the end of the study (480 minutes, 8 hours, following dosing with ¹⁴C-labelled PNMD). Methyl Isothiocyanate (MITC) was identified as a major metabolite representing 74.4% of total radioactivity at the last sampling point. It was proposed that MITC represented the majority of the radioactivity detected in the volatile phase, due to its relatively high vapour pressure (2427 Pa at 25°C, Lindemann, 2003). Given that MITC was clearly very rapidly eliminated (in the gas phase) from the system, it was not possible to calculate a DegT₅₀ rate for MITC. The DissT₅₀, though, was clearly much less than one day at 25°C.

EU guidance (SANCO, 2002) indicates that chronic risk assessments are not required where the DT₅₀ for the compound in the water column is < 2 days. Clearly, for MITC, the DT₅₀ in the water column is very much less than 2 days at 25°C. However, volatilisation is dependent on temperature, and so the likely volatilisation of MITC from the water column at a lower, more environmentally relevant temperature, has been investigated.

Estimation of volatile loss at 12°C

For the investigations presented here, an environmental temperature of 12°C was assumed. This is consistent with the standard temperature assumed for moderate latitudes in the EU Technical Guidance Document on Risk Assessment (European Commission, 2003).

Henry's law constant is an estimation of substance transfer from the aqueous phase to the gas phase and allows the air/water partitioning coefficient (K_{air-water}) to be determined. K_{air-water} describes the relationship of concentration in air to concentration in water. According to the EU Technical Guidance Document on Risk Assessment (European Commission, 2003) these parameters may be determined as follows:

$$HENRY = \frac{VP \cdot MOLW}{SOL} \quad (EU-TGD, Equation 21)$$

$$K_{air-water} = \frac{HENRY}{R \cdot TEMP} \quad (EU-TGD, Equation 22)$$

where:

Symbol	Parameter	Units	Value	Source
VP	vapour pressure	[Pa]	Temperature dependent	Data set
MOLW	molecular weight	[g.mol ⁻¹]	73.11	Data set
SOL	solubility	[mg.L ⁻¹]	Temperature dependent	Data set
R	gas constant	[Pa.m ³ .mol ⁻¹ .K ⁻¹]	8.314	Default
TEMP	Temperature at the air-water interface	[K]	Temperature dependent	Data set
HENRY	Henry's law constant	[Pa.m ³ .mol ⁻¹]		Output
K _{air-water}	air-water partitioning coefficient	[-]		Output

Vapour pressure and solubility inputs for Henry's law constant are temperature dependent. The water solubility of MITC is reported to be 8940 mg.L⁻¹ at 20°C (Flack, 1997), whilst the vapour pressure was measured as 2427 and 1231 Pa at 25 and 15 °C, respectively (Lindemann, 2003)¹. According to the EU-TGD, these parameters may be corrected to different environmental temperatures (in this case 25 and 12°C) using the following equations:

$$SOL(TEMP_{env}) = SOL(TEMP_{test}) . e^{\left(\frac{H_{0solute}}{R} \left(\frac{1}{TEMP_{test}} - \frac{1}{TEMP_{env}} \right) \right)} \quad (EU-TGD, Equation 3)$$

Symbol	Parameter	Units	Environmental Temperature		Source
			25 °C	12 °C	
Input					
SOL(TEMP _{test})	Solubility as in given data set	[mg.L ⁻¹]	8940	8940	data set
TEMP _{test}	Temperature of measured data	[K]	293	293	data set
TEMP _{env}	Environmental temperature	[K]	298	285	default
H _{0solute}	Enthalpy of solution	[J/mol]	1.10 ⁴	1.10 ⁴	default
R	gas constant	[Pa.m3.mol-1.k-1]	8.314	8.314	default
Output					
SOL(TEMP _{env})	Solubility at environmental temperature	[mg.L-1]	9577	7967	Output

$$VP(TEMP_{env}) = VP(TEMP_{test}) . e^{\left(\frac{H_{0vapour}}{R} \left(\frac{1}{TEMP_{test}} - \frac{1}{TEMP_{env}} \right) \right)} \quad (EU-TGD, Equation 2)$$

where:

¹ Lindemann (2003) also reports a vapour pressure for MITC of 1739 Pa at 20°C, interpolated from measurements at 15°C and 25°C

Symbol	Parameter	Units	Environmental Temperature		Source
			25°C	12°C	
Input					
VP(TEMP _{test})	Vapour temperature as in given data set	[Pa]	2427	2427	data set
TEMP _{test}	Temperature of measured data	[K]	298	298	data set
TEMP _{env}	Environmental temperature	[K]	298	285	default
R	gas constant	[Pa.m3.mol-1.k-1]	8.314	8.314	default
H _{0vapour}	Enthalpy of vapourisation	[J/mol]	5.10 ⁴	5.10 ⁴	default
Output					
VP(TEMP _{env})	Vapour pressure at environmental temperature	[Pa]	2427	967	Output

The resulting temperature-corrected vapour pressure and solubility values for MITC are summarised in Table 1.

Table 1: Solubility and Vapour Pressure at differing temperatures

Parameter	Units	Temperature [°C]	
		25	12
Solubility	[mg.L ⁻¹]	9577	7967
Vapour Pressure	[Pa]	2427	967

By applying the values shown in Table 1 to equations 21 and 22 from the EU-TGD, it is possible to derive temperature-dependent Henry's law constant and K_{air-water} values for MITC. The resulting values are shown in Table 2.

Table 2: Henry's law constant and K_{air-water} at differing temperatures

Parameter	Units	Temperature [°C]	
		25	12
Henry	[Pa.m ³ .mol ⁻¹]	18.53	8.87
K _{air-water}	[-]	0.0075	0.0037

Table 2 illustrates that with an approximate halving of temperature at the air water interface, both Henry's law constant and K_{air-water} values reduced by an equivalent magnitude. This suggests that volatilisation is reduced by approximately 50% at 12°C in comparison to the test temperature of 25°C. The study on aerobic aquatic metabolism of PNMDc reports that 63.6% of applied radioactivity is detected in the volatile phase at 25°C, and that this represents MITC. Therefore it can be assumed that with a 50% decrease in volatility, approximately 32% of MITC will be in the gaseous phase at 12°C, after 8 hours.

DT₅₀ for loss of MITC from the sediment/water system at 12°C

If volatile loss of MITC from the sediment/water system at 12°C is assumed to be according to simple first order kinetics:

$$\frac{dC}{dt} = -k C$$

The integrated form of the equation is:

$$C = C_0 e^{-k t}$$

Where:

C = concentration of MITC in sediment/water system at time t
 C_0 = initial concentration at time 0
 k = first-order rate constant (hour⁻¹)

Re-arranging the equation gives:

$$k = \frac{1}{t} \times \ln\left(\frac{C_0}{C}\right)$$

And DT₅₀ is:

$$DT_{50} = \frac{\ln 2}{k}$$

If 68% MITC is left in the system after 8 hours, the corresponding SFO rate constant (k) would be 0.04821 hours⁻¹ and the DT₅₀ would be 14.4 hours (0.6 days). Therefore the DissT₅₀ for MITC from the water column would be <1 day.

Conclusion

An environmental temperature of 12°C was assumed. This is consistent with the standard temperature assumed for moderate latitudes in the EU Technical Guidance Document on Risk Assessment (European Commission, 2003).

Based on the available information on solubility and vapour pressure, Henry's law constant and K_{air-water} were determined for 25°C and 12°C.

These parameters lead to the conclusion that the DissT₅₀ for MITC from the water column would be <1 day at 12°C. Hence a chronic aquatic risk assessment is not required and attempting to perform additional water/sediment studies would only confirm the rapid loss of MITC from the water column to air. Further water/sediment study is not required.

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.3, Applicant to calculate from data in the water sediment study Cohen, S.P. 1993a formation fractions and degradation rates (and associated DT₅₀) in the whole system.

The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

“According to reporting table comment 4(27), the concern raised relates to the amount of MITC remaining at the end of the study and the fact that no reliable DT50 may be derived from the data set presented in table 8.4.4-3.

It is acknowledged that no DT50 can be derived from the data on total MITC fraction (water+sediment+air).

However, the notifier respectfully points out that 63.3% MITC was present in the volatilised fraction at the end of the study, whilst total radioactivity in the water and sediment extracts were 8.5 and 4.8 % respectively. It is entirely logical that MITC will volatilise rather than remain in the sediment/water system.

For calculation of the predicted environmental concentration in surface water (PEC_{sw}) it is justified and realistic to use the DT50 values of MITC in water/sediment systems and to consider MITC in the air fraction in the loss term. In real-life conditions, volatilised MITC will dissipate to the atmosphere where it will be diluted and undergo atmospheric degradation. It is in the context of surface water (and sediment) concentrations not considered appropriate to build in the relatively slower degradation of MITC in the air phase because the major fraction of MITC is rapidly dissipating from the aquatic environment.

Details on the calculation can be found in attached document (Appendix IV to Jarvis, 2007, report No. TA18804-2A).

Conclusions of the peer review : point of clarification 4.3 addressed

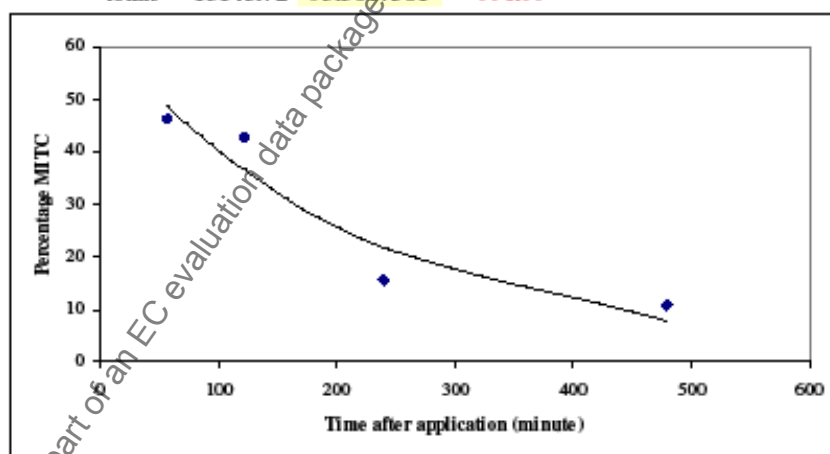
Report Number: TA18804-2A

APPENDIX IV: Re-calculation of DT_{50} value from existing sediment/water studies

The fate of MITC in the water/sediment system in the experiments by Cohen (1993a, b) was re-evaluated to obtain first order dissipation DT_{50} values (i.e. to include the volatilisation of MITC from the system into the loss term). Values of volatilised MITC were subtracted from the total MITC to obtain the amount of MITC remaining in the water/sediment system. These data were then fitted to a non-linear first order regression, using the Solver function in Excel. Outputs from the Excel spreadsheet are shown below.

Aerobic aquatic degradation (Cohen 1993a)

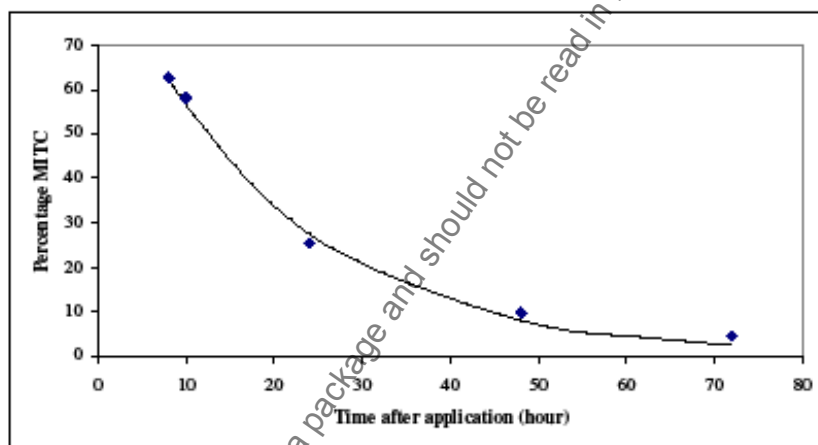
MITC		MITC			Solver function		
MAT	%obs	% calc.	(residuals)^2	total variation^2			
57	46.2	48.6	5.6353	301.02	Co	62.299735	
122	42.8	36.6	38.7867	194.60	k	0.0043662	
240	15.6	21.8	39.0292	175.56			
480	10.8	7.7	9.8505	325.80			
					half-life	158.75	mins
					DT90	527.37	mins
					SSE =	93.301758	
					SST =	996.99	
					R2 =	0.90642	
totals		13145.72	93.3017581	996.99			



Report Number: TA18804-2A

Anaerobic aquatic degradation (Cohen 1993b)

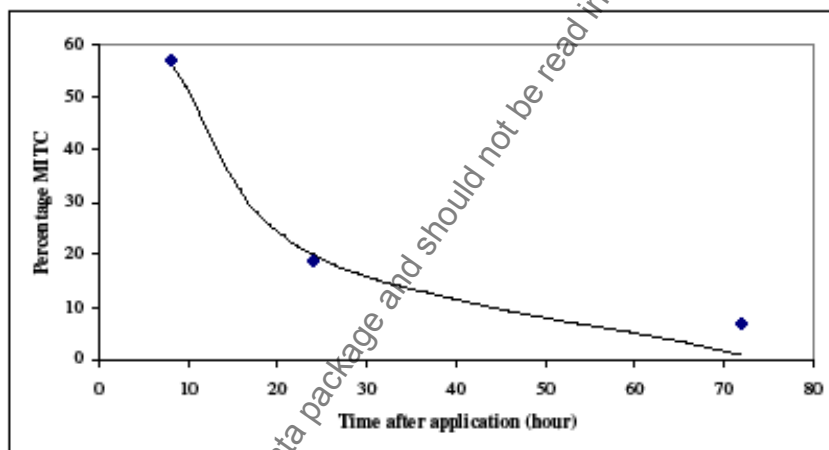
MITC		MITC		(residuals)^2	total variation^2	Solver function	
HAT	% obs	% calc.					
8	62.6	63.0	0.1748	932.69	Co	95.19763	
10	58.1	56.8	1.5806	678.08		0.051566	
24	25.3	27.6	5.3589	45.70	k		
48	9.7	8.0	2.8543	499.97	half-life	13.44	hr
72	4.6	2.3	5.1815	754.05	DT90	44.65	hr
					SSE =	15.150182	
					SST =	2910.492	
					R2 =	0.99479	
totals		24904.02	15.1501822	2910.492			



Report Number: TA18804-2A

Sterile aquatic degradation (Cohen 1993b)

MITC		MITC		total variation^2	Solver function			
HAT	% obs	% calc.	(residuals)^2					
8	57	56.7	0.0736	866.32	Co k	95.70935		
24	18.9	19.9	1.0600	75.11		0.0652796		
72	6.8	0.9	35.2344	431.25				
						half-life	10.60	hr
						DT90	45.22	hr
						SSE =	36.368073	
						SST =	1372.6867	
						R2 =	0.97351	
totals		6009.717	36.368073	1372.68667				



References:

Cohen, S.P. (1993a) Potassium N-methyldithiocarbamate (PNMDC) Aerobic aquatic metabolism of PNMDC. Center for Hazardous Materials Research, Pittsburgh USA., unpublished report No. ME 9100132

Cohen, S.P. (1993b) Potassium N-methyldithiocarbamate (PNMDC) Anaerobic aquatic metabolism of PNMDC + supplemental report. Center for Hazardous Materials Research, Pittsburgh USA, Unpublished report No. ME 9100133

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As open point 4.8, MS experts to discuss in a meeting the need for a second water sediment study. In this context discuss if the water sediment studies summarized in dazomet DAR are relevant for metam and its active metabolite MITC. The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

According to reporting table comment 4(29) the concern raised relates to the amount of MITC remaining at the end of the study and the possibility of further degradation of MITC. The notifier respectfully points out that acceptable mass balances were obtained at all timepoints and that at the final timepoint (480 minutes) 63.6% MITC was present in the volatilised fraction, whilst total radioactivity in the water and sediment extracts were 8.5 and 4.8% respectively. Therefore there is no realistic possibility of further degradation of MITC in the water or sediment that could lead to any other metabolites >10%. This was clearly stated in the study report and in the dossier provided by the Notifier.

The study itself was carried out according to accepted international guidelines and is not considered deficient in any way. It is entirely logical that MITC will volatilise rather than remain in the sediment/water system and hence there is no scientific basis to request a further sediment/water study to address the further degradation of MITC. Studies undertaken with dazomet (which also generates MITC) were provided for a different compound by a different notifier. Assuming that the study was conducted to internationally agreed guidelines with no deviations, there are still a number of reasons why the actual distribution of MITC between water and air could be different to the metam study provided by Taminco. These could include vigorousness of stirring, surface area of water, temperature etc. Nonetheless, none of these experimental design factors could be considered more relevant in the dazomet study than the metam study and the metam study conforms to the internationally agreed guideline. We therefore consider that the dazomet water/sediment study has no bearing on the evaluation of metam and it is unreasonable to place greater weight on the results of a study submitted by a different notifier for a different compound.

Conclusions of the peer review: open point 4.8 fulfilled

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.4, the applicant had to address the risk assessment of the aquatic metabolite DMTD. Only information already available in the dossier or in the raw data of studies in the dossier (including reanalysis of stored samples) may be used to finalize this risk assessment. In case information available in the dossier does not allow finalizing this assessment a data gap may be identified by the meetings of experts in fate and ecotox.

The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

The applicant agrees with the RMS. In one out of the three w/s systems, DMTD reached a maximum of 29.0% of the initial radioactivity at 122 minutes, then declined to 13.6% at time 240 minutes and was not detected at 480 minutes (8 hours). We do not see the need for a specific risk assessment for such a transient metabolite. Moreover, DMTD is a metabolite of metam, but metam is incorporated into the soil (no drift) and degrades very rapidly. As a consequence metam is not expected to reach the surface water therefore the DMTD metabolite cannot be formed in the aquatic environment.

Conclusion of the RMS:

The RMS considers that the statement of the notifier is valid. The RMS does not see the need to require a specific risk assessment for such a transient metabolite.

Conclusions of the peer review: Point of clarification 4.4 addressed

**B.8.4.5 Degradation in the saturated zone of active substance, metabolites, degradation and reaction products
(Annex IIA 7.2.1.4)**

Considering the supported uses of metam-sodium (Application into the soil by direct injection or through drip-irrigation system), it is not expected that metam-sodium or its volatile metabolite MITC would be exposed to anaerobic conditions.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.5 Impact on water treatment procedures (Annex IIIA 9.2.2)

Considering the supported uses of metam-sodium (Application into the soil by direct injection or through drip-irrigation system), it is not expected that metam-sodium or its volatile metabolite MITC would be exposed to anaerobic conditions.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.6 Predicted Environmental Concentrations in surface water and in groundwater (PEC_{sw}, PEC_{gw}) (Annex IIIA 9.2.1, 9.2.3)**B.8.6.1 Predicted environmental concentrations in ground water (PEC_{gw}) (Annex IIIA 9.21)**

At request of the RMS new calculations have been performed with PEARL 3.3.3. and taking into account the following points:

- the mean lab DT50 of MITC was used
- the crop interception is set at 0.
- The laboratory degradation studies were all undertaken at water contents above the theoretical pF 2 value. Hence no correction for moisture content is required and appropriate input value for modeling is 2.15 days (i.e. corrected to pF 2 and 20°C)

Predicted Environmental Concentrations of Metam-sodium (as MITC) in Groundwater in the EU using the FOCUS Groundwater Scenarios with the PRZM and PEARL models (Jarvis T., 2007a)

Models and assumptions:

Simulations with MITC applied to carrots, corn salad and tomatoes at rate of 1 x 172 = 344 kg MITC/ha corresponding to 600 l/ha to 1200 l/ha of a Metam-sodium 510 g/l end use solution, were conducted with the PRZM 2.4.1 and PEARL 3.3.3 models and covered all relevant scenarios (Chateaudun, Hamburg, Jokioinen, Kremsmunster, Piacenza, Porto, Seville, Thiva).

For the purposes of this assessment, simulations were carried out on the significant and representative crops of carrots (winter application), corn salad and tomatoes. These GAPs represent a wide range of application timing (winter, summer and spring application) and high application rates. Irrigation was applied according to the FOCUS (2000) recommendations (i.e. at Chateaudun, Piacenza, Seville and Thiva).

The agronomic parameters used as input for these simulations were therefore as follows. Cropping dates stated are those provided by FOCUS (2000) as part of the scenarios:

The dose rate of MITC is based on 100% conversion from metam-sodium and a molecular weight conversion of 73.11/129.19.

Table B.8.6.1-1: Crops and application parameters simulated

Application parameter	Carrot	Corn salad (cabbage surrogate FOCUS scenario)	Tomatoes
Application rate (kg MITC /ha) (0% crop interception)	229	172	344
Number of applications/year	1	1	1
Application date	15 Nov (PRZM), 1 Oct (or 16 Oct after harvest of carrots at Porto) for PEARL	10 day before 2 nd (or only) crop transplant	10 Mar
Incorporation depth (cm)	25	15	15

Table B.8.6.1-2: MITC compound properties

Properties	PRZM simulation	PEARL simulation
Molecular Mass (g mol ⁻¹)	73.11	73.11
Vapour Pressure (Pa)	-*	1739 at 20°C
Aqueous Solubility (mg/L)	-*	8940 at 20°C
Soil Adsorption Coefficient (K _{oc}) (ml/g)	36	36 (K _{om} = 21)
Freundlich Exponent	1.07	1.07
DT ₅₀ (days)	1.57 (field)**	2.15 at 20°C and pF2
Plant Uptake Coefficient	0.5	0

* Not required since field dissipation includes volatilisation losses

** Temperature and moisture corrections disabled

Findings:

Simulation results from PRZM 2.4.1 are shown in Tables 3-5 and those from PEARL 3.3.3 in Table 6. It should be noted that the 80th percentile concentration from the range of 20 years weather is combined with an 80th percentile worst case soil (already selected as part of the scenario). Therefore the predicted concentration is intended to be representative of the overall 90th percentile worst case scenario.

Table B.8.6.1-3: 80th Percentile average annual concentrations for MITC in carrots

80th Percentile Average Annual Concentration at 1 Meter Depth
CROP: Carrots, Applied Amount (g/ha) = *****

		Period	Conc. (ug/l)	Mass (g/ha)	Leachate (L/ha)
MITC	- C	13	0.1527E-03	0.3055E-03	0.2000E+07
MITC	- H	5	0.1711E-01	0.4636E-01	0.2710E+07
MITC	- J	4	0.6449E-03	0.2359E-02	0.3658E+07
MITC	- K	14	0.8049E-04	0.1708E-03	0.2122E+07
MITC	- O	16	0.7159E-04	0.2386E-03	0.3333E+07
MITC	- T	6	0.2256E-02	0.3053E-02	0.1353E+07

C:\FGRAT\PROJECTS\MITC\CARROTS\ANNUAL of FOCUS PRZM Groundwater Tool v2.4.1 (Mar., 2002)

C = Chateaudun, H = Hamburg, J = Jokioinen, K = Kremsmunster, O = Porto, T = Thiva

Table B.8.6.1-4: 80th Percentile average annual concentrations for MITC in corn salad (cabbage)

80th Percentile Average Annual Concentration at 1 Meter Depth
CROP: Cabbage, Applied Amount (g/ha) = *****

		Period	Conc. (ug/l)	Mass (g/ha)	Leachate (L/ha)
MITC	- C	11	0.1213E-07	0.1985E-07	0.1637E+07
MITC	- H	13	0.2631E-09	0.6674E-09	0.2537E+07
MITC	- J	18	0.7446E-04	0.2292E-03	0.3078E+07
MITC	- K	1	0.1903E-06	0.5665E-06	0.2977E+07
MITC	- O	19	0.7742E-16	0.2321E-15	0.2998E+07
MITC	- S	0	0.000	0.000	0.5818E+06
MITC	- T	1	0.1076E-18	0.2071E-18	0.1925E+07

C:\FGRAT\PROJECTS\MITC\LETTUCE\ANNUAL of FOCUS PRZM Groundwater Tool v2.4.1 (Mar., 2002)

C = Chateaudun, H = Hamburg, J = Jokioinen, K = Kremsmunster, O = Porto, S = Sevilla, T = Thiva

Table B.8.6.1-5: 80th Percentile average annual concentrations for MITC in tomatoes

80th Percentile Average Annual Concentration at 1 Meter Depth
CROP: Tomatos, Applied Amount (g/ha) = *****

		Period	Conc. (ug/l)	Mass (g/ha)	Leachate (L/ha)
MITC	- C	15	0.9881E-08	0.1829E-07	0.1851E+07
MITC	- P	6	0.8056E-03	0.3717E-02	0.4614E+07
MITC	- O	6	0.2169E-06	0.6746E-06	0.3110E+07
MITC	- S	3	0.000	0.000	0.1035E+07
MITC	- T	17	0.4093E-07	0.3517E-07	0.8592E+06

C:\FGRAT\PROJECTS\MITC\TOMATOES\ANNUAL5 of FOCUS PRZM Groundwater Tool v2.4.1 (Mar., 2002)

C = Chateaudun, P = Piacenza, O = Porto, S = Sevilla, T = Thiva

Table B.8.6.1-6: 80% percentile simulated concentrations of MITC at FOCUS scenarios after application to carrot, corn salad or tomatoes (PEARL – laboratory DT₅₀)

LOCATION	APPLICATION SCHEME	CROP_CALENDAR	IRRIGATION SCHEME	MITC (µg/l)
CHATEAUDUN	mitc-carrot	CHAT-CARROTS	CHAT-IRR-F	1.219851
CHATEAUDUN (application in every second year)	mitc-carrot	CHAT-CARROTS	CHAT-IRR-F	0.392449
HAMBURG	mitc-carrot	HAMB-CARROTS	No	8.973330
KREMSMUNSTER	mitc-carrot	KREM-CARROTS	No	2.435533
PORTO	mitc-carrot	PORT-CARROTS	No	0.217816
THIVA	mitc-carrot	THIV-CARROTS	THIV-IRR-F	0.058885
CHATEAUDUN	MITC_cabbage	CHAT-CABBAGE	CHAT-IRR-F	0.000221
HAMBURG	MITC_cabbage	HAMB-CABBAGE	No	0.023754
JOKIOINEN	MITC_cabbage 1 st	JOKI-CABBAGE	No	0.002737
KREMSMUNSTER	MITC_cabbage	KREM-CABBAGE	No	0.002558
PORTO	MITC_cabbage	PORT-CABBAGE	No	0.000072
SEVILLA	MITC_cabbage	SEVI-CABBAGE	SEVI-IRR-F	0.003623
THIVA	MITC_cabbage 1 st	THIV-CABBAGE	THIV-IRR-F	0.000000
CHATEAUDUN	MITC-toms	CHAT-TOMATOES	CHAT-IRR-F	0.002619
PIACENZA	MITC-toms	PIAC-TOMATOES	PIAC-IRR-F	0.883013
PORTO	MITC-toms	PORT-TOMATOES	No	0.000077
SEVILLA	MITC-toms	SEVI-TOMATOES	SEVI-IRR-F	0.000357
THIVA	MITC-toms	THIV-TOMATOES	THIV-IRR-F	0.000002

In all three sets of simulations with PRZM (using field DT₅₀ values), on carrots, corn salad and tomatoes the 80th percentile concentration was <0.1 µg/l.

In the simulations with PEARL (using laboratory DT₅₀ values) on carrots (229 kg MITC/ha), the simulated values were >0.1 µg/l, with the exception of Thiva (0.06 µg/l). The highest value obtained was 8.97 µg/l in the Hamburg scenario. For the simulations on corn salad (172 kg MITC/ha) and tomatoes (344 kg MITC/ha) values were <0.1 µg/l, with the exception of the Piacenza scenario where a value of 0.9 µg/l was simulated.

In practice, application of metam-sodium is unlikely to occur annually. Information indicated that application to carrots in every second year in France was much more likely and hence a simulation was also undertaken under these conditions. The PEC_{gw} was reduced significantly, from 1.22 µg/l with annual application to 0.39 µg/l with application in every second year.

The FOCUS groundwater models are generally accepted to be weak in their treatment of volatilisation processes, and this is likely to be a significant loss process for MITC.

Conclusions:

Simulations with MITC applied to carrots, corn salad and tomatoes at rate of 1 x 172 - 344 kg MITC/ha corresponding to 600 l/ha to 1200 l/ha of a Metam-sodium 510 g/l end use solution, were conducted with the PRZM 2.4.1 and PEARL 3.3.3 models and covered all relevant scenarios (Chateaudun, Hamburg, Jokioinen, Kremsmunster, Piacenza, Porto, Seville, Thiva).

Based on the very rapid degradation of Metam-sodium in soils, groundwater contamination with the parent compound can be excluded. The PEC_{gw} should only be calculated for MITC.

The FOCUS scenarios were appropriately chosen: representative crops are the field crops (no leaching for greenhouse crops; localized use, exceptional use in grapevine), application rate, one application/year.

The K_{oc}, Freundlich exponent were appropriately chosen.

The PRZM model (field DT_{50}) predicted that the concentrations of MITC at 1 m depth are below the 0.1 µg/l regulatory threshold. PRZM model is appropriate to calculate PEC based on field DT_{50} .

As RMS we have reservation on the choice of the DT_{50} MITC field used in the PRZM calculations. The application in the field was made by overhead-sprinkler system. The formulation was injected in the sprinkler irrigation pipeline, while water was applied to the plot. Incorporation of the a.s. in soil was achieved by post-application spray irrigation in some experiments. As the active substance has not been incorporated deeply into the soil by rotavation in the field experiments, it can be expected that the volatilisation at soil surface is very important. Consequently, the dissipation rate of MITC is overestimated (Field dissipation of MITC in the range 0.54-3 days with a mean of 1.57 days). The notifier indicated “that application by overhead sprinkler system is not supported in Europe. However, the common factor between all different application methods is the incorporation of metam in the top layer of the soil. The mean lab DT_{50} for MITC was 2.15 days. In view of the applicant the mean field DT_{50} of 1.57 days is realistic also in the case of the European application techniques since it is reflecting degradation in the soil as well as volatilisation to the air and is therefore expected to be lower than the lab DT_{50} . Based on this field DT_{50} the use of the PRZM model would be justified. “.

The PEARL model (laboratory DT_{50}) predicted concentrations generally <0.1 µg/l, in corn salad and tomatoes, but > 0.1 µg/l (0.06 to 8.97 µg/l) following autumn application to carrots. However, agricultural practice exists to cover treated soil for these crops with a plastic sheet to increase efficacy. In these situations there would be no water percolating through the soil and hence no chance of groundwater contamination for these uses either.

As a general conclusion, it is not expected that MITC would exceed the 0.1 µg/L threshold under practical situations.

- The indoor uses pose no concern for groundwater contamination (e.g. cucumber, eggplant/aubergine, pepper and tomato) whilst the outdoor uses on strawberries occur under a plastic film, thus also preventing percolation of water through the soil during the duration of effective compound exposure.
- The uses on grapes are as a spot treatment and are very localised. Hence the overall application rate (for instance over an entire hectare) will be much lower than the application rate stated by m².
- the PEARL and PRZM model calculations indicate that the PEC gw calculations for the outdoor uses up to the broadcast application rate of 612 kg a.s./ha are below 0.1 µg MITC/L for most scenarios. The PEC calculations have been performed under worst case situation since the volatilization is not well simulated by the FOCUS modeling softwares. The soil is cultivated after a few days, before plantation, in order to enhance MITC volatilization.
- The specific mode of use of this a.s. also mitigates the possible groundwater contamination (in practice, application of metam-sodium is unlikely to occur annually)

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.6, the applicant had to provide further clarification on the intended greenhouse use in order to define adequate particular conditions of use to justify the absence of exposure assessment for potential contamination of ground water. The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

A description of the technique of application in greenhouses through drip fumigation is provided here below. The product is applied via the micro-irrigation pipelines under a plastic film. The volume of product in water is fine tuned to the zone to be disinfected, afterward the treated soil surface remains undisturbed for at least 14 days until planting holes are made in the plastic.

During the fumigation with metam/MITC in greenhouses the treated surface will not be exposed to rainfall. The quantity of irrigation water is limited to the water needed to dilute the product and bring it to the required soil depth (rooting zone of the crop). Therefore no leaching to the groundwater is to be expected. “

Conclusions of the RMS:

The “description of the technique of application in greenhouses through drip fumigation” that has been submitted by the notifier is confirming that the indoor uses do not pose a concern for surface water contamination. (e.g. cucumber,

eggplant/aubergine, pepper and tomato) whilst the outdoor uses on strawberries occur under a plastic film, thus also preventing connectivity between soil and run-off water. Therefore no MITC contamination of surface bodies via run-off is possible for this use.

Conclusions of the peer review: Point of clarification 4.6 addressed

Application of Metam-sodium 510 g/l by micro-irrigation (drip-fumigation)



Introduction

METAM-SODIUM 510 G/L is a non halogenated soil fumigant which is applied before the installation of the crop.

Application by drip-fumigation is done in greenhouse, tunnel or field which are empty (free of crops, people and animals).

Drip fumigation allows saving water, while reducing severely the exposure of the environment, the operator and bystanders to the chemical. The product is directly applied under the plastic film used for the crop through the micro-irrigation pipes.

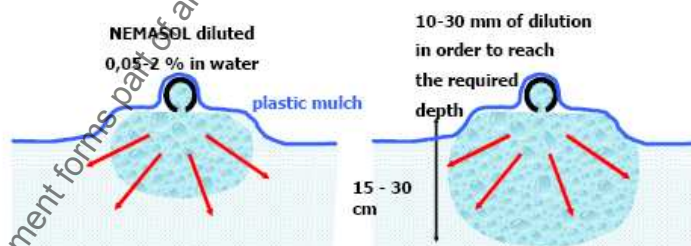
Application of Metam-sodium 510 g/l by drip-fumigation requires a very limited amount of human intervention, unlike conventional techniques of spraying.

The water solubility of Metam-sodium 510 g/l enables to "drip fumigate", consisting in applying the product diluted in water through the drip irrigation lines. As soon as it enters into contact with the soil, Metam-sodium 510 g/l is converted into methyl-isothiocyanate (MITC) which is the active ingredient. MITC moves upwards within the soil and partly laterally; zones located under or apart the area that received the product will not be disinfected.

Application through the micro-irrigation line

- 1) remove any people, animals and plant from the green-house, tunnel or field to be disinfected.
- 2) install the drip-irrigation network according to the agricultural practice
- 3) cover the irrigation network with the plastic much adapted to the crop.
- 4) install the pump and secure the water supply with anti return and shut-off valves as listed in § "Equipment and soil preparation"
- 5) before starting check the connections and repair the system if leakage occurs.
- 6) when everything is OK, open the drum of Metam-sodium 510 g/l and dip the sucking pipe of the pump into it for starting the injection. Inject a dilution of 0.05% to 2.0% of Metam-sodium 510 g/l in the drip irrigation lines in order to deliver the requested quantity of product in the proper amount of water (depending of the soil structure). It takes 1 to 2 hours to apply 10 to 20 mm of dilution
- 7) after 14 days when all product is degraded, cut the holes in the mulch for planting the crop

These operations from 1 to 7 are documented by a sequence of photographs on page 3.



Equipment and soil preparation

The preparation of the ground aims to obtain a fine structure that allows the fumigant diffusing properly in all parts of the soil. Soil must be freed of clods and crops residues. Pests and seeds of weeds to be destroyed must be in a living or pre-living stage; this in order to be sensitive to the fumigant.

Application occurs in a slightly humid soil (50 to 60% of the field capacity, as would requested for sowing or planting) when soil temperature at ten centimetres depth is not less than 10°C.

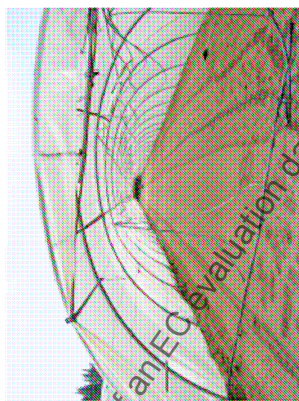
Hereafter the main characteristics of the network of drip-tubes:



Drip-fumigation with METAM-SODIUM 510 G/L on progress

- Tubes must be fitted with auto-regulated emitters, above all in case of slope delivering between 1.5 and 2.5 litres / hour at 1.5-2.5 bars pressure, placed each 0.20-0.30 cm on the line. When disinfection occurs in sandy soil, it is advisable to use two tubes laid in parallel 0.30-0.40 cm apart, in order to increase the lateral distribution of the fumigant.
- Inject METAM-SODIUM 510 G/L in the network of drip-tubes by mean of a dosing pump, mounted with a anti-return valve, for achieving a dilution of 0.05-2% (ratio hangs on the total volume of water needed for the application).

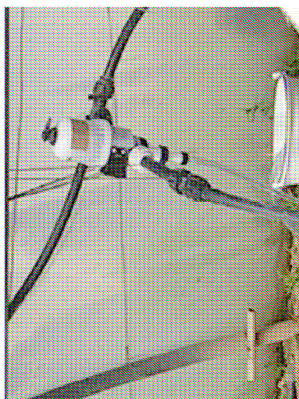
Application of Metam-sodium 510 g/l by drip-irrigation: pictures of the various stages



Installation of micro-irrigation network



Covering of irrigation pipes with plastic film



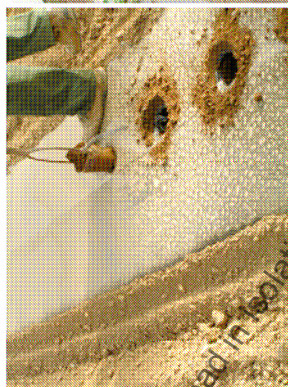
Installation of pump and security fittings



Opening of the drum



Connection of the pump to the drum (tube)



After 2 weeks, penetration of the plastic film



Planting

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

Added in August 2010

"A new data gap has been identified by EFSA after the meeting of experts to address the mobility of impurity DMTU in soil, in order to obtain adequate input parameters for ground water modelling."

Table B.8.6.1-7: Parameters for N,N'-dimethylthiourea (DMTU):

Parameter	Result	Reference
Water solubility	≥ 581.98 g/L	Habeck, 2009a *
n-octanol/water partition coefficient	Log Pow = -0.23	Habeck, 2009c *
Vapour pressure	912.00 Pa at 25°C 832.95 Pa at 20°C	Habeck, 2009b *
Henry constant	0.163 Pa m³/mol at 25°C 0.149 Pa m³/mol at 20°C	Habeck, 2009b *
DT ₅₀ in soil	0.121 d	Völkel, 2010; McMillan 2010**
K _{oc}	9	Völkel, 2009**

* : see chapter B.2

** : See chapter B.8 (above)

Added in August 2010

"A new data gap has been identified by EFSA after the meeting of experts, to address the potential ground water contamination of impurity DMTU."

PEC_{gw} calculations for DMTU, based on the above parameters, are presented in the following report :

Predicted Environmental Concentrations of N,N'-dimethylthiourea (DMTU) in Groundwater in the European Union using the FOCUS groundwater scenarios. (Franeý-Gardiner M., Terry A., 2010)

Modelling assumptions – input parameters:

The models used to calculate PEC_{GW} were FOCUS-PEARL 3.3.3 and FOCUS-PELMO 3.3.2. Simulations were conducted for applications to carrots (FOCUS-carrots), corn salad (FOCUS-cabbage) and tomatoes (FOCUS-tomatoes) at an extreme worst case "application rate" of 7 kg/ha.

Min/max. application rate is 153 – 1020 kg a.s./ha according to GAP table of intended uses. This corresponds to 299 – 1992 L metam-sodium TK/ha (cf. 510 g/L metam-sodium contained in TK). With DMTU at the max. content specified by Taminco (i.e. 3.5 g DMTU/L metam-sodium TK) this corresponds to 1 – 7 kg DMTU/ha. Note that the same result can be obtained by performing the following calculation: Min/max. application rate is 153 – 1020 kg a.s./ha. With a DMTU max. content of 7 g / kg metam-sodium (on dry weight basis), this corresponds to 1 – 7 kg DMTU/ha. An application rate of 612 kg a.i./ha gives approximately 4 kg DMTU/ha.

Table B.8.6.1-8: Summary of chemical input parameters used in the modelling of DMTU

Property	Value
Molar Mass (g/mol)	104.18
Vapour Pressure (Pa)	832.95 (20°C)
Solubility (mg/L)	581980 (20°C)
K _{OM} (L/kg)	5
K _{OC} (L/kg)	9
1/n	0.76
DT ₅₀ in soil (days)	0.121
Plant uptake	0
Q ₁₀ (PELMO)	2.58
Activation energy kJ/mol (PEARL)	65.4

Application Scenarios:

The FOCUS assessments were based on realistic conditions of use of Metam-sodium using the proposed GAP for Annex I listing in the EU re-registration process (Terry *et al.*, 2010). Representative simulations were carried out for DMTU on carrots, corn salad and tomatoes. The simulated applications are summarised in table below. Simulations were conducted as applications to FOCUS-carrots, FOCUS-cabbage and FOCUS-tomatoes for all available scenarios in both Northern and Southern Europe.

Table B.8.6.1-9: Simulated application of DMTU for FOCUS groundwater modelling

Crop	Application Rate (kg/ha)	Application Method	Soil incorporation depth (cm)
Carrots (FOCUS-CARROTS)	1 × 7	Incorporation	25
Corn salad (FOCUS-CABBAGE)	1 × 7	Incorporation	15
Tomatoes (FOCUS-TOMATOES)	1 × 7	Injection	15

Application dates:

The emergence, harvest and application dates used for the simulations are shown in table below. Applications were simulated on a yearly basis.

Table B.8.6.1-10: Emergence/transplanting, harvest and application dates used in the simulations

Location	Emergence/Transplanting	Harvest	Application date
Carrots			
Châteaudun	10-Mar	31-May	01-Oct
	10-Jul	20-Sep	
Hamburg	10-Mar	31-May	01-Oct
	10-Jul	20-Sep	
Kremsmünster	10-Mar	31-May	01-Oct
	10-Jul	20-Sep	
Porto	28-Feb	31-May	16-Oct
	22-Jul	15-Oct	
Thiva	05-Mar	22-May	01-Oct
	15-Jun	10-Sep	
Corn salad			
Châteaudun	20-Apr	15-Jul	21-Jul
	31-Jul	15-Oct	
Hamburg	20-Apr	15-Jul	21-Jul
	31-Jul	15-Oct	
Jokioinen	20-May	20-Sep	10-May
Kremsmünster	20-Apr	15-Jul	21-Jul
	31-Jul	15-Oct	
Porto	28-Feb	01-Jul	21-Jul
	31-Jul	15-Nov	
Sevilla	01-Mar	01-Jun	05-Jun
	15-Jun	15-Sep	
Thiva	15-Aug	30-Nov	05-Aug
Tomatoes			

Châteaudun	10-May	25-Aug	10-Mar
Piacenza	10-May	25-Aug	10-Mar
Porto	15-Mar	31-Aug	10-Mar
Sevilla	15-Apr	01-Jul	10-Mar
Thiva	10-Apr	10-Sep	10-Mar

Findings :

The 80th percentile annual average worst-case predicted environmental concentrations in groundwater (PECGW) for each scenario, calculated by the FOCUS-PELMO 3.3.2 and FOCUS-PEARL 3.3.3 models, at 1 m soil depth, for DMTU, are shown in the following tables.

Table B.8.6.1-11: Calculated 80th percentile annual average worst-case predicted environmental concentration at 1 m soil depth (µg/L) using the FOCUS-PELMO 3.3.2 groundwater scenarios- DMTU

Scenario	80 th Percentile Annual Average PEC _{GW} (µg/L)		
	FOCUS-carrots	FOCUS-cabbage	FOCUS-tomatoes
Châteaudun	0.000	0.000	0.000
Hamburg	0.000	0.000	N/A
Jokioinen	N/A	0.000	N/A
Kremsmünster	0.000	0.000	N/A
Okehampton	N/A	N/A	N/A
Piacenza	N/A	N/A	0.000
Porto	0.000	0.000	0.000
Sevilla	N/A	0.000	0.000
Thiva	0.000	0.000	0.000

N/A: Scenario not applicable to FOCUS crop

Table B.8.6.1-12: Calculated 80th percentile annual average worst-case predicted environmental concentration at 1 m soil depth (µg/L) using the FOCUS-PEARL 3.3.3 groundwater scenarios - DMTU

Scenario	80 th Percentile Annual Average PEC _{GW} (µg/L)		
	FOCUS-carrots	FOCUS-cabbage	FOCUS-tomatoes
Châteaudun	0.000	0.000	0.000
Hamburg	0.000	0.000	N/A
Jokioinen	0.000	0.000	N/A
Kremsmünster	0.000	0.000	N/A
Okehampton	N/A	N/A	N/A
Piacenza	N/A	N/A	0.000
Porto	0.000	0.000	0.000
Sevilla	N/A	0.000	0.000
Thiva	0.000	0.000	0.000

N/A: Scenario not applicable to FOCUS crop

Conclusions

The modelling undertaken in this exercise was based on the presence of DMTU at a 'worst case' application rate of 7 kg/ha. The results of the simulations indicate that predicted environmental concentrations of DMTU at 1 m soil depth would not exceed 0.1 µg/L for all crops and scenario simulations.

Added in August 2010

"A data gap was identified by the meeting of experts to recalculate MITC PECGW with adequate input parameters (when available) using FOCUS GW or higher tier approach if appropriate."

Predicted Environmental Concentrations of Methyl Isothiocyanate (MITC) in Groundwater in the European Union using the FOCUS groundwater scenarios. (Terry A., McMillan C. & Franey-Gardiner M. (2010))

Modelling assumptions – input parameters:

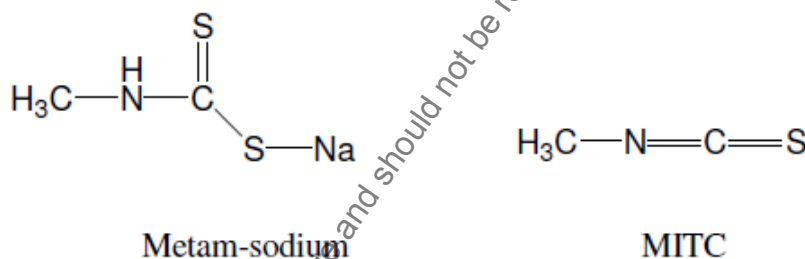
Introduction

Metam-sodium (sodium N-methyldithiocarbamate) is a soil fumigant intended for use in a variety of crops. Metam-sodium degrades very fast in soil ($DT_{90} < 1$ day) and the active substance is Methyl Isothiocyanate (MITC). As such, the risk to groundwater of MITC, only, has been investigated. The purpose of this study was to determine the leaching potential of MITC to groundwater, for 'open field' crops. The assessment was conducted using the FOCUS-PELMO 3.3.2 and FOCUS-PEARL 3.3.3 groundwater scenarios.

It should be noted that soil fumigants/steilants are a very specific group of pesticides, whose use and handling make them different to other compounds when considering environmental exposure pathways. There are a number of uses for metam-sodium where the crops are grown under protected conditions (e.g. cucumber, pepper, aubergine and tomatoes in glasshouse/polytunnels) where the soil is protected from precipitation and downward movement of water is unlikely. For these uses the risk to groundwater is low. Likewise, where the crop is covered with plastic film (e.g. strawberries) the risk to groundwater will be inherently low because downward movement of water is prevented.

Substance Properties

The structures of metam-sodium and MITC are shown in Figure below.



Chemical structures of metam-sodium and MITC (Jarvis, 2007)

The chemical input parameters used in the modelling were, with few exceptions, taken from the Draft Assessment Report (DAR) for MITC (2007) and the FOCUS kinetics report (McMillan, 2009). Where data were not available FOCUS default values (FOCUS, 2000) were employed. The chemical input parameters are summarised in table below.

Table B.8.6.1-13: Summary of chemical input parameters used in the modelling

Parameter	MITC	Reference source
Molar Mass (g/mol)	73.12	
Vapour Pressure (Pa)	1739 (20°C)	DAR (2007)
Solubility (mg/L)	8940 (20°C)	DAR (2007)
K_{OM} (L/kg)	7.83	$K_{OC}/1.724$
K_{OC} (L/kg)	13.5	Herrchen M (2009)
$1/n$	0.83	Herrchen M (2009)
DT50 in soil (days)	2.10	McMillan (2009)
Plant uptake	0	DAR (2007)
Q_{10}	2.58 (PELMO) 65.4 KJ/mol (PEARL)	Recommended values (EFSA, 2007)

Application Scenarios

The FOCUS assessments were based on realistic conditions of use (see table below; adapted from Jarvis, 2007). Representative simulations were carried out for MITC on carrots, corn salad, tomatoes and potatoes. The simulated applications are summarised in table below. Simulations were conducted as applications to FOCUS-carrots, FOCUS-cabbage, FOCUS-tomatoes and FOCUS-potatoes for all available scenarios in both Northern and Southern Europe.

Table B.8.6.1-14: The GAP supported for metam-sodium Annex I listing in the EU re-registration process (adapted from Jarvis, 2007)

Crop and/or situation	F, G or I ^a	Application			Application rate per treatment (Metam-sodium)	Equivalent MITC application rate ^b
		Method kind	Growth stage and season	Number Min max	Kg a.s/ha Min max	Kg a.s/ha Min max
Carrot	F	Soil injection + incorporation at 25 cm by rotavation	April-June	1	408	230.94
Carrot	F	Soil injection + incorporation at 25 cm by rotavation	Oct-Dec	1	408	230.94
Corn salad (= lambs lettuce)	F	Soil injection + incorporation at 15 cm by rotavation	April-Aug	1	306	173.21
Corn salad (= lambs lettuce)	F	Spray onto the soil + incorporation at 15 cm by irrigation	April-Aug	1	306	173.21
Cucumber	G	Drip-irrigation on the planting row	June-Aug	1	459	259.81
Eggplant/aubergine	G	Drip-irrigation on the planting row	June-Aug	1	612	346.41
Pepper	G	Drip-irrigation on the planting row	June-Aug	1	612	346.41
Potato	F	Soil injection + incorporation at 25 cm by rotavation	Sept-Nov	1	153	86.60
Strawberry	F	Drip irrigation under a plastic film on the planting row	Jul-Oct	1	612	346.41
Tomato	G	Drip-irrigation on the planting row	Feb-Aug	1	612	346.41
Tomato	F	Soil injection at 5 cm + coverage by 10 cm of soil	March	1	612	346.41
Grape	F	Soil injection at 40 cm at the site of the de-rooted vine (0.2 l/m ²)	Autumn, before replanting	1	1020	577.35

^a Outdoor or field use (F), glasshouse application (G) or indoor application (I)

^b Molecular weight conversion to MITC using molar masses of 128.18 g/mol for metam-sodium and 73.12 g/mol for MITC

Table B.8.6.1-15: Simulated application of MITC for FOCUS groundwater modelling

Crop	Application Rate (kg/ha)	Application Method	Soil incorporation depth (cm)
Carrots (FOCUS-CARROTS)	1 × 230.94	Incorporation	25
Corn salad (FOCUS-CABBAGE)	1 × 173.21	Incorporation	15
Tomatoes (FOCUS-TOMATOES)	1 × 346.41	Injection	15
Potatoes (FOCUS-POTATOES)	1 × 86.60	Incorporation	25

Application dates

The emergence, harvest and application dates used for the simulations are shown in table below. Applications to carrots, corn salad (FOCUS-cabbage) and tomatoes were simulated on a yearly basis. For carrots, an additional simulation was also made for the Thiva scenario of 1 application every 2 years. For potatoes, applications were simulated every three years.

Table B.8.6.1-16: Emergence/transplanting, harvest and application dates used in the simulations

Location	Emergence/Transplanting	Harvest	Application date
Carrots			
Châteaudun	10-Mar	31-May	01-Oct
	10-Jul	20-Sep	01-Jun
Hamburg	10-Mar	31-May	01-Oct
	10-Jul	20-Sep	01-Jun
Jokioinen	01-Jun	05-Oct	01-May**
Kremsmünster	10-Mar	31-May	01-Oct
	10-Jul	20-Sep	01-Jun
Porto	28-Feb	31-May	16-Oct
	22-Jul	15-Oct	01-Jun
Thiva	15-Mar	22-May	01-Oct
	15-Jun	10-Sep	23-May
Corn salad			
Châteaudun	20-Apr	15-Jul	21-Jul
	31-Jul	15-Oct	
Hamburg	20-Apr	15-Jul	21-Jul
	31-Jul	15-Oct	
Jokioinen	20-May	20-Sep	10-May
Kremsmünster	20-Apr	15-Jul	21-Jul
	31-Jul	15-Oct	
Porto	28-Feb	01-Jul	21-Jul
	31-Jul	15-Nov	
Sevilla	01-Mar	01-Jun	05-Jun
	15-Jun	15-Sep	
Thiva	15-Aug	30-Nov	05-Aug
Tomatoes			
Châteaudun	10-May	25-Aug	10-Mar (20 Apr*)
Piacenza	10-May	25-Aug	10-Mar (20 Apr*)

Porto	15-Mar	31-Aug	10-Mar
Sevilla	15-Apr	01-Jul	10-Mar
Thiva	10-Apr	10-Sep	10-Mar
Potatoes			
Châteaudun	30 Apr	01-Sep	02-Sep
Hamburg	10 May	15-Sep	16-Sep
Jokioinen	05-Jun	25-Sep	26-Sep
Kremsmünster	10-May	15-Sep	16-Sep
Okehampton	30-Apr	01-Sep	02-Sep
Piacenza	20-Apr	10-Sep	11-Sep
Porto	15-Mar	15-Jun	01-Sep
Sevilla	31-Jan	31-May	01-Sep
Thiva	01-Mar	30-Jul	01-Sep

* Additional simulations run for alternate date; **for efficacy considerations, autumn application not possible in Jokioinen (see Jarvis, 2007)

Volatilisation

Soil volatilisation is considered to be a significant loss mechanism for MITC (Jarvis, 2007). For both FOCUS-PELMO 3.3.2 and FOCUS-PEARL 3.3.3 water solubility and vapour pressure data were used by the models to calculate the total amount of pesticide volatilised from the soil as g/ha and kg/ha respectively.

Losses *via* volatilisation as a percentage of total applied pesticide was in general calculated to be higher in PELMO than PEARL with values ranging from 9.42% to 66.4% in PELMO and 0.87% to 47.09% in PEARL. It is known that these standard models do not simulate the movement of gases well and that the predicted levels of volatilisation obtained are likely to be conservative (Terry, 2010 and Van den Berg *et al.*). Therefore, even the PELMO volatilisation rates should be considered as conservative. Therefore, the PEC_{GW} values should be considered as being very conservative.

Findings :

The 80th percentile annual average worst-case predicted environmental concentrations in groundwater (PECGW) for each scenario, calculated by the FOCUS-PELMO 3.3.2 and FOCUS-PEARL 3.3.3 models, at 1 m soil depth, for MITC, are shown in the following tables. Values in bold type indicate PECGW less than 0.1 µg/L.

Table B.8.6.1-17: Calculated 80th percentile annual average worst-case predicted environmental concentration at 1 m soil depth (µg/L) using the FOCUS-PELMO 3.3.2 groundwater scenarios - MITC

Scenario	80 th Percentile Annual Average PEC _{GW} (µg/L)					
	FOCUS-carrots		FOCUS-cabbage	FOCUS-tomatoes		FOCUS-potatoes
	Winter	Spring		10 March	20 April	
Châteaudun	1.398	0.000	0.000	0.000	0.000	0.001
Hamburg	118.665	0.104	0.334	N/A	N/A	10.308
Jokioinen	N/A	0.000	0.000	N/A	N/A	197.734
Kremsmünster	20.888	0.000	0.000	N/A	N/A	0.540
Okehampton	N/A	N/A	N/A	N/A	N/A	1.208
Piacenza	N/A	N/A	N/A	2.040	0.039	0.645
Porto	0.367	0.000	0.000	0.000	*	0.000
Sevilla	N/A	N/A	0.000	0.000	*	0.000
Thiva	0.160	0.000	0.000	0.000	*	0.000
Thiva (1 year in 2)	0.050	*	*	*	*	*

N/A: Scenario not applicable to FOCUS crop

*Scenario not required

Table B.8.6.1-18: Calculated 80th percentile annual average worst-case predicted environmental concentration at 1 m soil depth (µg/L) using the FOCUS-PEARL 3.3.3 groundwater scenarios - MITC

Scenario	80 th Percentile Annual Average PEC _{GW} (µg/L)					
	FOCUS-carrots		FOCUS-cabbage	FOCUS-tomatoes		FOCUS-potatoes
	Winter	Spring		10 March	20 April	
Châteaudun	11.961	1.552	0.002	0.376	0.018	0.066
Hamburg	254.373	2.954	0.276	N/A	N/A	6.456
Jokioinen	N/A	0.378	0.003	N/A	N/A	49.264
Kremsmünster	43.011	0.301	0.061	N/A	N/A	0.827
Okehampton	N/A	N/A	N/A	N/A	N/A	1.947
Piacenza	N/A	N/A	N/A	48.561	1.262	0.591
Porto	7.038	0.000	0.000	0.001	*	0.000
Sevilla	N/A	N/A	0.013	0.002	*	0.000
Thiva	0.111	0.023	0.000	0.000	*	0.000
Thiva (1 year in 2)	0.060	*	*	*	*	*

N/A: Scenario not applicable to FOCUS crop

*Scenario not required

Conclusions:

A number of uses of metam-sodium occur under circumstances where downward movement of water is very unlikely. The applications to cucumber, pepper, aubergine and tomatoes in protected situations (glasshouse/polytunnel) are examples of such circumstances. In addition, application to strawberries outdoors involves covering the soil location with plastic film, which also prevents downward movement of water. The modelling undertaken in this exercise was based on the use of MITC as a soil fumigant.

The results of the simulations indicate that predicted environmental concentrations of MITC at 1 m soil depth could exceed 0.1 µg/L for some crop/scenario simulations. PEC_{GW} was simulated to be >0.1 µg/L for most winter carrot scenarios for both PELMO and PEARL. PEC_{GW} for carrots was lower for spring/summer applications. For FOCUS-cabbage, tomatoes and potatoes, PEC_{GW} for Porto, Sevilla and Thiva scenarios were all <0.1 µg/L. Simulations with FOCUS-cabbage were most likely to produce PEC_{GW} <0.1 µg/L. Consequently, in addition to glasshouse/polytunnel uses, safe use in 'open field' situations has also been demonstrated.

B.8.6.2 Predicted environmental concentrations in surface water (PEC_{sw}) (Annex IIIA 9.2.3)

Predicted Environmental Concentrations of Metam-sodium (as MITC) in Surface water for Selected Uses in the EU using the FOCUS Surface Water Scenarios (Jarvis T., 2007b)

Models and assumptions:

Metam-sodium is a soil fumigant which acts by decomposition to methyl isothiocyanate (MITC). Since Metam-sodium itself is subject to rapid degradation (laboratory DT₅₀'s ranged from 4 - 23 minutes) and is not expected to reach surface water, MITC is considered to be the active molecule and therefore all assessments of possible run-off/drainage were undertaken with this compound.

A number of safe uses (with respect to surface water) exist for metam-sodium by virtue of application to cucumber, pepper, aubergine and tomatoes in protected situations (glasshouse/polytunnel). In addition, application to strawberries

outdoors involves covering the soil with a plastic film by label requirement, hence preventing connectivity between soil and run-off water. Therefore no MITC contamination of surface water bodies via run-off is possible for this use.

Simulations with Metam-sodium applied to carrots, corn salad and tomatoes at rate of 1 x 172 - 344 kg MITC/ha corresponding to 600 l/ha to 1200 l/ha of a Metam-sodium 510 g/l end solution, were conducted with PRZM, MACRO and TOXSWA 2.2.1.F1 models for all relevant scenarios.

Table B.8.6.2-1: Crops and application parameters simulated

Application parameter	Carrot (root vegetables)	Corn salad (leafy vegetables)	Tomatoes (fruiting vegetables)
Application rate (kg MITC /ha) (0% crop interception)	229	172	344
Number of applications/year	1	1	1
Application date	30 Sept to 31 Oct	1 Feb to 3 Mar for R2, R3, R4 (all 1 st applications). 1 April to 1 May for D4 as well as D3 and R1 (both first applications). 1 June to 1 July for D6 as well as D3, R1, R2, R3, R4 (all second applications)	1 March to 31 March
Incorporation depth (cm)	25 cm for PRZM (CAM4), default for MACRO	15 cm for PRZM (CAM4), default for MACRO	15 cm for PRZM (CAM5), default for MACRO

One original set of simulations was undertaken with field soil dissipation data and a subsequent set of simulations were undertaken with laboratory soil degradation data and comprising of slightly different assumptions. MITC compound properties were used as follows:

Table B.8.6.2-2: MITC compound properties

MITC Properties	Field soil Values	Laboratory soil values
Molecular Mass (g mol^{-1})	73.11	73.11
Vapour Pressure (Pa)	0	1739
Aqueous Solubility (mg/L)	8940	8940
Soil Adsorption Coefficient (K_{om}) (ml/g)	20.9 ($K_{\text{oc}}=36$)	20.9 ($K_{\text{oc}}=36$)
Freundlich Exponent	1*	1*
DT_{50} (days)	1.57 (field) no temperature/moisture correction***	2.15 at pH 2 and 20°C
Plant Uptake Coefficient	0.5	0
Dissipation rate in sediment	0.37 day at 25°C**	0.37 day at 25°C****
Dissipation rate in water	0.37 day at 25°C**	0.37 day at 25°C****

* Value used due to limitations on Freundlich isotherm in TOXSWA at very low concentrations.

** As these are dissipation values including volatilisation, it is necessary to disable the routines in TOXSWA dealing directly with volatilisation. Also disable temperature dependence of degradation by setting activation energy to 0

*** $Q_{10}=1$ and moisture exponent =0 in PRZM; Exponent for temperature response =0, Exponent for moisture response =0 in MACRO

**** Although these are dissipation values including volatilisation, it was not possible to disable the routines in TOXSWA dealing directly with volatilisation since the SWASH shell required the vapour pressure to be input for soil. However, the simulated volatilisation was checked and found to be not significant. The temperature dependence of degradation could not longer be set to 0 due to a change in the model versions, but was effectively disabled by setting the activation energy to 100 J/mol (the smallest allowable value)

For Step 4 calculations, the the run-off was reduced by 90% and 97.5%, respectively for buffer zones of 10 and 20 m

Findings:

Summaries of $PEC_{sw-initial}$, TWAECsw2 day, TWAECsw4 day, TWAECsw21 day and TWAECsw28 day for MITC in all waterbody scenarios at FOCUS Step 3 and FOCUS Step 4, using field soil dissipation data and laboratory soil degradation data are shown below, for carrots, corn salad and tomatoes respectively.

Table B.8.6.2-3: FOCUS Step 3 calculations, using field soil dissipation data - Carrot

Scenario Location	Date of application	Date of $PEC_{sw-initial}$	Initial PEC_{sw} (µg/l)	TWAECsw2 (µg/l)	TWAECsw4 (µg/l)	TWAECsw21 (µg/l)	TWAECsw28 (µg/l)
D3-ditch	5 Nov 1992	2 Jan 1992*	0.000	0.000	0.000	0.000	0.000
D6-ditch	6 Nov 1986	2 Jan 1986*	0.024	0.024	0.024	0.020	0.020
R1-pond	14 Nov 1978	25 Nov 1978	0.579	0.205	0.106	0.020	0.015
R1-stream	14 Nov 1978	25 Nov 1978	9.136	1.757	0.879	0.167	0.126
R2-stream (1st crop)	8 Nov 1977	19 Nov 1977	4.542	1.001	0.647	0.124	0.093
R3-stream	15 Nov 1980	26 Nov 1980	15.935	5.315	2.754	0.525	0.393
R4-stream	5 Nov 1979	14 Nov 1979	36.607	6.165	3.083	0.587	0.440

* This represents the output to the waterbody from application to the soil in a previous year

Table B.8.6.2-4: FOCUS Step 3 calculations, using field soil dissipation data - Corn salad

Scenario Location	Date of application	Date of $PEC_{sw-initial}$	Initial PEC_{sw} (µg/l)	TWAECsw2 (µg/l)	TWAECsw4 (µg/l)	TWAECsw21 (µg/l)	TWAECsw28 (µg/l)
D3-ditch (1st crop)	4 Apr 1992	2 Jan 1992*	0.000	0.000	0.000	0.000	0.000
D3-ditch (2 nd crop)	14 June 1992	2 Jan 1992*	0.000	0.000	0.000	0.000	0.000
D4-stream	18 Apr 1985	27 Jan 1985	0.000	0.000	0.000	0.000	0.000
D4-pond	18 Apr 1985	3 Feb 1985	0.000	0.000	0.000	0.000	0.000
D6-ditch	1 June 1986	16 Aug 1986	0.000	0.000	0.000	0.000	0.000
R1-pond (1st crop)	26 Apr 1984	7 May 1984	0.003	0.001	0.001	0.000	0.000
R1-pond (2nd crop)	1 June 1978	11 June 1978	1.100	0.497	0.261	0.051	0.038
R1-stream (1st crop)	26 Apr 1984	7 May 1984	1.358	0.262	0.131	0.025	0.019
R1-stream (2 nd crop)	1 June 1978	11 June 1978	8.213	2.878	1.439	0.281	0.211
R2-stream (2 nd crop)**	4 June 1989	10 June 1989	73.075	16.16	8.08	1.614	1.211
R3-stream (2 nd crop)**	2 June 1975	9 June 1975	37.283	16.90	8.45	1.610	1.207
R4-stream (2 nd crop)	1 June 1985	7 June 1985	95.601	33.372	16.686	3.294	2.471

* This represents the output to the waterbody from application to the soil in a previous year

** applications of metam-sodium to corn salad occur in April to August. Therefore those simulations of PEC_{sw} following application to the first leafy vegetable crop are considered not to be relevant for the GAP supported and are therefore not included in the table above.

Table B.8.6.2-5: FOCUS Step 3 calculations, using field soil dissipation data -Tomatoes

Scenario Location	Date of application	Date of PEC _{sw-initial}	Initial PEC _{sw} (µg/l)	TWAECSw2 (µg/l)	TWAECSw4 (µg/l)	TWAECSw21 (µg/l)	TWAECSw28 (µg/l)
D6-ditch	5 Mar 1986	2 Jan 1986*	0.022	0.022	0.022	0.019	0.018
R2-stream	1 Mar 1977	11 Mar 1977	1.261	0.463	0.235	0.045	0.034
R3-stream	1 Mar 1980	8 Mar 1980	17.242	4.473	2.237	0.433	0.325
R4-stream	5 Mar 1984	16 Mar 1984	3.286	0.517	0.258	0.049	0.037

* This represents the output to the waterbody from application to the soil in a previous year

Summaries of PEC_{sw-initial}, TWAECSw2 day, TWAECSw4 day, TWAECSw21 day and TWAECSw28 day for MITC in all waterbody scenarios at FOCUS Step 3 using laboratory soil degradation data are shown below, for carrots, corn salad and tomatoes respectively.

Table B.8.6.2-6: FOCUS Step 3 calculations, using laboratory soil degradation data - Carrot

Scenario Location	Date of application	Date of PEC _{sw-initial}	Initial PEC _{sw} (µg/l)	TWAECSw2 (µg/l)	TWAECSw4 (µg/l)	TWAECSw21 (µg/l)	TWAECSw28 (µg/l)
D3-ditch	29 Sept 1992	3 Jan 1992*	0.003	0.003	0.003	0.0025	0.0023
D6-ditch	6 Oct 1986	30 Oct 1986	1.016	0.384	0.262	0.070	0.053
R1-pond	6 Oct 1978	25 Oct 1978	0.503	0.139	0.070	0.015	0.011
R1-stream	6 Oct 1978	17 Oct 1978	29.807	4.690	2.345	0.776	0.582
R2-stream (1 st crop)	9 Oct 1989	22 Oct 1989	8.555	3.520	1.880	0.367	0.275
R3-stream	22 Oct 1975	2 Nov 1975	85.828	15.278	7.639	1.490	1.118
R4-stream	30 Sept 1985	4 Oct 1985	60.463	26.829	13.464	2.564	1.923

* This represents the output to the waterbody from application to the soil in a previous year

** Due to additional information the application date was changed and hence the results from laboratory and field data cannot be directly compared

Table B.8.6.2-7: FOCUS Step 3 calculations, using laboratory soil degradation data - Corn salad

Scenario Location	Date of application	Date of PEC _{sw-initial}	Initial PEC _{sw} (µg/l)	TWAECSw2 (µg/l)	TWAECSw4 (µg/l)	TWAECSw21 (µg/l)	TWAECSw28 (µg/l)
D3-ditch (1 st crop)	4 Apr 1992	1 Nov 1992	0.000	0.000	0.000	0.000	0.000
D3-ditch (2 nd crop)	14 June 1992	2 Jan 1992*	0.000	0.000	0.000	0.000	0.000
D4-stream	18 Apr 1985	9 Jun 1985	0.011	0.011	0.011	0.008	0.007
D4-pond	18 Apr 1985	9 Jun 1985	0.000	0.000	0.000	0.000	0.000
D6-ditch	1 June 1986	16 Aug 1986	0.000	0.000	0.000	0.000	0.000
R1-pond (1 st crop)	26 Apr 1984	20 May 1984	0.074	0.024	0.012	0.004	0.003
R1-pond (2 nd crop)	1 June 1978	11 June 1978	0.359	0.135	0.068	0.014	0.011
R1-stream (1 st crop)	26 Apr 1984	7 May 1984	18.974	3.645	1.823	0.412	0.309
R1-stream (2 nd crop)	1 June 1978	11 June 1978	3.488	1.205	0.602	0.133	0.100

R2-stream (2 nd crop)**	4 June 1989	10 June 1989	82.287	17.648	8.824	1.899	1.424
R3-stream (2 nd crop)**	2 June 1975	9 June 1975	18.231	7.857	3.929	0.749	0.562
R4-stream (2 nd crop)**	1 June 1985	7 June 1985	39.275	13.496	6.748	1.423	1.068

* This represents the output to the waterbody from application to the soil in a previous year

** applications of metam-sodium to corn salad occur in April to August. Therefore those simulations of PEC_{sw} following application to the first leafy vegetable crop (i.e. 1st crop) are considered not to be relevant for the GAP supported and are therefore not included in the table above.

Table B.8.6.2-8: FOCUS Step 3 calculations, using laboratory soil degradation data -Tomatoes:

Scenario Location	Date of application	Date of PEC _{sw} -initial	Initial PEC _{sw} (µg/l)	TWAECSw2 (µg/l)	TWAECSw4 (µg/l)	TWAECSw21 (µg/l)	TWAECSw28 (µg/l)
D6-ditch	5 Mar 1986	30 Mar 1986	0.260	0.235	0.182	0.095	0.091
R2-stream	1 Mar 1977	11 Mar 1977	20.625	7.823	4.042	0.787	0.590
R3-stream	1 Mar 1980	8 Mar 1980	142.749	35.549	17.775	3.791	2.843
R4-stream	5 Mar 1984	16 Mar 1984	106.791	15.896	7.948	1.549	1.162

The PEC_{sw} values provided at Step 3 indicate that exposure concentrations from run-off into streams may need to be reduced in order to mitigate potential risks to aquatic organisms. Therefore run-off was reduced by 90% and 97.5%, consistent with buffer zones of 10m and 20m (Step 4). The relevant PEC_{sw} values for simulations undertaken with both field and laboratory soil data are shown below.

Table B.8.6.2-9: FOCUS Step 4 calculations, using field soil dissipation data

Scenario Location	Field soil dissipation values; Step 4 - 10 m Buffer zone				
	Initial PEC _{sw} (µg/l)	TWAECS _{sw} 2 (µg/l)	TWAECS _{sw} 4 (µg/l)	TWAECS _{sw} 21 (µg/l)	TWAECS _{sw} 28 (µg/l)
Carrots**					
R1-pond	0.058	0.021	0.011	0.002	0.002
R1-stream	0.914	0.176	0.088	0.017	0.013
R2-stream (1st crop)	0.454	0.100	0.065	0.012	0.009
R3-stream	1.594	0.532	0.275	0.053	0.039
R4-stream	3.661	0.617	0.308	0.059	0.044
Corn salad					
R1-pond (1st crop)	0.000	0.000	0.000	0.000	0.000
R1-pond (2nd crop)	0.110	0.050	0.026	0.005	0.004
R1-stream (1st crop)	0.136	0.026	0.013	0.003	0.002
R1-stream (2 nd crop)	0.821	0.288	0.144	0.028	0.021
R2-stream (2 nd crop)	7.308	1.616	0.808	0.161	0.121
R3-stream (2 nd crop)	3.728	1.690	0.845	0.161	0.121
R4-stream (2 nd crop)	9.560	3.337	1.669	0.329	0.247
Tomatoes					
R2-stream	0.126	0.046	0.024	0.005	0.003
R3-stream	1.724	0.447	0.224	0.043	0.033
R4-stream	0.329	0.052	0.026	0.005	0.004

** Due to additional information the application date was changed and hence the results from laboratory and field data cannot be directly compared

Table B.8.6.2-10: FOCUS Step 4 calculations, using field soil dissipation data

Scenario Location	Field soil dissipation values; Step 4 - 20 m Buffer zone				
	Initial PEC _{sw} (µg/l)	TWAECS _{sw} 2 (µg/l)	TWAECS _{sw} 4 (µg/l)	TWAECS _{sw} 21 (µg/l)	TWAECS _{sw} 28 (µg/l)
Carrots**					
R1-pond	0.014	0.005	0.003	0.001	0.000
R1-stream	0.228	0.044	0.022	0.004	0.003
R2-stream (1st crop)	0.114	0.025	0.016	0.003	0.002
R3-stream	0.398	0.133	0.069	0.013	0.010
R4-stream	0.915	0.154	0.077	0.015	0.011
Corn salad					
R1-pond (1st crop)	0.000	0.000	0.000	0.000	0.000
R1-pond (2nd crop)	0.028	0.012	0.007	0.001	0.001
R1-stream (1st crop)	0.034	0.007	0.003	0.001	0.000
R1-stream (2 nd crop)	0.205	0.072	0.036	0.007	0.005
R2-stream (2 nd crop)	1.827	0.404	0.202	0.040	0.030
R3-stream (2 nd crop)	0.932	0.423	0.211	0.040	0.030
R4-stream (2 nd crop)	2.390	0.834	0.417	0.082	0.062
Tomatoes					
R2-stream	0.032	0.012	0.006	0.001	0.001
R3-stream	0.431	0.112	0.056	0.011	0.008
R4-stream	0.082	0.013	0.006	0.001	0.001

Due to additional information the application date was changed and hence the results from laboratory and field data cannot be directly compared

Table B.8.6.2-11: FOCUS Step 4 calculations, using laboratory soil degradation data

Scenario Location	Laboratory soil degradation values; Step 4 - 10 m Buffer zone				
	Initial PEC _{sw} (µg/l)	TWAECS _{sw} 2 (µg/l)	TWAECS _{sw} 4 (µg/l)	TWAECS _{sw} 21 (µg/l)	TWAECS _{sw} 28 (µg/l)
Carrots**					
R1-pond	0.050	0.014	0.007	0.002	0.001
R1-stream	2.981	0.469	0.235	0.078	0.058
R2-stream (1st crop)	0.856	0.352	0.188	0.037	0.028
R3-stream	8.583	1.528	0.764	0.149	0.112
R4-stream	6.046	2.683	1.346	0.256	0.192
Corn salad					
R1-pond (1st crop)	0.007	0.002	0.001	0.000	0.000
R1-pond (2nd crop)	0.036	0.014	0.007	0.001	0.001
R1-stream (1st crop)	1.897	0.365	0.182	0.041	0.031
R1-stream (2 nd crop)	0.349	0.121	0.060	0.013	0.010
R2-stream (2 nd crop)	8.229	1.765	0.882	0.190	0.142
R3-stream (2 nd crop)	1.823	0.786	0.393	0.075	0.056
R4-stream (2 nd crop)	3.928	1.350	0.675	0.142	0.107
Tomatoes					
R2-stream	2.063	0.782	0.404	0.079	0.059
R3-stream	14.275	3.555	1.778	0.379	0.284
R4-stream	10.679	1.590	0.795	0.155	0.116

** Due to additional information the application date was changed and hence the results from laboratory and field data cannot be directly compared

Table B.8.6.2-12: FOCUS Step 4 calculations, using laboratory soil degradation data

Scenario Location	Laboratory soil degradation values; Step 4 - 20 m Buffer zone				
	Initial PEC _{sw} (µg/l)	TWAECS _{sw} 2 (µg/l)	TWAECS _{sw} 4 (µg/l)	TWAECS _{sw} 21 (µg/l)	TWAECS _{sw} 28 (µg/l)
Carrots**					
R1-pond	0.013	0.003	0.002	0.000	0.000
R1-stream	0.745	0.117	0.059	0.019	0.015
R2-stream (1st crop)	0.214	0.088	0.047	0.009	0.007
R3-stream	2.146	0.382	0.191	0.037	0.028
R4-stream	1.512	0.671	0.337	0.064	0.048
Corn salad					
R1-pond (1st crop)	0.002	0.001	0.000	0.000	0.000
R1-pond (2nd crop)	0.009	0.003	0.002	0.000	0.000
R1-stream (1st crop)	0.474	0.091	0.046	0.010	0.008
R1-stream (2 nd crop)	0.087	0.030	0.015	0.003	0.003
R2-stream (2 nd crop)	2.057	0.441	0.221	0.047	0.036
R3-stream (2 nd crop)	0.456	0.196	0.098	0.019	0.014
R4-stream (2 nd crop)	0.982	0.337	0.169	0.036	0.027
Tomatoes					
R2-stream	0.516	0.196	0.101	0.020	0.015
R3-stream	3.569	0.889	0.444	0.095	0.071
R4-stream	2.670	0.397	0.199	0.039	0.029

** Due to additional information the application date was changed and hence the results from laboratory and field data cannot be directly compared

Conclusions:

Simulations with MITC applied to carrots, corn salad and tomatoes at rate of 1 x 172 - 344 kg MITC/ha corresponding to 600 l/ha to 1200 l/ha of a Metam-sodium 510 g/l end use solution, were conducted with the PRZM, MACRO and TOXSWA 2.2.1.F1 models for all relevant scenarios (Chateaudun, Hamburg, Jokioinen, Kremsmunster, Piacenza, Porto, Seville, Thiva). Step 3 and step 4 calculations were performed using field soil dissipation and laboratory soil degradation data.

- The FOCUS sw models were not developed with soil fumigants in mind. It is therefore probable that the results obtained by these models for MITC (volatile) highly overestimate the actual surface water contamination.
- Based on the very rapid degradation of Metam-sodium in soils, surface water contamination with the parent compound can be excluded. The PEC_{sw} should only be calculated for MITC.
- Based on the application technique, drift to surface water can be excluded.
- STEP 1-2 calculations are not sufficiently demonstrating safe uses and are therefore not reported. The run-off/drainage contributions of 2-5% of the application rate that are assumed in step 1-2 calculations would lead to unrealistically high PEC levels.
- The FOCUS scenarios were appropriately chosen: representative crops are the field crops (no leaching for greenhouse crops; localized use, exceptional use in grapevine), application rate, one application/year
- The Koc, Freundlich exponent were appropriately chosen

As RMS we have reservation on the choice of the DT50 MITC field used in the modelling calculations. The application in the field was made by overhead-sprinkler system. The formulation was injected in the sprinkler irrigation pipeline while water was applied to the plot. Incorporation of the a.s. in soil was achieved by post-application spray irrigation in some experiments. As the active substance has not been incorporated deeply into the soil by rotavation in the field experiments, it can be expected that the volatilisation at soil surface is very important. Consequently, the dissipation rate of MITC is overestimated (Field dissipation of MITC in the range 0.54-3 days with a mean of 1.57 days). The notifier indicated "that application by overhead sprinkler system is not supported in Europe. However, the common factor between all different application methods is the incorporation of metam in the top layer of the soil. The mean lab DT50 for MITC was 2.15 days. In view of the applicant the mean field DT50 of 1.57 days is realistic also in the case of the European application techniques since it is reflecting degradation in the soil as well as volatilisation to the air and is therefore expected to be lower than the lab DT50. Based on this field DT50 the use of the PRZM model would be justified. "

- The indoor uses pose no concern for surface water contamination. (e.g. cucumber, eggplant/aubergine, pepper and tomato) whilst the outdoor uses on strawberries occur under a plastic film, thus also preventing connectivity between soil and run-off water. Therefore no MITC contamination of surface bodies via run-off is possible for this use.
- In the DAR we based the risk assessment for aquatic organisms on PEC sw step 4 considering mitigation by 20 m buffer zones. Laboratory soil degradation data were used as input data. However, the PEC overestimation should be held in mind when evaluating the acceptability of the TER aquatic organisms (FOCUS models were not developed with soil fumigants in mind. It is that the models do not properly consider the volatilisation and therefore highly overestimate the actual surface water contamination)
- The initial PEC_{sw} step 4 were in the range of 0.002 (R1-pond, corn salad) to 3.569 (R3-stream, tomatoes) µg MITC /L, considering 20 m buffer zones.
- The assessment of risk to sediment organisms is not justified since
 - The properties of MITC (low Koc, high solubility in water) exclude exposure of the sediment organisms.
 - low level of MITC observed transiently in the sediment phase of the w/s study (1.5-4.5 % AR in the sediment after 72 h)
- The assessment of chronic risk to aquatic organisms is not justified since
 - The DT50 MITC, whole water-sediment system is clearly below 2 days.
 - The a.s. is applied once a year. Moreover, soil sterilants are generally not used every year.

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.5, Applicant to provide new PEC SW calculations. For field uses FOCUS Step 4 calculations may be provided if different mitigation options (such spray drift buffer zones [up to 100 m] and vegetative buffer strips for run off mitigation) are presented in separated (stepwise) calculations. For mitigation of run off FOCUS Landscape document together with the Opinion of the Scientific Panel on Plant protection products and their residues (PPR) related on the Final Report of the FOCUS Working Group on Landscape and Mitigation Factors in Ecological Risk Assessment (adopted date: 13/12/2006) has to be considered. Effect of potential volatilization deposition may need to be assessed and / or justified. Separated calculations may be provided for the greenhouse if a worst case for volatilization deposition is accounted for. . The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

"As stated in the DAR, based on the very rapid degradation of Metam-sodium in soils, surface water contamination with the parent compound can be excluded. The PEC_{sw} should only be calculated for MITC. Based on the application technique (soil injection or micro-irrigation) drift to the surface water can be excluded. The relevant routes of surface water contamination for FOCUS_{sw} are therefore run-off or drainage.

The applicant wishes to stress that for most drainage scenarios (D), FOCUS Step 4 calculations resulted in acceptable risk assessments for aquatic organisms, therefore no further refinements (step 4) are required for drainage scenarios. Further, application of metam through drip irrigation lines in greenhouses are not expected to result in surface water exposure of MITC through run-off as the treated areas are not exposed to rain. Safe uses for surface water have therefore been demonstrated.

Only for the run-off scenarios in field, FOCUS Step 4 calculations were performed and submitted in the dossier, taking into account 90 and 97.5% reduction factors for 10 m and 20 m vegetative strips. These factors were applicable for national registration in Germany at the time of submission of the dossier and the only guidance available for refining run-off exposure through vegetative strips. It should be noted that realistically soil treatment with metam will not take place if heavy rainfall is expected, which indirectly also reduces the potential for surface water contamination by run-off.

The reduction factors for run-off exposure at FOCUS Step 4 have been clarified since the original submission and the 90% and 97.5% reduction factors are apparently no longer supportable. In the opinion of the applicant, the evaluators should take into account knowledge and guidance that was in force at the time of submission of a dossier. For applicants, it is not always manageable to implement new guidance documents or information from FOCUS reports in risk assessments after submission of the EU dossier for annex I inclusion. Moreover, when implementation of these new guidance documents leads to other conclusions than those presented in the dossier, submission of new data/studies allowing further refinements is not longer accepted for consideration. Under such circumstances, the implementation of the new guidance documents should be part of the ANNEX III procedure.

Due to the short timeframe (1 month comment time), new risk assessments for the run-off scenarios are not yet available, but recalculations (using the Laboratory DT50) with the currently approved run-off reductions in the FOCUS Landscape and Mitigation report are expected to lead to a 2-3 fold reduction in PEC_{sw} on average and hence are likely not to result in acceptable TER ratios for most run-off scenarios.

However, for the specific use of metam in run-off situations, there are several options for further refinement of the modelling, eg. GIS/Landscape analysis, ... Should there be remaining critical intended uses, higher tier field data or monitoring data can be developed. These steps however, are preferably taken at Member State level, in preparation of the Annex III dossiers, in discussion with the national evaluation authorities in order to carefully select the most relevant approach. Implementation of risk mitigation measures, if necessary, are also to be discussed at Member state level as for the inclusion in Annex I safe uses can be demonstrated.

EFSA indicated that the effect of potential volatilization deposition may need to be assessed and/or justified. There is currently no approved guidance for this exposure route. There is a draft FOCUS guidance document but this was heavily criticised by the EFSA PPPR Panel in their opinion from Summer 2007. In these circumstances the applicant cannot be expected to address this particular request. It is deemed unreasonable for further PEC_{sw} data on a completely new exposure route to be required at this late stage when there is no approved guidance to follow.

Conclusions of the RMS:

Spray drift: Considering the mode of application by soil injection or drip irrigation, spray drift is totally excluded.

Run-off mitigation: As RMS we have considered that the FOCUS calculations (steps 3 and 4) that were provided in the original DAR were worst case PEC_{sw}. We also indicated in the DAR the points that have to be taken into account in this type of assessment:

- Risk is negligible for several uses under glasshouse protection or under plastic foil
- the mode of application (intensive cultivation of the soil, soil injection,...) reduces the run-off contribution.
- Considering its high volatility, the transport of MITC in flowing water or on soil particles is expected to be negligible
- The FOCUS models do not properly consider the volatilisation and therefore highly overestimate the actual surface water contamination.
- Even if the exact contribution of run-off mitigations measures is not known, a large proportion of the fields treated with metam are not close to surface water bodies and are therefore not at risk.

It is not clear whether the report of the FOCUS working group on landscape and mitigations factors in ecological risk can be used as basis of PEC calculations considering run-off mitigations. Contradictory guidance is given in the reporting table (according to comment 4(40), the FOCUS guidance should not be used) and in the evaluation table (according to Point of clarification for the applicant 4.5, the FOCUS guidance should be used).

Effect of potential volatilisation: According to the opinion of the PPR panel on the final report of the FOCUS air working group, the available models seem to be not robust enough. In absence of a robust modelling tool agreed at EU level, the RMS has considered that the available field studies are more appropriate than modelling results.

Several no-residue situations (greenhouse, plastic film covering,...) as well as acceptable situations (FOCUS step3 scenarios considering drainage, some FOCUS step 4 run-off scenarios) have been identified and would lead to acceptable risk for the aquatic environment. Further risk refinement for specific uses should be required in the framework of re-assessment of formulations at national level. Implementation of risk mitigations measures should be proposed at national level.

Conclusions of the peer review on point of clarification 4.5 : new data gaps have been proposed

Added in August 2010:

"A data gap for worst case PEC_{sw} estimations of MITC taking into consideration short range transport and deposition to surface water bodies and potential exposure via drainage with adequate input parameters was identified by the meeting of experts."

Predicted environmental concentrations of methyl isothiocyanate (MITC) in surface waters in the European Union using the Focus surface water scenarios. (Terry A.& Franey-Gardiner M., 2010)

Modelling assumptions – input parameters:**Objectives**

To undertake surface water modelling of methyl isothiocyanate (MITC) in support of registration activities in the European Union under EC Directive 91/414/EEC.

It should be noted that soil fumigants/sterilants are a very specific group of pesticides, whose use and handling make them different to other compounds when considering environmental exposure pathways. There are a number of uses for metam-sodium where the crops are grown under protected conditions (e.g. cucumber, pepper, aubergine and tomatoes in glasshouse/polytunnels) where the soil is protected from precipitation and lateral movement of water is unlikely. For these uses the risk to groundwater is low. Likewise, where the crop is covered with plastic film (e.g. strawberries) the risk of contact between lateral moving water and MITC in soil is low.

Surface Water Exposure Modelling

The results of a number of modelling assessments are summarised in this document. The strategy employed is a conservative assessment to generate PEC_{SW} and PEC_{SED} values. The assumptions made at each stage are summarised and results interpreted with respect to regulatory significance.

Scope of Modelling - Evaluating the GAP

It is important to base aquatic risk assessments on realistic conditions of use, as far as is possible. MITC is derived from metam-sodium, a soil sterilant with a wide range of applications. Metam-sodium degrades very fast in soil ($DT_{90} < 1$ day) and the active substance is MITC. This study considers the risk arising from MITC from application of metam-sodium to carrots, corn salad, tomatoes and potatoes, and simulations have been performed using MITC as parent in the calculations. The proposed GAP for metam-sodium (adapted from Jarvis, 2007) is shown in table below.

Table B.8.6.2-13: The GAP supported for Metam-sodium Annex I listing in the EU re-registration process (adapted from Jarvis, 2007)

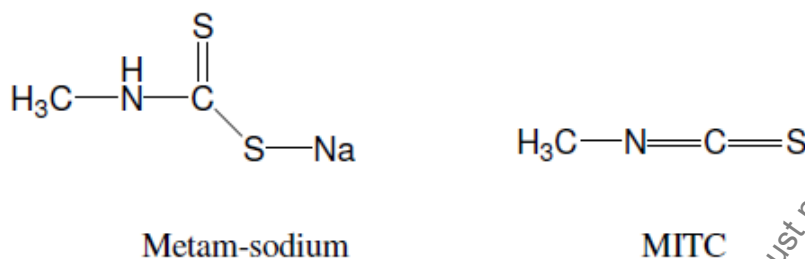
Crop and/or situation	F, G or I ^a	Application			Application rate per treatment (Metam-sodium)	Equivalent MITC application rate ^b
		Method kind	Growth stage and season	Number Min max	Kg a.s/ha Min max	Kg a.s/ha Min max
Carrot	F	Soil injection + incorporation at 25 cm by rotavation	April-June	1	408	230.94
Carrot	F	Soil injection + incorporation at 25 cm by rotavation	Oct-Dec	1	408	230.94
Corn salad (= lambs lettuce)	F	Soil injection + incorporation at 15 cm by rotavation	April-Aug	1	306	173.21
Cucumber	G	Drip-irrigation on the planting row	June-Aug	1	459	259.81
Eggplant/aubergine	G	Drip-irrigation on the planting row	June-Aug	1	612	346.41
Pepper	G	Drip-irrigation on the planting row	June-Aug	1	612	346.41
Potato	F	Soil injection + incorporation at 25 cm by rotavation	Sept-Nov	1	153	86.60
Strawberry	F	Drip irrigation under a plastic film on the planting row	Jul-Oct	1	612	346.41
Tomato	G	Drip-irrigation on the planting row	Feb-Aug	1	612	346.41
Tomato	F	Soil injection at 5 cm + coverage by 10 cm of soil	March	1	612	346.41
Grape	F	Soil injection at 40 cm at the site of the de-rooted vine (0.2 l/m ²)	Autumn, before replanting	1	1020	577.35

^a Outdoor or field use (F), glasshouse application (G) or indoor application (I)

^b Molecular weight conversion to MITC using molar masses of 128.18 g/mol for metam-sodium and 73.12 g/mol for MITC

Chemical Characteristics

The structures of metam-sodium and MITC are shown in Figure below.



Chemical structures of metam-sodium and MITC (Jarvis, 2007)

The chemical input parameters used in the modelling are summarised in table below. Where data were not available FOCUS default values (FOCUS, 2000) were employed.

Table B.8.6.2-14: Summary of chemical input parameters used in the modelling

Parameter	MITC	Reference source
Molar Mass (g/mol)	73.12	
Vapour Pressure (Pa)	1739 (20°C)	DAR (2007)
Solubility (mg/L)	8940 (20°C)	DAR (2007)
K _{OM} (L/kg)	7.83	K _{OC} /1.724
K _{OC} (L/kg)	13.5	Herrchen (2009)
1/n	0.83	Herrchen (2009)
DT ₅₀ in soil (days)	2.10	McMillan (2010)
Plant uptake	0	DAR (2007)
DT ₅₀ water	1000	worst case default
DT ₅₀ sediment	1000	worst case default
Q ₁₀	2.58 (PRZM)	Recommended values (EFSA, 2007)
	65400 (TOXSWA)	
	0.0948 (MACRO)	

Step 3 FOCUS Surface Water Assessments

Step 3 calculations were carried out to assess the movement and fate of MITC in surface waters and sediment. The FOCUS Surface Water methodology at Step 3 has ten scenarios that together represent realistic worst-case combinations of soil, agriculture and weather across Europe (FOCUS, 2001). These simulations are used in conjunction with a suite of models to generate predicted environmental concentrations in surface water (PEC_{SW}) and sediment (PEC_{SED}). The models include: SWASH v.2.1; Drift calculator v.1.1; MACRO v.4.4.2; PRZM_SW v.1.1.1 and TOXSWA v.2.2.1.

The pesticide use pattern determines which scenarios have to be completed for the safety assessment. The scenarios with relevance to the GAP for carrots (FOCUS-root vegetables), corn salad (FOCUS-leafy vegetables), tomatoes (FOCUS-fruited vegetables) and potatoes (FOCUS-potatoes) are summarised in table below.

Table B.8.6.2-15: Relevant FOCUS surface water scenarios

Crop	Drainage scenarios		Runoff scenarios	
	Northern Europe	Southern Europe	Northern Europe	Southern Europe
Carrots (FOCUS-root vegetables)	D3	D6	R1	R2, R3, R4
Corn salad (FOCUS-leafy vegetables)	D3, D4	D6	R1	R2, R3, R4
Tomatoes (FOCUS-fruited vegetables)	--	D6	R1	R2, R3, R4
Potatoes (FOCUS-potatoes)	D3, D4	D6	R1	R2, R3

Application Scenarios

It is important to base FOCUS assessments on realistic conditions of use, as much as is possible. MITC is intended for use as summarised in **Error! Reference source not found..** The simulated applications are provided in table below.

Table B.8.6.2-16: Simulated application of MITC

Crop	Application Rate (kg/ha)	CAM*	Soil incorporation depth (cm)
Root vegetables (carrots)	1 × 230.94	4	25
Leafy vegetables (Corn salad)	1 × 193.21	4	15
Fruiting vegetables (Tomatoes)	1 × 346.41	5**	15
Potatoes	1 × 86.60	4	25

*Chemical Application Method for PRZM

**in this case fresh soil is added on top of the treated soil and so an even distribution of MITC throughout the soil i.e. CAM 4, is not considered appropriate.

The emergence and harvest dates, application windows and actual application dates for the FOCUS scenarios appropriate to root vegetables (carrots), leafy vegetables (corn salad), fruited vegetables (tomatoes) and potatoes are given in table below. For tomatoes, two possible spring application windows were simulated to consider the differences in the effect of application timing on PEC_{SW}.

Table B.8.6.2-17: Summary of emergence and harvest dates, application windows and application dates for FOCUS-root vegetables, FOCUS-leafy vegetables and FOCUS-potatoes (FOCUS, 2002)

Scenario	Emergence date	Harvest date	Possible window of application	Application date generated by PAT *
Carrots (Root vegetables)				
D3	25-Apr	15-Aug	30 Sep-31 Oct	29-Sep-1992
D6	25-Feb	13-May	30 Sep-31 Oct	06-Oct-1986
R1	20-Apr	10-Aug	30 Sep-31 Oct	06-Oct-1978
R2 (1 st crop)	28-Feb	31-May	30 Sep-31 Oct	09-Oct-1989
R2 (2 nd crop)	22-Jul	15-Oct	Not simulated*	
R3	26-Feb	13-May	30 Sep-31 Oct	22-Oct-1975
R4	26-Feb	13-May	30 Sep-31 Oct	30-Sep-1985
Corn salad (Leafy Vegetables)				
D3	25-Apr	20-Jul	01 Apr-01 May	04-Apr-1992
D3	05-Aug	20-Oct	01 Jun-01 Jul	14-Jun-1992
D4	10-May	26-Sep	01 Apr-01 May	18-Apr-1985
D6	15-Aug	30-Nov	01 Jun-01 Jul	01-Jun-1986
R1	20-Apr	15-Jul	01 Apr-01 May	26-Apr-1984
R1	31-Jul	15-Oct	01 Jun-01 Jul	01-Jun-1978
R2	28-Feb	01-Jul	Not simulated**	
R2	31-Jul	15-Nov	01 Jun-01 Jul	04-Jun-1989
R3	01-Mar	01-Jun	Not simulated**	
R3	15-Jun	15-Sep	01 Jun-01 Jul	02-Jun-1975
R4	01-Mar	01-Jun	Not simulated**	
R4	15-Jun	15-Sep	01 Jun-01 Jul	01-Jun-1985
Tomatoes (Fruiting vegetables (March application))				
D6	10-Apr	10-Aug	01 Mar-31 Mar	05-Mar-1986
R2	15-Mar	31-Aug	01 Mar-31 Mar	01-Mar-1977
R3	10-May	25-Aug	01 Mar-31 Mar	01-Mar-1980
R4	20-Apr	15-Jul	01 Mar-31 Mar	05-Mar-1984
Tomatoes (Fruiting vegetables (April application))				
D6	10-Apr	10-Aug	31 Mar-30 Apr	03-Apr-1986

R2	15-Mar	31-Aug	31 Mar-30 Apr	22-Apr-1977
R3	10-May	25-Aug	31 Mar-30 Apr	04-Apr-1980
R4	20-Apr	15-Jul	31 Mar-30 Apr	08-Apr-1984
Potatoes				
D3	10-May	15-Sep	16 Sep-16 Oct	26-Sep-1992
D4	22-May	23-Sep	24 Sep-24-Oct	28-Sep-1985
D6 (1 st crop)	10-Apr	15-Jul	01 Sep-01 Oct	04-Sep-1986
D6 (2 nd crop)	05-Aug	25-Nov	26 Nov-26 Dec	06-Dec-1986
R1	05-May	08-Sept	09 Sep-09 Oct	17-Sep-1978
R2	15-Mar	15-Jun	01 Sep-01 Oct	29-Sep-1989
R3	10-Apr	01-Sep	02 Sep-02 Oct	23-Sep-1975

*PAT – Pesticide Application Timer: included in FOCUS surface water models

*application would have been at same time as R1 first crop, and would have generated same answer

**application prior to planting would be in February which is outside GAP window

Implementing Large application Rates in MACRO

Where the application rate is particularly high, the MACRO program generates an application rate in the output *.m2t file (macro to toxswa) which is not the same as that used by the TOXSWA *.txw input file. This leads to incompatibility between the two models and TOXSWA will not run where there is an affected file. When this occurs, it is necessary to manually alter the *.m2t file to correct the application rate. This was the case with Fruiting Vegetables, scenario D6 where the application rate in the *.m2t file was calculated as 346409.970 g a.i./ha for the March application window and 346409.984 g a.i./ha for the April application window as opposed to the required value of 346410 g a.i./ha.

Step 4 modelling

The PEC_{SW} values obtained from Step 3 indicate that additional mitigation is required in order to reduce the potential risk to aquatic environments. Vegetative filter strips can significantly reduce run-off of pesticides into water bodies (FOCUS, 2004). The amount of mitigation that can be achieved appears to depend on many different factors, including many which are linked to the specific location being considered. In the case of MITC it is reasonable to assume that as it is carried across the rough vegetative filter strip a significant proportion of the substance would be lost from the thin water transport layer *via* volatilisation. As such, the maximum mitigation of 97.5% currently allowed according to German national guidelines for a 20 m buffer zone has been considered, as representative of what might be achievable with the implementation of vegetative filter strips at the national level.

Therefore, FOCUS Step 4 calculations have been undertaken where the run-off concentrations have been reduced by 97.5% (run-off volume, run-off flux, erosion mass and erosion flux). Step 4 simulations were set up using the same application scheme as used in Step 3 simulations. Run-off mitigation was applied using the Surface Water Assessment eNabler (SWAN v.1.1.4). SWAN v.1.1.4 modifies the Step 3 *.txw files to account for the reduction in pesticide loading *via* spray drift and/or run-off. It copies all existing files from the existing Step 3 folder, plus the modified *.txw, and provides a batch file that can be used to initiate the Step 4 simulations.

Findings:**Table B.8.6.2-18: Step 3 PEC_{SW} and PEC_{SED} for MITC following application to carrots (FOCUS-root vegetables)**

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
D3	Ditch	0.2740	0.3760	0.2730	0.2730	0.2700	0.2670	0.2560	0.2450	0.2370
D6	Ditch	1.6640	0.1540	0.8840	0.6670	0.4540	0.3020	0.1730	0.1180	0.0891
R1	Pond	0.2840	0.0461	0.2190	0.1710	0.1110	0.0685	0.0411	0.0281	0.0211
R1	Stream	43.2370	2.4000	10.3130	5.1600	2.5810	1.4750	1.0580	0.7060	0.5290
R2	Stream	5.2130	0.5920	2.8640	1.8200	0.9360	0.5380	0.2700	0.1800	0.1350
R3	Stream	115.4920	7.9930	43.1230	21.5770	10.3920	6.1680	3.1000	2.0670	1.5500
R4	Stream	49.7660	5.8790	39.0220	21.1170	10.5870	6.0500	3.0250	2.0170	1.5130

Table B.8.6.2-19: Step 3 PEC_{SW} and PEC_{SED} for MITC following application to corn salad (FOCUS-leafy vegetables)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
D3	Ditch	0.0002	0.0006	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001
D3	Ditch	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
D4	Pond	0.0129	0.0142	0.0128	0.0126	0.0120	0.0108	0.0100	0.0078	0.0063
D4	Stream	0.4280	0.3190	0.4240	0.4180	0.3980	0.3590	0.3230	0.2630	0.2180
D6	Ditch	0.0000	0.0000	N/A	N/A	N/A	N/A	N/A	N/A	N/A
R1	Pond	0.1230	0.0187	0.0935	0.0712	0.0447	0.0269	0.0168	0.0137	0.0103
R1	Stream	40.7640	3.2110	15.7520	7.8800	3.9410	2.2520	1.1850	0.7910	0.5930
R1	Pond	0.4290	0.0603	0.3270	0.2410	0.1420	0.0867	0.0452	0.0301	0.0226
R1	Stream	2.6630	0.3520	1.8580	0.9300	0.4650	0.3030	0.1530	0.1020	0.0767
R2	Stream	78.4160	6.5440	34.0310	17.0210	8.5120	4.8650	2.6250	1.7500	1.3120
R3	Stream	10.7750	1.4630	9.2480	4.7150	2.3590	1.3480	0.6740	0.4500	0.3370
R4	Stream	28.6220	3.2870	19.8350	9.9230	4.9630	3.0680	1.5400	1.0270	0.7700

N/A The simulated period was too short for calculation of PEC_{SW}

Table B.8.6.2-20: Step 3 PEC_{SW} and PEC_{SED} for MITC following application to tomatoes (FOCUS-fruited vegetables)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
D6	Ditch	0.8410	0.4650	0.8210	0.7530	0.5820	0.4240	0.3360	0.3030	0.2900
R2	Stream	25.0930	2.7080	14.6930	8.4610	4.2740	2.4540	1.2270	0.8180	0.6140
R3	Stream	184.6650	15.8750	94.9340	47.5660	23.7960	13.6020	7.2900	4.8650	3.6490
R4	Stream	114.8120	6.5240	33.0880	17.8840	8.9440	5.1120	2.5860	1.7300	1.2970

Table B.8.6.2-21: Step 3 PEC_{SW} and PEC_{SED} for MITC following application to potatoes (FOCUS-potatoes)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
D3	Ditch	0.0319	0.0728	0.0318	0.0318	0.0317	0.0316	0.0314	0.0309	0.0304
D4	Pond	0.5980	0.2530	0.5930	0.5780	0.5520	0.4950	0.3680	0.2940	0.2350
D4	Stream	3.3540	1.3000	2.8920	2.6940	2.6090	2.3530	1.7350	1.3910	1.1310
D6 (1 st crop)	Ditch	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
D6 (2 nd crop)	Ditch	9.0840	2.8030	8.3550	7.6220	6.8140	5.6700	3.7440	2.7030	2.1650
R1	Pond	0.0858	0.0126	0.0605	0.0436	0.0272	0.0181	0.0094	0.0063	0.0047
R1	Stream	13.0580	1.0790	4.3770	3.1090	1.5550	0.9120	0.4560	0.3040	0.2290
R2	Stream	0.1190	0.0170	0.0659	0.0444	0.0231	0.0133	0.0067	0.0044	0.0033
R3	Stream	0.3280	0.0397	0.1650	0.0904	0.0452	0.0262	0.0131	0.0087	0.0066

Table B.8.6.2-22: Step 4 PEC_{SW} and PEC_{SED} for MITC in all run-off scenarios with 97.5% run-off reduction following application to carrots (FOCUS-root vegetables)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
R1	Pond	0.0071	0.0015	0.0055	0.0043	0.0028	0.0017	0.0010	0.0007	0.0005
R1	Stream	1.1090	0.0752	0.2590	0.1300	0.0648	0.0371	0.0286	0.0190	0.0143
R2	Stream	0.1620	0.0229	0.0897	0.0570	0.0293	0.0169	0.0085	0.0056	0.0042
R3	Stream	3.1860	0.2650	1.1650	0.5830	0.2920	0.1670	0.0838	0.0559	0.0419
R4	Stream	1.5490	0.2240	1.2210	0.6600	0.3310	0.1890	0.0947	0.0631	0.0473

Table B.8.6.2-23: Step 4 PEC_{SW} and PEC_{SED} for MITC in all run-off scenarios with 97.5% run-off reduction following application to corn salad (FOCUS-leafy vegetables)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
R1	Pond	0.0031	0.0006	0.0023	0.0018	0.0011	0.0007	0.0004	0.0003	0.0003
R1	Stream	1.0340	0.1010	0.3970	0.1990	0.0995	0.0568	0.0302	0.0202	0.0151
R1	Pond	0.0110	0.0020	0.0083	0.0061	0.0036	0.0022	0.0012	0.0008	0.0006
R1	Stream	0.0831	0.0137	0.0585	0.0293	0.0146	0.0095	0.0048	0.0032	0.0024
R2	Stream	2.4020	0.2420	1.0400	0.5200	0.2600	0.1490	0.0804	0.0536	0.0402
R3	Stream	0.3360	0.0566	0.2900	0.1480	0.0743	0.0424	0.0212	0.0142	0.0106
R4	Stream	0.8930	0.1260	0.6240	0.3120	0.1560	0.0966	0.0485	0.0323	0.0242

Table B.8.6.2-24: Step 4 PEC_{SW} and PEC_{SED} for MITC in all run-off scenarios with 97.5% run-off reduction following application to tomatoes (FOCUS-fruited vegetables)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
R2	Stream	0.7820	0.1040	0.4600	0.2650	0.1340	0.0767	0.0384	0.0256	0.0192
R3	Stream	5.7780	0.5970	3.0450	1.5260	0.7640	0.4370	0.2330	0.1560	0.1170
R4	Stream	3.5220	0.2440	1.0130	0.5420	0.2710	0.1550	0.0783	0.0524	0.0393

Table B.8.6.2-25: Step 4 PEC_{SW} and PEC_{SED} for MITC in all run-off scenarios with 97.5% run-off reduction following application to potatoes (FOCUS-potatoes)

Scenario	Waterbody	Max PEC _{SW} (µg/L)	Max PEC _{SED} (µg/kg)	1 day TWAEC _{SW} (µg/L)	2 day TWAEC _{SW} (µg/L)	4 day TWAEC _{SW} (µg/L)	7 day TWAEC _{SW} (µg/L)	14 day TWAEC _{SW} (µg/L)	21 day TWAEC _{SW} (µg/L)	28 day TWAEC _{SW} (µg/L)
R1	Pond	0.0022	0.0004	0.0015	0.0011	0.0007	0.0005	0.0002	0.0002	0.0001
R1	Stream	0.3890	0.0391	0.1290	0.0876	0.0438	0.0258	0.0129	0.0086	0.0065
R2	Stream	0.0037	0.0007	0.0020	0.0014	0.0007	0.0004	0.0002	0.0001	0.0001
R3	Stream	0.0101	0.0015	0.0051	0.0028	0.0014	0.0008	0.0004	0.0003	0.0002

Conclusions :

The input parameters that have been used in the FOCUS calculations have been appropriately chosen. PEC_{SW} and PEC_{SED} values for MITC have been calculated at Step 3 at appropriate application rates for the EU GAP. FOCUS Step 4 modelling has also been conducted to explore mitigation arising from the use of run-off reduction measures. The potential exposure at Step 4 was reduced for all PEC_{SW} values for run-off scenarios. Calculated PEC_{SW} values should be considered as unrealistically worst case, because FOCUS-MACRO and FOCUS-PRZM do not satisfactorily account for loss of volatile substances from the soil.

A number of uses of metam-sodium occur under circumstances where lateral movement of water is very unlikely. The applications to cucumber, pepper, aubergine and tomatoes in protected situations (glasshouse/polytunnel) are examples of such circumstances. In addition, application to strawberries outdoors involves covering the soil location with plastic film, which also prevents contact between lateral moving water and MITC in soil.

For the other uses, FOCUS surface water (SW) scenarios (FOCUS, 2001) provide a standard assessment tool. The use of MITC on carrots, corn salad, tomatoes and potatoes was simulated at application rates of 230.94 kg/ha, 173.21 kg/ha, 346.41 kg/ha and 86.60 kg/ha respectively using FOCUS surface water Steps 3 and 4. These PEC_{SW} have been taken as input for the TER aquatic organisms.

It has been demonstrated that safe uses are possible, but some Focus surface water scenarios are more relevant for some countries than others. Therefore, more detailed considerations should be taken at Member State level. This is demonstrated in the following study :

FOCUS Surface Water Scenario Contextualisation for Potatoes and Root Vegetables. Hughes G.O. (2010)

This investigation contextualises the relevance of the FOCUS Surface Water Scenarios ($FOCUS_{SWS}$) simulation modelling results with respect to potato and root vegetable (representative of carrots) production in the EU member states under consideration, these being Belgium, Germany, Spain, France, Greece, Hungary, Ireland, Italy, Netherlands, Poland, Portugal and the UK.

The $FOCUS_{SWS}$ were constructed to represent EU agriculture as a whole and as such each scenario does not have pedo-climatic relevance to all member states. In addition, they were constructed with the best available datasets at the time (*circa* 2000) and these have been superseded by more recent and higher resolution datasets. Through construction of more up-to-date and higher resolution versions of the $FOCUS_{SW}$ scenarios the pedo-climatic relevance of each of the scenarios to the member states under consideration is outlined. This analysis demonstrates that each scenario is relevant to between 1 and 9 member states, with most pedo-climatically relevant to 5 or less.

In addition, a spatial analysis to determine the possible area of crop grown on soils vulnerable to runoff or drain flow was undertaken. This analysis suggests that between 0.02% and 37.2% of potatoes and 0.03% and 40.2% of root vegetables may possibly be grown on surface runoff vulnerable soils. In the majority of member states under consideration less than 10% of the cropped area of potatoes and root crops would be vulnerable to surface runoff. The analysis also suggests that between 0.8% and 80.2% of potatoes and 0.8% and 95% of root vegetables may possibly be grown on soils vulnerable to drain flow. In a third of the member states the vulnerability to drain flow is below 10% of the cropped area and below 25% for half of them.

Both analyses indicate that failure of a $FOCUS_{SW}$ scenario may have limited relevance at a member state or EU zonal level and that there are many member states where a safe use is likely.

Prediction of redeposition of MITC to surface waters in the EU following application of metam-sodium. Terry A.& McMillan C (2010)

Project methodology

There are currently no validated approaches for estimating PEC_{SW} following redeposition of volatilised pesticides in the EU. The PEC_{SW} arising from the redeposition route will depend on many different factors, all of which will vary depending on the exact local conditions and practices. Essentially, a scenario-based approach would be required, and no such EU (or Member State) scenarios are available.

Therefore, an alternative approach has been taken. In the absence of a scenario approach that would be suitable to consider local circumstances, an attempt has been made to consider the redistribution of MITC amongst the various environmental compartments once it has entered the air from treated soil, at the EU-regional scale, using the EU wide model, EUSES 2.1. EUSES 2.1 allows redistribution of MITC among the environmental compartments to be calculated on a regional scale according to the EU-TGD. This approach has the advantage that EUSES 2.1 is an accepted regulatory simulation tool at the EU-level, already used in the context of the Biocidal Products Directive (98/8/EC) and REACH (2006/121/EC).

Modelling assumptions – input parameters:

The substance input is regarded as continuous and equivalent to continuous diffuse emission. The outputs from the model are steady-state concentrations which can be regarded as estimates of long-term average exposure levels.

EUSES 2.1 uses a defined area of 200 km by 200 km with 20 million inhabitants for regional calculations. It is assumed that 10% of the EU production and use of the product takes place within this area i.e. 10% of the estimated emission is used as input for the region.

Approximately 19 380 metric tonnes of metam-sodium is used annually in the EU (from all suppliers). Assuming 100% conversion of metam-sodium to MITC within the soil, approximately 10 970 tonnes of MITC is released annually in the EU. This assessment is an investigation of the redistribution of MITC throughout environmental compartments at the regional scale following application of metam-sodium to soil and subsequent emission to air. Therefore the fraction of tonnage released to air was set to 1. This is a conservative assumption given that volatile release of MITC to air is very unlikely to be 100% of that generated in soil from metam-sodium, the very rapid degradation of MITC in soil, and the agronomic measures taken to limit rapid volatile loss to aid efficacy. The input parameters employed in EUSES 2.1 are summarised in table below.

Table B.8.6.2-26: Input parameters used in EUSES 2.1 simulations for MITC

Parameter	Value
Molecular mass (g/mol)	73.12
Melting point (°C)	34
Boiling point (°C)	118
Vapour pressure at 20°C (Pa)	1739
Water solubility at 20°C (mg/L)	8940
Log P at 20°C	1.05
K _{OC} (ml/g)	13.5
DT ₅₀ water (d)	50
DT ₅₀ soil (d)	2.1
DT ₅₀ air (d)	8.9
Tonnage per year	10970
Fraction of EU volume for region (%)	10
Industry category	Agricultural chemicals
Use category	Plant protection products, agricultural
Fraction of tonnage released to air	1

Findings:

EUSES 2.1 provides regional predicted environmental concentrations (PECs) for the different environmental compartments; surface water, air, agricultural soil, pore water of agricultural soil, natural soil, industrial soil and sediment. The predicted regional environmental concentrations for MITC in these different compartments is summarised in table below.

Table B.8.6.2-27: Regional PECs for MITC in different environmental compartments

Compartment	PEC	Unit
Surface water	0.0153	µg/L
Air	6.63E-05	µg/L
Agricultural soil	1.84E-03	µg/kg _{wwt}
Pore water of agricultural soil	5.15E-03	µg/L
Natural soil	4.12E-03	µg/kg _{wwt}
Industrial soil	4.12E-03	µg/kg _{wwt}
Sediment	0.015	µg/kg _{wwt}

Conclusions :

The input parameters that have been used in the EUSES calculations have been appropriately chosen. EUSES 2.1. predicts a worst case (19380 tonnes of metam-sodium, 100% emitted to air as MITC). EU-regional PEC_{SW} of 0.0153 µg/L following redistribution of MITC lost to air via volatilisation from treated soil which can be considered to assess the risk related to short range transport.

The risk to soil organisms related to short range transport (1.84 to 4.12 E-06 mg/kg soil) is covered by the risk assessment that has been performed for in-field exposure (max PEC = 153 mg MITC/kg soil)

The risk to aquatic organisms related to short range transport of MITC (0.0153 µg/L) is covered by the risk assessment that has been performed for edge-of-field exposure (max PEC_{sw} = 184 µg/L)

B.8.7 Monitoring data

Pesticides in groundwater: occurrence and ecological impacts. (Notenboom *et al.*, 1999).

RIVM, Published report 601506002

This study describes a groundwater monitoring program that has been performed in the Netherlands around 1990-1995.

“Monitoring data from shallow (<10 m below soil surface) and deep groundwater in the Netherlands. The shallow groundwater samples were use related, it concerned aimed sampling after pesticide. Only the sampling of deeper groundwater is considered to be actual “monitoring”

“MITC was only detected in shallow groundwater samples. An LOD was not stated in the report but clearly it is <0.1 µg/l (since the median value from the flower bulbs was 0.05). The location of the exceedences is not known, hence no information is available on whether the compound was used according to the GAP.”

2-3 samples out of 126 were in the range 0.1-2.5 µg MITC/L. All other samples were below 0.1 µg MITC/L.

“In the deeper groundwater, MITC was one of the compounds that was analyzed by drinking water companies in the period 1992-1995, but not detected (VEWIN database, 1992-1995).”

Conclusion:

This study can be considered as additional information on the groundwater contamination by MITC.

The IPS Raw Water Monitoring and in depth analysis of the occurrence of the active ingredients of pesticides in drinking water resources.

This study describes a groundwater monitoring program that has been performed in Germany in 1985-1986. MITC was analyzed in the program, but not found in any of the sampling points.

Conclusion:

This study can be considered as additional information on the groundwater contamination by MITC.

Flavour compounds in weakly polluted rivers as a means to differentiate pollution sources. (Jüttner F.,1992). Published. Wat. Sci. Tech. Vol 25. No. 2 pp 156-164

“The volatile organic compounds of eight weakly polluted small rivers and brooks in SW Germany were studied by GC-MS.

More than a hundred different compounds were identified in the eight rivers and brooks. MITC was found only in one river water (River Schussen) and in samples which were several months apart. The source of MITC in those samples could not be established, but a possible explanation could be the formation of MITC by microorganisms (*Pseudomonas*).”

Conclusion:

This study is not useful for the final assessment.

Concentrations of methyl isothiocyanate in the air near villages in the Northeast of the Netherlands (van den Berg F. et al., 1988)

Experimental Design:

Monitoring of air quality was conducted near villages in the Northeast of the Netherlands in the autumns of 1985 (Emmer-Compascuum, Borgercompagnie), 1986 (Valthermond, Borgercompagnie) and 1987 (Valthermond, Borgercompagnie).

One sampler (sampling height 1.5 m above the soil surface) has been placed in each location. Very limited information is given on the respective position of the treated field and of the sampler.

Limited information is given on the analytical procedures.

Findings:

Conclusions from the study report: “All of the concentrations of methyl isothiocyanate measured in air were below the determination limit of 5 µg/m³ in autumn 1985. Subsequently, improved analytical procedures were developed which allowed measurements down to a determination limit of 2.0 µg/m³ in autumn 1986 and then down to 1.0 µg/m³ in autumn 1987.

Most (93%) of the 6-hour concentration of methyl isothiocyanate measured in 1986 and 1987 ranged from less than 1 µg/m³ to 2 µg/m³. As the concentration approaches the determination limit, there is an increased risk of interfering

substances contributing to the response. Some of the 6-hour concentrations of methyl isothiocyanate (3%) measured in 1986 and 1987 were in the somewhat higher range of 3.0 to 6.2 $\mu\text{g}/\text{m}^3$.

In some cases, the concentrations measured could be explained from the fumigation of a nearby field upwind of the measuring site. However, in other cases there was no explanation for the somewhat higher values. A comparatively high 6-hour concentration of 96 $\mu\text{g}/\text{m}^3$ measured in the autumn of 1986 could not be explained. The explanation of the higher values was hampered because not all fumigations are reported to the Plant Protection Service and the dates of the reported fumigations were uncertain.”

Conclusions:

Study of limited quality.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.8 Fate and behaviour in air (Annex IIA, 7.2.2; Annex IIIA 9.3)

“Metam-sodium is a soil fumigant which is active against nematodes, soil-borne diseases, weed seeds and seedlings and soil pests. Metam-sodium is acting by decomposition to Methylisothiocyanate (MITC) and is used as a soluble concentrate (SL) containing 510 g/L (42.1 % w/w) Metam-sodium. Application of Metam-sodium is carried out by a soil-injection technique using tractor mounted equipment as well as by a drip irrigation technique the latter of which does not require the presence of an operator except for coupling the drum to the drip irrigation installation. In addition, Metam-sodium is also applied for soil fumigation in greenhouses. Metam-sodium is an aqueous solution and will be applied at a rate of up to 1200 L/ha corresponding to 612 kg Metam-sodium/ha and the product will be marketed in 60, 200 and 1,000 L containers or drums, respectively.”

The method of application for the supported uses of metam-sodium in Europe is as follows:

- injection of the undiluted formulation in the soil followed by incorporation by rotavation and soil surface sealing with a roller (carrots, lamb's lettuce, potato, tomato)
- injection of the undiluted formulation in the soil (grape replanting)
- drip irrigation under a plastic film on the planting row (strawberry)
- drip irrigation on the planting row in glasshouse (cucumber, eggplant, pepper, tomato)

B.8.8-1: Overview of the supported uses

Crop	Field or greenhouse	Application rate of metam-sodium		Incorporation depth (cm)
Carrot	F	800 L/ha	408 kg a.s./ha	25 cm
Lamb's lettuce	F	600 L/ha	306 kg a.s./ha	15 cm
Potato	F	300 L/ha	153 kg a.s./ha	25 cm
Strawberry	F	1200 L/ha	612 kg a.s./ha	Drip irrigation under plastic
Tomato	F	1200 L/ha	612 kg a.s./ha	15 cm
Grape	F	2400 L/ha	1020 kg a.s./ha	40 cm
Cucumber	G	900 L/ha	459 kg a.s./ha	Drip irrigation on the planting row
Eggplant, pepper, tomato	G	1200 L/ha	612 kg a.s./ha	Drip irrigation on the planting row

The notifier submitted several monitoring studies investigating the MITC concentrations in air. The rapporteur summarized the data in terms of MITC air concentrations expressed in mg/m³

Blootstelling van de toepasser aan methylisothiocyanaat tijdens de grondontsmetting met metam-natrium in het fabrieksaardappelgebied (Exposure of the user to methylisothiocyanate during soil decontamination with Metam-sodium on industrial potato land) (Mulder, A. et al, 1994)

Guidelines:

no specific guideline indicated; study meets good scientific practice

GLP:

No

Materials and methods:Test substance:

Monam (Metam-sodium 510 g/L), batch: not specified, purity: not specified

Experimental design:

Metam-sodium was applied onto 15 different parcels at 12 different field locations in the Netherlands during soil fumigation of industrial potato land in the autumn (end of September until mid of November) of 1992. Tractor-drawn equipment was used with 12 parcels treated with spade injector and 3 parcels treated with cultivator injection equipment, respectively. In order to avoid exposure during turning at the headlands all injection equipments used were fitted with an anti-drip systems, ie. anti-drip caps or blow-through system. Irrespective of the injection equipment used

all tractors were fitted with one to two flat driven roller for sealing of the soil. Soil fumigation was carried out by contractors taking part in the exposure measurements and all contractors were representative for the group of soil fumigants applicators as was the selected area of the parcels. Contractors wore overalls and were using gloves. During injection gloves were stored inside or outside of the tractor cabin or in the overall. Furthermore, filling times and the number of filling operations, spills during filling and number of drip during turns at the headlands were recorded. Application rate of Monam was 300 L/ha (153 kg a.s./ha). Eleven soils were classified as sandy soils and the four soils were classified as reclaimed moor soils. Soil parameters such as soil temperature, pH, soil humidity and organic content were determined for each treated soil in addition to meteorological parameters such as wind speed, wind direction, air humidity and air temperature, respectively.

Measurements of MITC in air were performed on the operators (outlet of the pump attached to the overall), within the tractor cabins and outside of the tractor cabin near the tractor driver). MITC concentrations were determined by using Dupont P4LC air pumps with a flow-through of 40 L/h. Pumps were connected to an SKC adsorbent tube which activated carbon as the adsorbent material.

Analytical methods:

After termination of sampling adsorbent material extracted with acetone and analyzed by gas chromatography (GC). Blank tests for determination of the MITC background concentration conducted in addition to penetration measurements for the investigation of the adsorption capacity of the adsorbent tubes used were performed for both personal and tractor cabin measurements. In addition, recovery measurements were performed to assess extraction efficiency and recovery of MITC of spiked adsorbent material.

B.8.8-2: Injection equipment and soil parameters for decontamination of soils with Metam-sodium/MITC

Sandy soil	Reclaimed moor soil
Injection equipment specification	
- 11 parcels fumigated - 9 parcels treated with spade injectors: 7 with antidrip caps, 2 with blow through system (1 turned on and 1 turned off) - 2 parcels treated with cultivator injector fitted with blow through system, 1 turned off and 1 turned on - flat driven rollers - soil sealing efficiency moderate to excellent	- 4 parcels fumigated - 3 parcels treated with spade injectors: 2 with antidrip caps, 1 with blow through system turned on - 1 parcel treated with cultivator injector fitted with antidrip caps - flat driven rollers - soil sealing efficiency moderate to good
Soil parameters	
pH: 4.4 – 5.6	pH: 4.2 – 5.8
Moisture: 13.4 – 23.7 %	Moisture: 21.5 – 32.6 %
Organic content: 4.2 – 9.1 %	Organic content: 13.3 – 28.6 %

Findings:

Analytical investigations:

Recovery experiments demonstrated that average recovery of MITC in spiked acetone solutions to which the content of an SKC adsorbent tube was added amounted to 87 %.

On the basis of the analytical method used the limit of detection (LOD) was shown to be $< 0.01 \mu\text{g/mL}$ in acetone as the solvent. After recalculation for recovery, flow rate and pumping duration, This LOD is equivalent to $\sim 1 \mu\text{g MITC/ m}^3$ air. All blank tests performed prior to injection application of Metam-sodium on the respective fields demonstrated background values in the range of $< 0.01 \mu\text{g/mL}$ to $0.08 \mu\text{g/mL}$ of acetone. There were two outliers with figures of 0.15 and $0.24 \mu\text{g/mL}$ which were due to contaminations from adjacent fields. In addition, penetration experiments did not reveal breakthrough of the adsorbent material used since no penetration of MITC to a second SKC tube could be demonstrated and MITC was efficiently adsorbed onto the activated carbon. On four parcels exposure measurements were performed in duplicate. The reproducibility of the method used was investigated in the tractor cabin air of four different parcels by performing duplicate measurements. Variations between values of duplicate measurements of the cabin air were within a range of 0.5 – 29 %.

The flow rate of the air pumps used was shown to be within 10 % of the set flow-through of 40 L/h or about 667 mL/min.

Results of personal, cabin and outside exposure measurements:

The average exposure figures were comparable for personal and cabin measurements (about 145 µg MITC/h for personal measurements vs. about 141 µg/h in the cabin) while measurements outside of tractor cabin were considerably lower (27.0 µg/h) when not taking into account respective figures for parcel BG2. The cause for this difference is due to a higher ventilation while in the closed cabins generated MITC cannot escape which results in both higher and also comparable figures for personal and cabin exposure.

Personal and, cabin and outside air MITC exposure measurements showed that in 13 of 15 measurements exposure towards MITC was up to 211 µg MITC/hour.

- During soil fumigation of parcel BG2 high exposure towards MITC was found on personal measurements while exposure figures in the cabin and outside of the tractor were comparable to all other parcels treated. The higher exposure figure was the result of filling of the tractor tanks from 200 L drums during which the operator/driver was wearing gloves and subsequent storage of the contaminated gloves in the overall pockets of the driver thereby contributing to a high exposure towards MITC during the application period. The somewhat lower exposure figures in the cabin of the tractor were due to open cabin windows thereby lowering cabin MITC concentration by dilution with fresh air.

- In parcel BG11 exceptional high MITC concentrations were found on personal and cabin measurements due to damage to one of the injector spades which were repaired on the field that was already treated with Metam-sodium. As a consequence thereof both the overall and footwear of the operator/driver became contaminated with treated soil that released MITC and which resulted in the observed high MITC exposure levels. This has been confirmed by the second period of treatment on the same parcel where comparatively low MITC concentrations were demonstrated on both personal and cabin measurements with MITC concentrations of about 200 µg/h.

Exposure figures for parcels BG12 and BG13 –which are at the same location and treated at the same date- demonstrate that although exposure figures for both personal, cabin and outside air measurements were in general low, the use of blow-through equipment reduces exposure by a factor of about 2 – 3 in the tractor cabin and by a factor of about 9 outside of the tractor which confirms the effectiveness of anti-drip equipment for exposure mitigation.

B.8.8-3: MITC air concentrations and operator exposure during soil injection

Field Code	Type of injector	Area (in ha) treated	Duration of measurement (min)	Air concentration (in mg MITC/m ³)			Inhalation exposure in µg MITC/h = Air concentration (in µg/m ³) X 1.25 m ³ /hour		
				Personal measurement	Cabin measurement	measurement on the outside front of the Tractor	Personal measurement	Cabin measurement	measurement on the outside front of the Tractor
BG1	Spade inj.	1.28	145	0.039	0.037	0.019	48.4	45.7	23.9
BG2	Spade inj.	3.50	250	0.546	0.187	0.046	683.1	234.1	58.0
BG3	Spade inj.	2.34	215	0.046	0.037	0.006	57.1	46.6	7.4
BG4	Cultivator inj.	5.54	245	0.058	0.073	0.005	72.4	91.6	6.4
BG5	Spade inj.	1.64	130	0.034	0.027	0.013	41.9	33.3	16.6
BG6	Spade inj.	4.84	315	0.086	0.083	0.017	107.9	104.3	21.3
BG7	Spade inj.	5.41	300	0.120	0.142	0.036	149.4	177.7	44.6
BG8	Spade inj.	5.15	310	0.117	0.116	*	146.4	144.4	*
BG9	Spade inj.	2.70	145	0.097	0.098	0.054	121.1	122.7	68.0
BG10	Spade inj.	2.44	150	0.104	0.103	0.049	130.1	128.3	61.0
BG11	Spade inj.	2.75	230	0.592	0.565	*	739.8	706.6	**
BG12	Cultivator inj.	2.38	135	0.012	0.013	0.002	14.4	16.7	1.9
BG13	Cultivator inj.	2.93	200	0.029	0.042	0.015	36.3	53.1	18.6
BG14	Spade inj.	3.93	220	0.117	0.098	*	146.6	122.7	*
BG15	Spade inj.	2.93	245	0.169	0.143	*	211.4	178.4	*
Average		3.32	216	0.144	0.118	0.024	180.4	147.1	29.8
Average (w/o BG2)		3.30	213	0.116	0.103	0.022	144.5	140.9	27.0

ad: fitted with anti-drip caps

db: fitted with blow-through equipment switched on

-db: fitted with blow-through equipment switched off

*: not conducted (BG8: rainy weather; BG14+15: technical difficulties in mounting the respective pump units to the tractor)

**: measurement lost due to strong vibration of the tractor during application

Conclusions:

Metam-sodium was applied at application rate of 153 kg a.s./ha onto 15 different parcels at 12 different field locations in the Netherlands during soil fumigation of industrial potato land in the autumn (end of September until mid of November) of 1992. Tractor-drawn equipment was used with 12 parcels treated with spade injector and 3 parcels treated with cultivator injection equipment, respectively. Soil fumigation was carried out by contractors taking part in the exposure measurements and all contractors were representative for the group of soil fumigants applicators as was the selected area of the parcels. Contractors wore overalls and were using gloves. During injection gloves were stored inside or outside of the tractor cabin or in the overall. Furthermore, filling times and the number of filling operations, spills during filling and number of drip during turns at the headlands were recorded.

The aim of this study was to determine the MITC concentration in air at operator level (on the operator's overall, within the tractor cabin and outside of the tractor cabin near the tractor driver) during the application of metam-sodium

Personal cabin air MITC exposure measurements showed that 13 of 15 measurements were in the range of 0.012-0.169 mg MITC/m³

In 2 cases where repair work had to be performed or contaminated gloves were stored in the tractor cabin against the label recommendations, the MITC concentrations were 0.189-0.592 mg MITC/m³

The MITC concentrations in open air outside of the tractor cabin were in the range ND-0.054 mg MITC/m³

The notifier proposes that “In cases where unforeseen maintenance has to be performed on the treated field appropriate respiratory protection is recommended for the operator.”

Blootstelling van de toepasser aan methylisothiocyanaat tijdens de grondontsmetting van bloembollenpercelen met metam-natrium (Exposure of the user to methylisothiocyanate during soil decontamination of bulb parcels with Metam-sodium) (De Rooij, M. et al, 1993)

Guidelines:

no specific guideline indicated; study meets good scientific practice

GLP:

No

Test substance:

BASF monam, AAmomam, Shell-NMC and Luxan monam (Metam-sodium 510 g/L), batch: not specified, purity: not specified

Experimental design:

Metam-sodium was applied for soil decontamination purposes onto 11 representative bulb parcels during 25 July and 29 August 1992 at an application rate ranging from 420 L/ha to 700 L/ha (214 to 357 kg a.s./ha). Four of the parcels were located in South Holland (Bloembollenstreek) and 7 were located in North Holland (Noordelijk Zandgebied). The average area of the fields treated in South and North Holland was 1.1 ha and 4 ha, respectively, and the fields were classified as sandy soils in both areas. Soil and environmental parameters such as soil moisture content, soil and air temperature, relative humidity, wind direction and wind speed during soil decontamination of parcels in addition to general weather conditions were determined.

Soil fumigation was conducted by eight different contractors who voluntarily took part in the exposure measurements during representative application of Metam-sodium. Three of the eight contractors were treating two parcels each. Prior to application of Metam-sodium the status of the contractors' personal equipment with regard to work clothes, type of footwear, gloves and face masks was recorded. All parcels were treated using specialized equipment, i.e. cultivator injectors which inject Metam-sodium into the soil at a depth of about 18 – 20 cm. One equipment used for this purpose was fitted with a blow-through device on the injector thereby reducing the loss of Metam-sodium when turning at the headlands. Immediately after injection the soil was compressed by one or two flat rollers one of which was a driven roller to ensure that the soil was well compressed and sealed. In all cases the injection activities were commenced on the downwind side of the parcel thereby reducing additional exposure as a consequence of emission of MITC from parcels that were already treated.

The average tank capacity of the tractors was 450 – 500 L which were filled from 3,000 L supply tanks or 200 L drums. Transfer of Metam-sodium from storage tanks or drums to the tractor tanks were accomplished by means of a positive pressure or vacuum system. Positive pressure systems are used for 3,000 L supply tanks while both systems were in place for 200 L storage containers. The following parameters for the application of Metam-sodium on each treated parcel were recorded:

- Type and capacity of stock container
- Filling system used, injector tank capacity, number of filling procedures per parcel, filling time and total filling volume
- Injector type, working width, number of rollers, injection depth and type of caps (anti-drip caps etc.)
- Dosage applied per parcel and product used
- Working direction, number of work sessions per parcel, work duration and sealing level of soil

For the determination of exposure of MITC only the inhalation route of exposure was considered. Exposure via the dermal and/or oral route of exposure was not measured. Representative measurements were performed during filling to gain an impression on possible exposure during operations other than soil injection. MITC exposure measurements were performed on the operators/tractor drivers (personal measurements) and within the tractor cabin. MITC concentrations were determined by using Dupont D4LC air pumps operating at a flow-through of 40 L/h connected to an SKC adsorbent tube with activated carbon as the adsorbent material. SKC tubes were fastened to the lapel of the operators and in the tractor cabin.

Analytical methods :

After termination of sampling adsorbent material extracted with acetone and analyzed by a suitable gas chromatography (GC) method with NP (nitrogen-phosphorus) detection. The robustness and stability of the method used for exposure measurements was verified by conduction of flow rate controls, blank tests for MITC background concentrations, extraction efficiency (recovery) experiments and penetration measurements to investigate the capacity of the used SKC adsorbent tubes. Within the tractor cabins MITC concentration was determined in duplicate while single determinations were carried out for 'personal' measurements

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B.8.8-4: Injection equipment and soil parameters for decontamination of soils with Metam-sodium/MITC

Parcel No.	Soil Parameters	Injection equipment*
1	- Sandy soil - moisture content: 9.4 % - soil temperature (5 – 20 cm): 19-22°C - wind speed: 3-5 m/sec. - air temperature (1m): 17-21°C - air humidity: 81-93 %	- cultivator injector - anti-drip caps: no - flat rollers: 2 - powered rollers: yes - application rate: 700 L/ha
2	- sandy soil - moisture content: 12.3 % - soil temperature (5 – 20 cm): 16-18°C - wind speed: 2 m/sec. - air temperature (1m): 18-20°C - air humidity: 51-63 %	- cultivator injector - anti-drip caps: no - flat rollers: 1 - powered rollers: yes - application rate: 420 L/ha
3	- sandy soil - moisture content: 10.3 % - soil temperature (5 – 20 cm): 22-26°C - wind speed: 4-5 m/sec. - air temperature (1m): 25-27°C - air humidity: 31-32 %	- cultivator injector - anti-drip caps: no (leaks) - flat rollers: 1 - powered rollers: yes - application rate: 700 L/ha
4	- sandy soil - moisture content: 4.8 % - soil temperature (5 – 20 cm): 17-20°C - wind speed: 3-5 m/sec. - air temperature (1m): 19-22°C - air humidity: 59-92 %	- cultivator injector - anti-drip caps: no - flat rollers: 2 - powered rollers: yes - application rate: 525 L/ha
5	- sandy soil - moisture content: 14.5 % - soil temperature (5 – 20 cm): 16-16.5°C - wind speed: 2-3 m/sec. - air temperature (1m): 14-16°C - air humidity: 97-98 %	- cultivator injector - anti-drip caps: yes - flat rollers: 1 - powered rollers: yes - application rate: 700 L/ha
6	- sandy soil - moisture content: 12-12.5 % - soil temperature (5 – 20 cm): 16.5-19°C - wind speed: 0-3 m/sec. - air temperature (1m): 18-19°C - air humidity: 75-82 %	- cultivator injector - anti-drip caps: yes - flat rollers: 1 - powered rollers: yes - application rate: 700 L/ha
7	- sandy soil - moisture content: 10-14 % - soil temperature (5 – 20 cm): 15-16°C - wind speed: 4-6 m/sec. - air temperature (1m): 16°C - air humidity: 74-77 %	- cultivator injector - anti-drip caps: yes - flat rollers: 2 - powered rollers: yes (1) - application rate: 560 L/h
8	- sandy soil - moisture content: 10.5-12 % - soil temperature (5 – 20 cm): 17-22°C - wind speed: 2-4 m/sec. - air temperature (1m): 16-22°C - air humidity: 65-89 %	- cultivator injector - anti-drip caps: yes - flat rollers: 2 - powered rollers: yes (1) - application rate: 700 L/h
9	- sandy soil - moisture content: 11-11.2 % - soil temperature (5 – 20 cm): 17-18°C - wind speed: 4-11 m/sec. - air temperature (1m): 16-19°C - air humidity: not measured (defective device)	- cultivator injector - anti-drip caps: no - flat rollers: 2 - powered rollers: yes (2) - application rate: 560 L/h

B.8.8-4: Injection equipment and soil parameters for decontamination of soils with Metam-sodium/MITC

Parcel No.	Soil Parameters	Injection equipment*
10	- sandy soil - moisture content: 7.6-8.4 % - soil temperature (5 – 20 cm): 17°C - wind speed: 5-6 m/sec. - air temperature (1m): 19-20°C - air humidity: > 90 %	- cultivator injector - anti-drip caps: no (blow-through) - flat rollers: 2 - powered rollers: yes (2) - application rate: 700 L/h
11	- sandy soil - moisture content: 7.6-8.4 % - soil temperature (5 – 20 cm): 17°C - wind speed: 5-6 m/sec. - air temperature (1m): 17-18°C - air humidity: > 90 %	- cultivator injector - anti-drip caps: no (w/o blow-through) - flat rollers: 2 - powered rollers: yes (2) - application rate: 700 L/h

*: cabin windows and doors were closed in tractors of all 11 parcels; with the exception of tractors on parcels 2 + 3, all tractors were equipped with ventilation

Findings:*Analytical investigations:*

Recovery experiments demonstrated that average recovery of MITC in spiked acetone solutions to which the content of an SKC adsorbent tube was added amounted to 66 %.

On the basis of the analytical method used the limit of detection (LOD) was shown to be < 0.01 µg/mL in acetone as the solvent. Blank tests performed prior to injection application of Metam-sodium on 5 representative parcels (parcels 1, 4, 8, 9 and 10) demonstrated background levels of MITC below the limit of detection (< 0.01 µg/mL). Good repeatability could be shown for the duplicate measurements within the tractor cabin since measured figures differed on average by 3.15 % only.

Penetration experiments did not reveal breakthrough of the SKC adsorbent tubes since no penetration of MITC to a second SKC tube could be demonstrated and MITC was efficiently adsorbed onto the activated carbon. MITC quantities in the first adsorbent tube were 3.2 µg and 34 µg indicating that the adsorbent capacity of one tube is high and that MITC figures obtained after work up of the tubes accurately reflect the actual airborne MITC concentrations.

The average flow rate of the air pumps used was shown to be 39.6 L/h (or 660 mL/min) which was within 1 % of the set flow-through of 40 L/h (or 667 mL/min).

Results of personal, cabin and outside exposure measurements:

Nearly all contractors were wearing suitable and effective protective equipment, i.e. shoes or boots, overalls and gloves, during filling and soil injection of Metam-sodium. Gloves were stored outside the tractor cabin. Only one contractor working on parcel no. 2 was wearing no gloves but washing the hands immediately after filling at the company. None of the contractors used a face mask.

During the MITC measurements performed after soil injection application of Metam-sodium it could be demonstrated that in most cases obtained figures for personal measurements were comparable to or slightly higher than corresponding figures for cabin measurements in the respective parcels. Only in parcels no. 5 and 6 figures for cabin measurements were higher than for personal measurements in the same parcel and it was indicated that this might have been the result of a defective injector construction. Furthermore, large differences in the measured MITC exposure levels were noted among the various parcels which might be due to a combination of influencing factors such as wind speed and wind direction, moisture content in the soil and rate of transformation of Metam-sodium to MITC. The measurement results gave no clear indication for a connection between the level of MITC exposure and the presence of special equipment in the cabin or the type of soil sealing technique used.

In general, highest exposure figures for both personal or cabin MITC exposure were measured particularly at the end of the decontamination period when decontamination of the endlands was performed which is explainable by release of MITC from Metam-sodium that leaked on the ground of the end lands or into shallow soil when the tractor was turning. In parcels 10 and 11 soil injection was performed by the same contractor using soil injection equipment with blow-through system. When the blow-through system was switched on considerably lower MITC exposure levels (about 6-

times lower) were measured in parcel 10 as compared to parcel 11 when the blow-through equipment was not operating. In parcel 11 leakage of Metam-sodium was reported from the injector thereby contributing to higher MITC exposure levels on personal and cabin measurements, respectively

The contribution of filling operations to exposure towards MITC was investigated on five separate measurements. For the treatment of parcels 2 and 9 a positive pressure filling system was used and virtually no MITC was detected during filling and measured personal and cabin MITC levels were in good agreement with each other. For the treatment of parcels 5 and 6 a vacuum filling system was used and relatively high MITC exposure levels amounting to 35, 58 and 77 $\mu\text{g MITC}/\text{m}^3$ were detected during filling. However, no clear conclusion can be drawn for parcels 5 and 6 since higher personal MITC exposure would have to be expected if filling contributes largely to exposure towards MITC. In addition, filling is assumed to represent a small fraction of the whole working period which relativises the exposure towards MITC found in parcels BG5 and 6 during filling operations, respectively.

B.8.8-5: Results of MITC concentration in air and operator exposure after application of Metam-sodium on bulb parcels

Parcel No. (Application rate L/ha)	MITC concentration in air (mg MITC /m ³)		MITC exposure (mg/person/d)*	
	Personal measurements	Tractor cabin measurements	Personal measurements	Tractor cabin measurements
1 (700)	0.045	0.041	0.397	0.359
2 (420)	0.006	0.006	0.056	0.054
3 (700)	0.037	0.025	0.325	0.216
4 (525)	0.047	0.031	0.412	0.267
5 (700)	0.109	0.119	0.951	1.044
6 (700)	0.170	0.187	1.491	1.637
7 (560)	0.044	0.042	0.388	0.370
8 (700)	0.105	0.070	0.918	0.612
9 (560)	0.162	0.159	1.421	1.392
10 (700)	0.011	0.013	0.100	0.116
11 (700)	0.068	0.066	0.597	0.574
Average parcels 1 - 11	0.073	0.069	0.641	0.604

*: assuming 7 h per working day, body weight: 70 kg/person, inhalation of 1.25 m³/hour

Conclusions:

Metam-sodium was applied for soil decontamination purposes onto 11 representative bulb parcels located in Province Holland during 25 July and 29 August 1992 at an application rate ranging from 420 L/ha to 700 L/ha (214 to 357 kg a.s./ha). The fields were classified as sandy soils in both areas.

Soil fumigation was conducted by eight different contractors who voluntarily took part in the exposure measurements during representative application of Metam-sodium. Three of the eight contractors were treating two parcels each. Prior to application of Metam-sodium the status of the contractors' personal equipment with regard to work clothes, type of footwear, gloves and face masks was recorded. All parcels were treated using specialized equipment, i.e. cultivator injectors which inject Metam-sodium into the soil at a depth of about 18 – 20 cm. One equipment used for this purpose was fitted with a blow-through device on the injector thereby reducing the loss of Metam-sodium when turning at the headlands. Immediately after injection the soil was compressed by one or two flat rollers one of which was a driven roller to ensure that the soil was well compressed and sealed. In all cases the injection activities were commenced on the

downwind side of the parcel thereby reducing additional exposure as a consequence of emission of MITC from parcels that were already treated.

The aim of this study was to determine the MITC concentration in air at operator level (outlet of the pump attached to the overall, within the tractor cabin) during the application of metam-sodium. No difference is observed between the measurements on the operator's overall and within the tractor cabin.

The MITC concentrations in air during metam-sodium application was in the range 0.006-0.187 mg MITC/m³. The MITC concentrations measured during the filling of the application equipment are within this range (0.035, 0.058 and 0.077 mg MITC/m³)

Methyl isothiocyanate volatilisation from fields treated with metam-sodium (Saeed et al, 2000)

Conclusions:

The publication properly describes the experimental design, analytical methods and results obtained.

The MITC concentrations in air after application of Metam-sodium by means of soil injection on two fields in Wisconsin are reported. Concentration of MITC in air at three heights (10, 100 and 200 cm) above 2 arable fields were measured following application of Metam-sodium formulation at an application rate of 480 l/ha corresponding to 166 kg a.s./ha. Maximum MITC concentrations in air were 7.4 µg/m³ recorded 10 cm above ground 6-8 h following application and minimum concentrations of 0.2 µg/m³ recorded 200 cm above ground 30 - 35 h following application.

Measured and computed concentrations of Methyl Isothiocyanate in the air around fumigated fields (van den Berg F., 1993)

Guidelines:

none

GLP:

No

Material and Methods :

The behaviour of Metam sodium and MITC in soil as well as the emission of MITC in the air was described by a computer simulation model and results compared with measured figures after soil injection application of Metam sodium into the soil of two selected fields in the Netherlands (field A near Valtermond and field B near Eeserveen). For both fields, Metam sodium was applied at an application rate of 300 L/ha (510 g Metam sodium/L) and injected at a depth of approx. 18 cm using a horizontal blade injector with spray nozzles below the blades and subsequent compression of the soil with a roller. The treated area comprised 5.9 ha for both fields. The two soils (A/B) had pH values of 4.3 (A) and 5.2 (B), the organic matter content was 13.8 % (A) and 6.2 % (B), the mineral fraction < 2 µm was 2.5 % (A) and 2.2 % (B), and the mineral fraction ranging from 2 – 50 µm was 7.2 % (A) and 6.2 % (B). During the first few weeks after soil injection the average temperatures in the plough layer of fields A and B were 12 °C and 11 °C, respectively. The concentration of MITC in the air around the two fields was measured four to five times in a period of 7 – 9 days following soil injection of Metam sodium. Sampling of MITC was accomplished by charcoal tubes and air samples were taken in a height of 1.5 m above the soil on each sampling day. Samples were collected at different sampling points with one to two samples taken upwind of the treated field and four to six samples taken at sites downwind of the treated field. Samples were stored under cool and dark conditions prior to extraction with acetone and analysis by GC with NP (nitrogen-phosphorus) detection.

The LOD was given with 2.0 µg/m³ for the measurements on field A (performed 1986) and 1.0 µg/m³ for the measurements on field B (performed 1987). The concentration patterns of MITC in the air around the treated field were calculated with the PAL (point-area-line) model which is based on the Gaussian plume concept where it is assumed that dispersion from point, area and line sources results in Gaussian distributions in both the lateral and vertical directions through the plume dispersing from that source. Input data for this model comprise field size (km) and orientation, source strength/rate of emission (g/m²/sec.) and source height (m). Hourly values of the MITC emission rate into the air were taken as the source strength and the source height was set to 0 m. In the PAL model the downwind concentration in the air calculated is proportional to the source strength. Further data required by the PAL model are wind speed, wind direction, atmospheric stability and mixing height.

Findings:

B.8.8-6: Measured concentrations of MITC in the air downwind of fields A and B * after injection of metham-sodium

Time after injection (days)	Emission rates ($\mu\text{g}/\text{m}^2/\text{sec}$)	Downwind distance (m)	Concentration in air ($\mu\text{g}/\text{m}^3$)	
			computed	measured
Field A				
1.9	0.80	0	4.7	< 2.0
1.9	0.80	51	2.4	< 2.0
1.9	0.80	192	0.8	3.1
2.9	1.30	0	3.9	2.7
2.9	1.30	55	2.0	2.6
5.0	1.10	0	14.0	2.1
5.0	1.10	150	8.2	2.9
6.9	0.79	0	1.8	< 2.0
6.9	0.79	51	1.0	< 2.0
6.9	0.79	99	0.7	< 2.0
Field B				
1.1	0.03	0	0.1	1.8
1.1	0.03	50	0.1	3.1
1.1	0.03	90	0.1	1.1
1.1	0.03	130	0.0	1.0
1.1	0.03	170	0.0	< 1.0
3.1	0.53	0	2.1	< 1.0
3.1	0.53	45	0.9	< 1.0
3.1	0.53	125	0.3	< 1.0
5.2	0.95	0	3.9	1.6
5.2	0.95	40	3.2	1.2
5.2	0.95	74	2.5	< 1.0
5.2	0.95	111	2.1	< 1.0
5.2	0.95	178	1.6	< 1.0
6.9	0.92	36	3.6	1.3
9.1	0.77	0	3.0	< 1.0
9.1	0.77	47	1.4	< 1.0
9.1	0.77	82	1.0	< 1.0
9.1	0.77	130	0.6	< 1.0
9.1	0.77	214	0.4	< 1.0

*Field A: pH 4.3; organic matter 13.8%; soil particle size: < 2 μm : 2.5%, 2-50 μm : 7.2%

Field A covered an area of 5.9 ha and was treated in early Oct. 1986

Field B: pH 5.2; organic matter 6.2%; soil particle size: < 2 μm : 2.2%, 2-50 μm : 6.2%

Field B covered an area of 3.4 ha and was treated end of Sep. 1987

Conclusions:

During the first 5 days after the injection of metam-sodium into the soil of the first field, the concentrations of MITC in air measured at downwind sites (sampling height 1.5 m above the soil surface) ranged up to a about 3 $\mu\text{g}/\text{m}^3$. Thereafter, the MITC concentration was below the detection limit of 2.0 $\mu\text{g}/\text{m}^3$. At sites downwind from the second field, concentrations of MITC in air of up to 3 $\mu\text{g}/\text{m}^3$ were measured one day after injection of metham-sodium. Measurements during the following 6 days resulted in concentrations up to 1.6 $\mu\text{g}/\text{m}^3$. Thereafter the concentrations were below the detection limit that was lowered from 2 to 1 $\mu\text{g}/\text{m}^3$.

Operator and bystander inhalatory exposure to MITC during and after breaking of the seal after soil fumigation with Metam-sodium (Schepel, E.G. and Dijksterhuis, A., 2003)

Guidelines:

no specific guideline indicated

GLP:

Yes

Materials and methods:*Test substance:*

Luxan Monam (Metam-sodium 510 g/L), batch: G070009514 (batch 1); G0A010564 (batch 2), purity: 508 g/l (batch 1); 501 g/l (batch 2)

Experimental design:

Metam-sodium was applied onto three sandy soil fields in the Northeast of the Netherlands with a rate of 300 l/ha of a 510 g/l Metam-sodium solution (153 kg a.s./ha). In every field of the study, two separate parts (2 ha each) were cultivated at different time points. Cultivation means breaking of the seal to let the remaining MITC dissipate from the soil. The breaking of the seal took place 14 to 17 days after fumigation (first time) and 21 to 33 days after fumigation (second time). All the investigations were done in the autumn (mid of October until mid of December) of 2001.

During the breaking of the seal (from the beginning until the end of cultivation of each test plot) air at the level of the tractor cabin and air from the breathing zone of the driver was sampled and was investigated for the amount of MITC. Furthermore, MITC concentration in the surroundings of the fields was measured by means of sampling pumps set up at 50 and 100 m downwind and at right angles to the wind direction. The pumps were installed at 1.5 m height. Sampling was performed at different time intervals after the soil breaking; 8 h sampling starting with the beginning of cultivation (subdivided in 2, 2, and 4 h sampling periods) and 4 h sampling starting 24 h after the cultivation.

The MITC exposure on the fields was measured under controlled conditions by means of tunnels with sampling pumps at the inlet and outlet of the air. Sampling was performed during different time intervals after the soil breaking to determine the emission flux for MITC directly at the soil surface.

Soil parameters such as soil temperature, pH, organic matter content were determined for each treated soil in addition to meteorological parameters such as wind speed, wind direction, air humidity and air temperature, respectively. Soil samples were taken one to two days before the breaking of the seal, in order to determine the MITC residue in the top layer of the soil.

MITC concentrations in air were determined by using air pumps with a flow-through of 40 L/h. Pumps were connected to an SKC adsorbent tube with petroleum based charcoal as the adsorbent material. After termination of sampling adsorbent material was extracted and extract analysed by GC/NPD.

Analytical methods:

Blank tests for determination of potential MITC background concentration in air were taken 25 meters from the edge of the field (windward side) for 8 h starting with the beginning of cultivation. Twenty-four hours after cultivation another measurement was made for 4 h. In addition the adsorption capacity of the adsorbent tubes used were investigated for the MITC air measurements and for the MITC emission flux measurements (i.e. breakthrough samples). In addition, a test was conducted to check if a known quantity of applied MITC is still quantifiable after 2 or 4 h of aeration and after sample preparation as for the other samples taken (fortification of SKC tubes – field spikes).

Findings:*Analytical investigations:*

Fortification experiments with SKC tubes (field spikes) demonstrated that average recovery of MITC at a level of 0.01 mg/l was 84 % and at a ten-fold higher level it was 82 %. These results are within the criteria for method validation (SANCO/825/00 rev. 6 “Guidance document on residue analytical methods” dated 20 June 2000).

On the basis of the analytical method used the limit of detection (LOD) was shown to be 0.01 mg/L in the extract. No penetration of MITC to a second SKC tube could be demonstrated and MITC was efficiently adsorbed onto the activated carbon (no breakthrough).

MITC concentrations in soil:

In untreated fields no MITC was found (controls). In treated fields MITC was found at levels of about 0.1 up to 14.96 µg/g dried soil 13 to 31 days after fumigation with Metam-sodium, which demonstrates the effectiveness of the sealing after application.

MITC concentrations at the breathing zone of driver and in the tractor cabin:

During the first soil cultivation 14-17 days after fumigation an amount of MITC was detected with an average exposure to MITC of 1.96 µg/m³ in the breathing zone and 2.09 µg/m³ in the cabin. When the soil cultivation was performed after 3 to 4.5 weeks, MITC was not detected in the driver's breathing zone nor in the cabin.

The highest MITC concentration was 4.62 µg/m³ at the breathing zone of a driver that did the cultivation 14 days after fumigation.

Table B.8.8-7: MITC concentrations in the driver's breathing zone and in the tractor cabin

Location/ fumigation date	Days after fumigation	MITC – breathing zone ($\mu\text{g}/\text{m}^3$)	MITC – cabin ($\mu\text{g}/\text{m}^3$)
Field 1/ 15 Oct 2001	17	<LOQ ¹⁾	0.97
	22	<LOQ	<LOQ
Field 2/ 25 Oct 2001	14	4.62	3.42
	21	<LOQ	<LOQ
Field 3 7 Nov 2001	14	1.26	1.88
	33	<LOQ	<LOQ

¹⁾ LOQ = Limit of quantification = 0.01 mg/l MITC in extract

MITC in the surroundings of the fields:

No MITC was detected in the air surrounding the fields 1 and 2 with one exception; for field 2, which was cultivated 15 days after fumigation and at < 50 m distance to the field a maximum concentration of MITC in air of $0.67 \mu\text{g}/\text{m}^3$ was determined.

In the surroundings of field 3, MITC was found in the air, when cultivation took place 14 days after fumigation. The downwind concentration of MITC in air was $8.88 \mu\text{g}/\text{m}^3$ at 50 m during the first 2 h but a rapid decrease to $0.63 \mu\text{g}/\text{m}^3$ was noted 6 to 10 h after the cultivation. At 100 m, MITC concentration in the air was $4.70 \mu\text{g}/\text{m}^3$ initially, but decreasing to $0.45 \mu\text{g}/\text{m}^3$ after 6 to 10 h after cultivation. When cultivation was done 33 days after fumigation, no MITC was detected in the surroundings

Table B.8.8-8: MITC concentrations in air surrounding the fields cultivated after fumigation

Field 1	0-2 h after cultivation	2-4 h after cultivation	4-8 h after cultivation	24-28 h after cultivation
day 17	<LOQ ¹⁾	n.a. ²⁾	n.a.	n.a.
day 21	<LOQ	n.a.	n.a.	n.a.
Field 2	0-2 h after cultivation	1-3 h after cultivation	6-10 h after cultivation	24-28 h after cultivation
day 14	<LOQ	<LOQ except left 50 m: $0.6660 \mu\text{g}/\text{m}^3$	<LOQ	<LOQ
day 21	<LOQ	<LOQ	<LOQ	<LOQ
Field 3	0-2 h after cultivation	2-4 h after cultivation	6-10 h after cultivation	24-28 h after cultivation
day 14	<LOQ except downwind: 50 m: $8.8834 \mu\text{g}/\text{m}^3$; 100 m: $4.6951 \mu\text{g}/\text{m}^3$	<LOQ except downwind: 50 m: $2.6038 \mu\text{g}/\text{m}^3$; 100 m: $1.2490 \mu\text{g}/\text{m}^3$	<LOQ except downwind: 50 m: $0.6331 \mu\text{g}/\text{m}^3$; 100 m: $0.4461 \mu\text{g}/\text{m}^3$	<LOQ
day 33	<LOQ	<LOQ	<LOQ	<LOQ

¹⁾ LOQ = Limit of quantification = 0.01 mg/l MITC in extract

²⁾ n.a. = not analysed

MITC emission flux:

For field 1, only in the first 2 h after breaking the seal a detectable flux of $8 \mu\text{g}/\text{m}^2\cdot\text{h}$ was found. On field 3, MITC was detected in the air in the tunnels with the highest flux ($18317 \mu\text{g}/\text{m}^2\cdot\text{h}$) determined in the first 2 h after cultivation 14 days after fumigation. The following day (24 h after breaking the seal) the flux was $610 \mu\text{g}/\text{m}^2\cdot\text{h}$.

Conclusion:

Inhalatory exposure to MITC for workers re-entering the fumigated field and potential bystanders was assessed during and after the first breaking of the seal after soil fumigation with Metam-sodium. MITC concentrations determined in the breathing zone of the drivers and in the tractor cabin (mean of 1.96 and $2.09 \mu\text{g}/\text{m}^3$, respectively; maximum level of $4.62 \mu\text{g}/\text{m}^3$) as well as concentrations from measurements surround the fields (maximum of $8.88 \mu\text{g}/\text{m}^3$ seen 2 h after cultivation) can be used to estimate potential worker and bystander exposure to MITC.

Emissie en Verspreiding van Methylisothiocyanat bij Grondontsmetting in Kassen (Emission and Spreading of Methyl Isothiocyanate with Soil Decontamination in Glasshouses) (den Tonkelaar and Heidema, 1988)

Guidelines:

no specific guideline indicated

GLP:

no

Materials and methods:

Test substance:

AAmonam GC (Metam-sodium 510 g/L), batch: not specified, purity: not specified

Experimental design:

The soil disinfection at an application rate of 1950 L/ha of a 510 g/L formulation (995 kg a.s./ha) was performed in a glasshouse (0.123 ha) located in 's-Gravensande (The Netherlands). The disinfection took place in the morning of 15 October 1986 by means of self-propelled tooth injector. Injection took place at a depth of 5-10 cm. After injection, the soil was covered within 5 to 10 minutes with a low-density polyethylene foil with a thickness of 30µm. After 7 days (morning of 22 October), the foil was thrown open and finally removed on 24 October.

The following parameters were continuously measured during the experiment:

- concentration of MITC in the glasshouse
- temperature under the foil in the glasshouse (2 places) and outside the glasshouse
- humidity in the glasshouse
- wind speed and direction outside the glasshouse

Several air samples were also taken outside the glasshouse at lee side and at 20 m distance of the glasshouse.

Analytical methods:

The MITC in the glasshouse was determined by infrared spectrometry (20 places for the samplings).

MITC concentrations in air outside the glasshouse were determined by using air pumps with a flow-through of 0.5-1.125 L/min. Pumps were connected to an SKC adsorbent tube with active carbon as the adsorbent material. After termination of sampling adsorbent material was extracted and extract analysed by GC/NPD. Samplings were made downwind of the glasshouse at two locations on the lee side and on two locations at 20 m distance

Findings:

Table B.8.8-9: Course of MITC concentrations in the greenhouse during a period of 5 days after soil injection application of Metam sodium at a rate of 1,950 L/ha

Time (h)	12	24	36	40	48	54	60	72	78	84	96	108	120
MITC (mg/m ³) ¹	65	52	40	49.5	33.7	51.6	42	22.6	27.9	17.9	8.4	8.4	4.7

¹: only approximate concentrations given, derived from the graphs in the study reports

The MITC concentrations on the lee side and at 20 m of the glasshouse were at levels of 0.15-0.25 mg/m³ for the first 100 hours after application. The MITC concentrations sharply decrease afterwards and reached a constant level of around 0.01 mg/m³ for 100-200 hours after application. The values are approximate concentrations derived from the graphs in the study reports.

Conclusions:

The study presents several shortcomings (reporting of raw data, reporting of the analytical validation). The RMS however considers that this data bring valuable information for the final risk assessment.

The soil disinfection at an application rate of 995 kg a.s./ha was performed in a glasshouse (0.123 ha) located in 's-Gravensande (The Netherlands).

MITC concentrations in the air of the greenhouse ranged from 65 mg/m³ on the day of application to 4.7 mg/m³ on day 5 after application (transient increase of MITC level at plastic removal). The MITC concentrations on the lee side and

at 20 m of the glasshouse were at levels of 0.15-0.25 mg/ m³ for the first 100 hours after application. The MITC concentrations sharply decrease afterwards and reached a constant level of around 0.01 mg/m³ for 100-200 hours after application.

Operator exposure to methyl isothiocyanate (MITC) and methyl isocyanate (MIC), and air monitoring of MITC, MIC, carbon disulfide and methylamine following use of metam sodium (Links IHM, et al., 2006)

Guidelines:

no specific guideline indicated

GLP:

no

Materials and methods:

Test substance:

Soluble concentrate (Metam-sodium 510 g/L), batch: G5A0041796, purity: not specified

Experimental design:

The soil disinfection at an application rate of 300 L/ha of a 510 g/L formulation (153 kg a.s./ha) was performed in a 6.5 hectare field located in Raven/ Eyendorf (Germany). The disinfection took place on 2nd November 2005, between 13:16 h and 18 h by means of a tractor mounted with a Rumpstad shear injector. The machine featured a working width of 3 meters. Metam sodium was loaded in the tank that was located at the front of the tractor. Via a flexible pressure tubing, metam-sodium was transported under pressure to the spray valves below the plough. The Rumpstad injected metam-sodium at a depth of 15 to 20 cm and worked the soil with a roto-tiller. After injection the soil was flattened with a roller that was part of the application equipment.

MITC and MIC concentrations in air were monitored at 16 locations at field boundaries (locations 1 to 8) and at 100-225 m distance from the field (locations 9 to 16). CS₂ and methylamine concentrations in air were monitored at 4 locations (1 to 4) at field boundary. The measurements started at 14:20-15:50 (during application) and lasted for 4 days (2-5 November).

The following meteorological parameters were continuously measured during the experiment: temperature relative humidity, wind speed and direction. Cloudiness was also reported twice a day.

The concentrations of MITC and MIC were measured at 16 locations around the field. The concentrations of CS₂ and methylamine were measured at 4 locations around the field.

Analytical methods:

MITC, CS₂, MIC and methylamine concentrations in air in the field were determined by using air pumps connected to an adsorbent tube. After termination of sampling adsorbent material was extracted and extract analysed by GC-NPD (MITC), GC-MS (CS₂) or HPLC (MIC and Methylamine).

Findings:

Table B.8.8-10: MIC and MITC concentrations (µg/ m³ air) at operator level during the application of metam sodium (one measurement on a 5 hour duration)

	On the operator	Inside tractor	Outside tractor
MIC	< 4	< 4	Sample lost
MITC	76.51	70.33	107.88

Table B.8.8-11: Range of MITC concentrations (µg/m³ air) in the field during a period of 0-4 days after soil injection application of Metam sodium

Location	Range of MITC concentration in µg/m ³	
1 (field boundary, upwind)	< 0.042	Measurements during the whole study duration
2 (field boundary, upwind)	< 0.042	Measurements during the whole study duration
3 (field boundary, downwind)	4.47 - 23.71	Measurements during the whole study duration

4 (field boundary, downwind)	< 0.042 – 1.82	Measurements during the whole study duration
5 (field boundary, upwind)	No valid result	-
6 (field boundary, downwind)	4.77 – 24.35	Measurements during the whole study duration
7 (field boundary, downwind)	4.21 – 13.31	Measurements during the whole study duration
8 (field boundary)	< 0.042 – 6.85	Measurements during the whole study duration
9 (100 m of the field, upwind)	(0.08)	Two valid measurements on 2/11 and 4/11
10 (100 m of the field, upwind)	(0.09)	One valid measurement on 4/11
11 (100 m of the field, upwind)	(0.04)	One valid measurement on 2/11
12 (100 m of the field, downwind)	0.66 – 3.62	Measurements during the whole study duration
13 (100 m of the field, downwind)	2.10 – 13.19	Measurements during the whole study duration
14 (100 m of the field, downwind)	< 0.042 – 35.96	Measurements during the whole study duration
15 (200 m of the field, upwind)	(0.10)	One valid measurement on 5/11
16 (200 m of the field, upwind)	(0.09)	One valid measurement on 5/11

* : The measurements on locations 5, 9, 10, 11, 15 and 16 were not considered in the final conclusions of the study.

Conclusions:

The soil disinfection at an application rate of 300 L/ha of a 510 g/L formulation (153 kg a.s./ha) was performed in a 6.5 hectare field located in Raven/ Eyendorf (Germany). The disinfection took place on 2nd November 2005.

MITC concentrations in the air at a distance of 0 to 100 m of the field during a period of 0-4 days after application were in the range <0.00004 to 0.036 mg/m³. MITC concentrations in the tractor cabin were at level of 0.070-0.076 mg/m³ during application.

Levels of CS₂, methylamine and MIC were respectively <0.4 mg/m³, <0.027 mg/m³, <0.004 mg/m³ (<LOD) at day 0-4 after application, for all samplings.

Predicted Emission rates of MITC into air in the EU using the FOCUS Groundwater Scenarios with the PRZM model (Jarvis, T., 2004)

Guidelines:

not applicable

GLP:

No (not applicable)

Modelling procedure:

“The operator exposure studies performed by Mulder et al (1994) and de Rooij et al (1993) were conducted in climates which are representative for the climatic conditions in Northern Europe. However, no corresponding studies after soil injection application of Metam sodium by field tractor-mounted equipment were performed in Southern Europe where climates are much warmer. In Southern Europe transformation rates of Metam sodium to MITC are assumed to be much higher which results in greater MITC emission rates and MITC concentrations and thus, a higher operator exposure towards MITC during soil injection application of Metam sodium. For extrapolation of the measured operator exposure figures obtained in the exposure studies performed under climatic conditions representative for Northern Europe to climatic conditions commonly observed in Southern Europe, modelling with PRZM within the Focus GW (groundwater) shell was conducted to estimate emission rates of MITC on the first day of application for different representative scenarios. The mean daily emission rates (in g/cm²/day) based on simulation of 26 years for application scenarios during spring, autumn and summer were estimated for different locations in Europe and application rates and the results of the estimates are presented in Table B.8.8-12. Applications in Hamburg during autumn and applications during summer in Seville are considered to be representative for typical applications in Northern and Southern Europe, respectively. In addition, the application scenario in Hamburg is comparable to that used in the study of de Rooij et al (1993) as regards application timing, dose rate and climate. The modelling results obtained from the Focus GW shell can therefore be applied for both extrapolation of the MITC concentration above treated fields and operator exposure assessment in Southern Europe. The comparison of the mean emission rates in Hamburg for applications during autumn (9.26E-06 g/cm²/day) with the mean emission rates estimated for applications in Seville during summer (2.73E-04 g/cm²/day) yield 30-fold higher emission rates for Seville. It can be reasonably estimated that 30 times higher emission rates on day one in the hot climates of Southern Europe will result in 30-times higher MITC concentration in the air when compared to the results of the operator studies performed by de Rooij et al (1993). For this assumption the faster photodegradation of MITC in the air is neglected.

Table B.8.8-12: PRZM modelling results for the mean volatilisation of MITC (in g/cm²/day) on the day of application in different climates and at different Metam sodium application rates

PRZM modelling results							
Carrots (Autumn, 800 l/ha)							
Chateaudun	Hamburg	Jokioinen	Kremsmunster	Piacenza	Porto	Seville	Thiva
1.01E-05	9.26E-06	9.67E-06	9.3E-06	-	1.82E-05		2.22E-05
Lettuce (Summer, 600 l/ha)							
Chateaudun	Hamburg	Jokioinen	Kremsmunster	Piacenza	Porto	Seville	Thiva
1.33E-05	6.62E-05	4.4E-05	5.76E-05	-	0.000173	0.000273	7.26E-05
Tomatoes (Spring, 1200l/ha)							
Chateaudun	Hamburg	Jokioinen	Kremsmunster	Piacenza	Porto	Seville	Thiva
8.48E-07	-	-	-	8.2E-06	7.29E-06	4.7E-05	4.91E-06

Conclusions:

On the basis of the volatilisation modelling, the notifier estimated that the operator exposure in Southern Europe (Sevilla) is 30 times higher than in the conditions of autumn uses in Northern Europe (Jokioinen) (where the various monitoring studies have been performed). (0.000273/ 9.67E-6).

This modelling indicated that the volatilisation is in the range 0.491-27 kg MITC/ ha/ day . This would correspond to 24 - 1350 mg MITC/m³ air if we assume equal distribution of MITC in a 2 m air layer above the field, with complete air renewal after 24 hours.

Focus models have been developed with the aim to provide accurate PEC_{gw}. It is not proven that these models are able to provide realistic PEC air for highly volatile substances. The results were included as additional information.

Betteley, 2001 (UCB 811/013383)

Method of calculation:

Calculation with Atmospheric Oxidation Program (based on Atkinson method, AOPWIN v1.90)

Findings and conclusions:

Metam-sodium:

Hydroxyl rate constant = $64,3 \cdot 10^{-12}$ cm³/molecule-sec

⇒ DT₅₀ = 1.997 hours

(assuming a hydroxyl radical concentration of 1.5×10^6 OH radicals/cm³)

Conclusions

Study is Acceptable. Metam-sodium is expected to be very rapidly degraded in air.

Photochemical degradation of Methyl isothiocyanate (MITC) in the gas phase (Parlar H. et al. 1987)

Guidelines:

OECD Test guideline on Photochemical Oxidative Degradation, UBA Berlin, 1986

GLP:

Yes

Material and Methods :

Test substance:

MITC, chemical purity: > 99%, supplier: Fluka

Experimental design:

To determine the direct photostability of MITC in the gas phase, the substance was irradiated with wavelengths above 290 nm at 30°C. Starting concentrations were 10^{-5} and 10^{-4} mol/l. The concentration of MITC and volatile conversion products were determined every 10-60 sec with a mass analyzer. All photoproducts with a concentration of 0.5% of the starting material were identified.

In addition, the stability of MITC towards OH-radicals was determined. The substance was irradiated with wavelengths above 230 nm at 30°C in the presence of HONO₂, which reacts under these conditions directly to HO- and NO₂-radicals. The starting concentration was 10^{-4} mol/l for MITC and 10^{-1} mol/l for HONO₂.

A xenon lamp with water-cooled Pyrex filter was used as the light source for irradiation above 290 nm. In the case of the OH-radicals experiment, a quartz filter was used for the wavelength area above 230 nm. Quantification was performed by a gas-phase mass analyzer which was directly connected to the irradiated reaction vessel.

Findings:

Table Irradiation of MITC with wavelengths above 290 nm in nitrogen and air

Initial concentration (mol/l)	Humidity (%)	Gas phase	K (sec ⁻¹)	DT ₅₀ (hours)
6.0×10^{-5}	40	Nitrogen	1.19×10^{-4}	1.6
4.0×10^{-5}	40	Nitrogen	5.20×10^{-5}	3.6
4.0×10^{-5}	40	Air	2.55×10^{-5}	7.6
4.8×10^{-5}	40	Air	2.90×10^{-5}	6.2
6.4×10^{-5}	40	Air	2.95×10^{-5}	6.4

"MITC can easily be degraded at wavelengths above 290 nm, which are representative for the troposphere. The half-life in the air varies between 6.2 and 7.6 hours. The reaction is accelerated if the experiments are done under nitrogen atmosphere. Under these conditions a half-life of 1.6 hours was observed, at an initial concentration of 6.0×10^{-5} mol/ml, corresponding to 150 ppm.

With the mass analyzer system and capillary GC/MS investigations some conversion products were identified after 5 hours irradiation: COS, CH₃NH₂, CO₂, CO, SO₂, CH₃CN and NH₃. The main reaction is the formation of SO₂ and CH₃CN. Addition of water leads to methylamine and COS. All substances formed react under the experimental conditions subsequently to mineralisation products such as NH₃, CO and CO₂.]

The results from this experiment with OH-radicals and irradiation showed that MITC reacts very rapidly with OH-radicals in the gas phase. A relative reaction constant of $16.0 \times 10^{12} \text{ cm}^3/\text{mol} \times \text{sec}$ was observed. In the presence of OOH-radicals, MITC is completely degraded in 30 min.”

Conclusions:

The study has been reevaluated. See below

Photochemical oxidative degradation of Methyl isothiocyanate in the gas phase (Zetzsch C. 1992(a))

Guidelines:

OECD Test guideline: Absolute methods to determine the rate of reaction with OH radicals, OECD/UBA, Berlin 1990

GLP:

Yes

Material and Methods :

Test substance :

Methyl isothiocyanate, chemical purity: >99.5%, supplier: Fluka

Experimental design :

The experimental technique used throughout this study is flash photolysis-resonance fluorescence. OH-radicals are produced by photolysis of water vapour by means of a VUV flash lamp, and the hydroxyl radical concentration is monitored by observation of the 308 nm resonance fluorescence after excitation with a gas discharge resonance lamp. From time-resolved detection of OH decays in the presence of reactive species the gas kinetic rate constant of the hydroxyl radical reaction with the test substance is deduced.

Findings:

The gas phase reaction of MITC with OH-radicals was studied in Argon at temperatures between 296 and 353 K with the flash photolysis-resonance fluorescence technique. All observed OH decays in the presence of the test substance were strictly monoexponential indicating pseudo first-order conditions. The apparent rate constants vary from 3.9 to $4.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ between 295 and 353 K, respectively. The observed reaction was probably an abstraction of an H atom, i.e. an OH attack at the methyl group.

From $k = 3.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at $T = 296 \text{ K}$ and a global tropospheric OH-radical concentration of $5 \times 10^5 \text{ cm}^{-3}$ the half-life of MITC was calculated to be 40 days. The degradation via reaction with OH radical is a relatively limited process.

Conclusions:

The study has been reevaluated. See below

Smog chamber investigation of the tropospheric degradation paths of Methyl isothiocyanate (Zetzsch C. 1992(b))

Guidelines:

OECD Draft Test guideline: Absolute methods to determine the rate of reaction with OH radicals, OECD/UBA, Berlin 1990

GLP:

Yes

Material and methods:

Test substance

MITC

Experimental design:

The experiments were performed at 300 ± 2 K in a 2.4 m^3 glass vessel in nitrogen atmosphere at 50% relative humidity and atmospheric pressure. The smog chamber was irradiated by metal vapour lamps with 3.5 mm borosilicate filter glass and a cut-off wavelength of 300 nm. The chamber was flushed by pure N_2 , known amounts of O_2 were added to achieve a mixing ratio between 60 ppm and atmospheric composition (21%). The OH-radicals are produced from different sources, such as direct photolysis of H_2O_2 or photolysis of HONO or from photochemical degradation of NO_2 . Ozone was produced by photolyzing O_2 under slow flow conditions.

MITC and the indicator compounds for OH were constantly monitored at 50 min intervals by capillary GC and FID/ECD detection.

Findings:

The tropospheric degradation of MITC was simulated in a smog chamber experiment at room temperature (300 K) in order to assess the environmental half-life of the compound. With the full spectrum of the solar simulator (cut-off at 300 nm) and using H_2O_2 as a precursor of OH, direct photolysis is observed to dominate in the observed decay, OH-radicals contributing less than 15% to the degradation. The photolytic rate constant was observed to be $2.2 \times 10^{-5} \text{ s}^{-1}$. The photolytic rate constant increases slightly with increasing levels of MITC, but drastically with decreasing levels of O_2 by more than a factor of three at 60 ppm O_2 in N_2 . This autocatalytic behaviour closely resembles that of CS_2 photolysis and may explain the observed quantum yield of almost 3 at initial levels of 30 ppb MITC and 21% O_2 .

For environmental solar irradiation conditions of July at sea level in middle Europe and assuming a quantum yield of one, a photolytic rate constant of $1.8 \times 10^{-6} \text{ s}^{-1}$ was obtained leading to a half-life of 4.5 days. If the determined quantum yield of 3 is considered, the half-life would be only 1.5 days, since the half-life is directly proportional to the quantum yield. This half-life is in very good agreement to the photolytic half-life of MITC determined in air.

Direct photolysis

Directed photolysis is observed to dominate in the observed decay of MITC. The photolytic rate constant was observed to be $2.2 \times 10^{-5} \text{ s}^{-1}$. For environmental solar irradiation conditions of July at sea level in middle Europe and assuming a quantum yield of one, a photolytic rate constant of $1.8 \times 10^{-6} \text{ s}^{-1}$ was obtained leading to a half-life of 4.5 days.

Reaction with OH radicals

Degradation by reaction with OH-radicals is a limited process (results in good agreement with the previous study by Zetzsch C. 1992(a))

Reaction with O₃ in the dark

The reaction of MITC with ozone is limited ($k_{(1000 \text{ ppm } \text{O}_3, \text{ in the dark})} = (3.0 \pm 2.2) \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$)

Products appearing from the degradation processes

The major degradation product is methyl isocyanate (CH_3NCO) that has been recovered at levels ranging from 31 to 63% of the MITC consumed, irrespective of the experimental conditions. The only other degradation products COS and SO_2 were found at lower level. No quantitative information on the production of these compounds could be obtained.

Conclusions:

The study has been reevaluated. See below

Added in June 2008 (< addendum dated June 2008) – peer reviewed in June 2008:

As point of clarification 4.7, the applicant had to provide a calculation on the photochemical degradation of active metabolite MITC in the atmosphere. The Notifier's position and the RMS conclusion which were reported in the addendum dated June 2008 are reported hereunder as the conclusion of the peer review.

Methylisothiocyanate (MITC) – stability in air (photochemical degradation) (Hooke K., Jarvis T, 2008)

The decomposition rate constant of methylisothiocyanate (MITC) in air occurring through reaction with hydroxyl radicals was estimated according to the method of Atkinson using the Atmospheric Oxidation Program (AOPWIN version 1.92, US EPA). This method estimates the rate constant for the atmospheric gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals and between ozone and olefinic/acetylenic compounds.

The decomposition rate constant of MITC in air following reaction with hydroxyl radicals was calculated to be $0.1360 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Assuming that the 12 hour daytime hydroxyl radical concentration is $1.5 \times 10^6 \text{ molecules.cm}^{-3}$, the half-life was calculated to be 78.6 days (12 hr day).

The decomposition rate constant of MITC in air following reaction with ozone was not calculated since only olefins and acetylenes are calculated.

However studies according to OECD guidance have been performed and provide further refinement of the half-life determination :

Study 1:

Photochemical degradation of Methyl isothiocyanate in the gas phase (Parlar H. et al. 1987)

Direct photolysis : 6.2-7.6 hours

In presence of OOH radicals, MITC is completely degraded in 30 minutes

Study 2:

Photochemical oxidative degradation of methyl isothiocyanate in the gas phase (Zetsch C. 1992a)

Half life: 40 days.

Study 3:

Smog chamber investigation of tropospheric degradation paths of Methyl isothiocyanate (Zetsch C. 1992b).

July, sea level middle Europe DT50: 4.5 days (quantum yield 1). If the determined quantum yield of 3 is considered, half life would only be 1.5 days.

The above studies were submitted in the EU dossier and summarized in the DAR. However, their results have not been considered in the final assessment since it is not possible to check the relevance of the study and to relate the DT50 determinations to real operator exposure situations.

The RMS has considered that the numerous field studies investigating the actual MITC concentrations in air were more appropriate to assess the behaviour in air. These studies were performed during the various steps of metam-sodium application (soil injection, seal breaking, soil injection in glasshouse) by professionals under the conditions of the practice (material, protective equipments, application period in autumn, realistic duration of the work). Data on the MITC concentrations in air at operator level (in the tractor) and at bystander level (at several meters of the field, outside the glasshouse) are available.

Conclusions of the peer review: a new data gap has been proposed

Added in August 2010

"A data gap to address the atmospheric fate and behaviour of MITC including global warming ozone depletion, long range transport and deposition, and to address the potential contamination of surface water and soil by deposition in the vicinity of the applied areas was identified by the meeting of experts."

Fate of methyl isothiocyanate (MITC) in air. (Terry A. (2010b)

Introduction

Metam-sodium, a soil fumigant, rapidly degrades to form the major degradation product Methyl Isothiocyanate (MITC). MITC has a high vapour pressure and is released as a gas upon degradation of metam-sodium. Consequently, there is known to be volatile loss of MITC from fields treated with metam-sodium. It is necessary to provide information on the fate of volatile pesticides in air as part of the registration/re-registration of pesticides in the European Union (EU) according to Directive 91/414/EEC (the Authorisation Directive; Anon, 1991).

The FOCUS Air Working Group (FOCUS, 2008) have suggested a tiered approach to evaluating the risk from volatile pesticides. Here the long term, long range risk from MITC will be examined, as the short range, short term risk associated with volatile loss of MITC has been investigated elsewhere (Terry, 2010).

Structure of atmosphere

The atmosphere can be divided into a surface boundary layer (the troposphere; ca 15 km high), the stratosphere (which includes the ozone layer and extends to 50 km above the earth's surface) and the mesosphere and ionosphere. The troposphere has a more stable, restricted movement phase closest to the ground (extending up to a few kilometres), and a more free-moving phase beyond that. Dispersion of a pesticide released into the stratified, more stable troposphere at the regional scale (defined by FOCUS as long-range transport; over ca 1000 km) is on the order of from hours to several days. Movement into the more free moving troposphere tends to take on the order of a few weeks to months. Therefore, the distance that a volatile pesticide will be transported depends on how long it resides in the atmosphere. Substances can be removed from the atmosphere *via* two mechanisms: transformation and deposition.

Transformation

Transformation of pesticides in air is not a consideration for short range transport, but becomes a significant factor for long range transport (LRT), because the “capacity for pesticides to be transported over long distances is a function of their atmospheric lifetime, which is the result of emission and removal processes” (FOCUS, 2008, page 45). In fact “long-range transport of pesticides will occur when compounds have a significant lifetime” (FOCUS, 2008, page 45).

There are two main transformation pathways for pesticides in the atmosphere:

- Photooxidative processes (indirect photolysis), reactions with photo-induced reactive species such as hydroxyl radicals (OH), ozone (O₃) and nitrate radicals (NO₃),
- light-induced reactions (direct photolysis), where pesticides are directly transformed following absorption of light. This is possible only for molecules absorbing at wavelengths greater than 290 nm.

Generally, the indirect processes are more important, with the reactions with hydroxyl radicals being the most significant. Reaction with ozone and nitrate radicals tends to be more significant for molecules with double or multiple bonds.

Deposition

Deposition is the removal of a substance from the air compartment to the aquatic or terrestrial compartment. Wet deposition is the removal of substances in precipitation, whereas dry deposition from the gaseous phase is the partitioning of substances to the soil or water phases, or uptake by plants. Pesticides can be in the gaseous phase or adsorbed to particles, and are usually distributed between these two phases. From the gaseous state, wet deposition occurs *via* dissolving of the substance in rain, and dry deposition by molecular, dispersive deposition. Material adsorbed to particles (aerosols) is subjected to wet deposition by rain out of aerosols, whereas loss of material adsorbed to particles by fall out constitutes dry deposition. There are many different factors, apart from the physico-chemical properties of the pesticide, that affect wet and dry deposition. No standard calculation frameworks with respect to the individual importance of these processes are available.

FOCUS trigger for Long Range Transport

The FOCUS air Working Group (FOCUS, 2008) concluded that a tiered approach for determining whether LRT needs to be considered can be applied. If the DT₅₀ in air obtained *via* a Structure Activity calculation is less than 2 days, then further consideration of LRT is not required. The 2 day trigger is somewhat arbitrary, but the workgroup considered this value conservative enough to give confidence that a DT₅₀ below 2 days would mean that a pesticide would not be subject to LRT. If the trigger is exceeded then the DT₅₀ in air can be experimentally determined in the laboratory. If this determination credibly returns a DT₅₀ value of less than 2 days then no further consideration of LRT is required. Where a DT₅₀ of less than 2 days cannot be established then LRT needs to be considered, but only generic advice was given about how to go about this. Consequently, determining the DT₅₀ in air constitutes an important first step in the evaluation of fate in air.

Transformation of MITC in air

Structure Activity (Atkinson calculation)

The Atkinson calculation uses a structural approach (based on a large database of measured values) to estimate the rate at which the test molecule might react with hydroxyl radicals, ozone and nitrate radicals. For MITC, the Atkinson calculation returns a DT₅₀ value of 78.6 days (12 hour day; 1.5 x 10⁶ hydroxyl radicals/cm³; Hooke and Jarvis, 2008).

Laboratory determinations of the fate of MITC in air

Three studies are available. The last of these (Zetzsch, 1992b) is the most informative and comprehensive and will be reported here in more detail than the other two.

Parlar (1987)

A study was conducted to investigate the degradation of MITC in air, in the laboratory, according to the EPA Guideline 161-4. This was prior to GLP. The study report gives a comprehensive description of the apparatus used and the analytical aspects of the study. An attempt was made to measure the direct photostability of MITC, with irradiation at >290 nm and this revealed that direct photodegradation was an important transformation process for MITC. However, no control substances were employed, and no direct measure of light intensity used was measured, such that the rate constant for the degradation (4×10^{-5} mol/L; corresponding to a half life of 7.6 hours) could not be extrapolated to environmentally relevant conditions.

In addition, the rate of reaction with hydroxyl radicals was measured by introducing hydroxyl radical-precursors and irradiating at >230 nm. In this case control substances with known reaction rates with hydroxyl radicals were also included such that a rate for reaction of MITC with hydroxyl radicals was derived ($k_{OH} 16 \times 10^{12}$ cm³/mol/sec, which is 2.657×10^{-11} cm³/molecule/sec). This translates to an environmental DT₅₀ (12 hour day; 1.5×10^6 hydroxyl radicals/cm³) of just 4.83 hours. However, no attempt was made to exclude the direct degradation of MITC, and this almost certainly led to an unreliable k_{OH} value.

Zetzsch (1992a)

An investigation was carried out to measure the degradation of MITC via reaction with hydroxyl radicals (Zetzsch, 1992a), according to the OECD guideline "Absolute methods to determine the rate of reaction with hydroxyl radicals" in "The rate of photochemical transformations of gaseous organic compounds in air under tropospheric conditions (1990)", under GLP.

This study employed Flash photolysis – Resonance Fluorescence (FP-RF), whereby hydroxyl radicals were formed in a reaction vessel by photolysis of water vapour by means of a flash lamp, in argon, and the decline of the produced hydroxyl radicals monitored by observation of the 308 nm resonance fluorescence after excitation with a gas discharge resonance lamp. From the time-resolved detection of the hydroxyl radical decays in the presence of the MITC the gas kinetic rate constant of the hydroxyl radical reaction with the test substance was deduced. The rate of reaction was measured at five different temperatures and the rate constant (3.9×10^{-13} cm³/sec at 23°C) deduced. This corresponds to an environmentally relevant DT₅₀ of 27.4 days (12 hour day; 1.5×10^6 hydroxyl radicals/cm³). It was determined that there was a small amount of direct photolytic degradation of MITC under these conditions, but that it was quantitatively insignificant.

Zetzsch (1992b)

The third investigation was a very intensive study of the fate in air of MITC using a very sophisticated smog chamber (Zetzsch), under GLP, carried out (as was Zetzsch, 1992a) at the Fraunhofer Institute in Germany. This experimental set up consisted of a 2.4 m³ reaction vessel, up to seven lamps (with assorted filters) and very sophisticated control and analytical facilities. The experiments were run in a nitrogen environment with variable, but precisely measured amounts of oxygen present. The investigation was prompted by the Zetzsch, 1992a study, because it wasn't clear what the theoretical transformation processes had been. This smog chamber investigation was designed to more closely examine the degradation process.

However, it became clear early on in the investigations that, against expectations, the direct photodegradation of MITC was a more important transformation process than the reaction of MITC with hydroxyl radicals. As such, investigations were undertaken which minimised the presence of hydroxyl radicals (or other reactive species) so that the direct photodegradation process could be studied more thoroughly. Conditions were found such that the direct photodegradation to be expected under environmentally relevant conditions could be measured (excluding an autocatalytic tendency of MITC, and at environmentally relevant oxygen levels). The absolute intensity and spectrum of the lamps were measured, as was the quantum yield. These data were compared to the spectrum and intensity of natural sunlight in July, at sea level, in middle Europe, and a rate constant of 1.8×10^{-6} /sec derived for these conditions. A first order DT₅₀ of 8.9 days (12 hour day) can be calculated from this rate constant.

These various reaction rates can be combined, as all these processes will be proceeding independently in the troposphere. Table 1 summarises the consequent rate constants and environmentally relevant DT_{50} values associated with them.

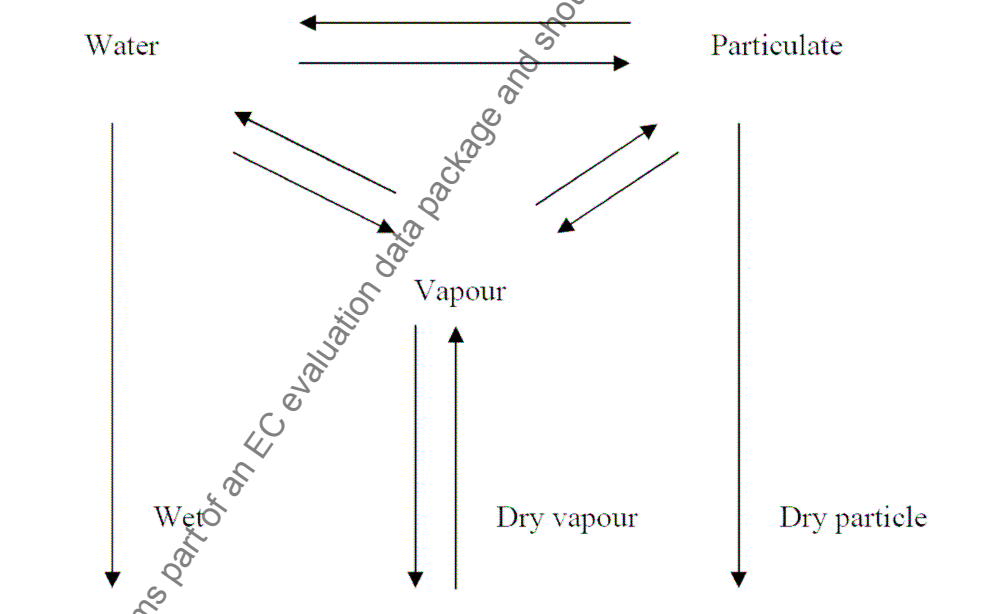
Table 1 Summary of Reaction Rates for MITC in Air (derived from Zetzsch, 1992b)

	Process	Rate Constant	DT ₅₀ in troposphere (12 hr, days)
1	Direct photodegradation	$1.8 \times 10^{-6}/\text{sec}$	8.9
2	Reaction with hydroxyl radicals	$7.65 \times 10^{-7}/\text{sec}$	22.0
3	Reaction with O(³ P) species	$7.5 \times 10^{-7}/\text{sec}$	21.4
4	Direct photodegradation and Reaction with hydroxyl radicals	$2.565 \times 10^{-6}/\text{sec}$	6.3
5	Direct photodegradation and Reaction with hydroxyl radicals and Reaction with O(³ P) species	$3.315 \times 10^{-6}/\text{sec}$	4.8

It can be seen that the maximum environmentally relevant DT₅₀ in air is 8.9 days, arising from direct photolysis alone, but that when the reaction with hydroxyl radicals is also factored in the DT₅₀ reduces to 6.3 days. Although there is uncertainty associated with the rate constant derived for the transformation mediated by the O(³P) species, this is clearly an important degradation pathway and including this process reduces the air DT₅₀ to 4.8 days. Given that transformation is only one of the removal processes at work in the troposphere (loss by deposition being the other significant process), these derived air transformation DT₅₀ values are worst case as a measure of the removal of MITC from air.

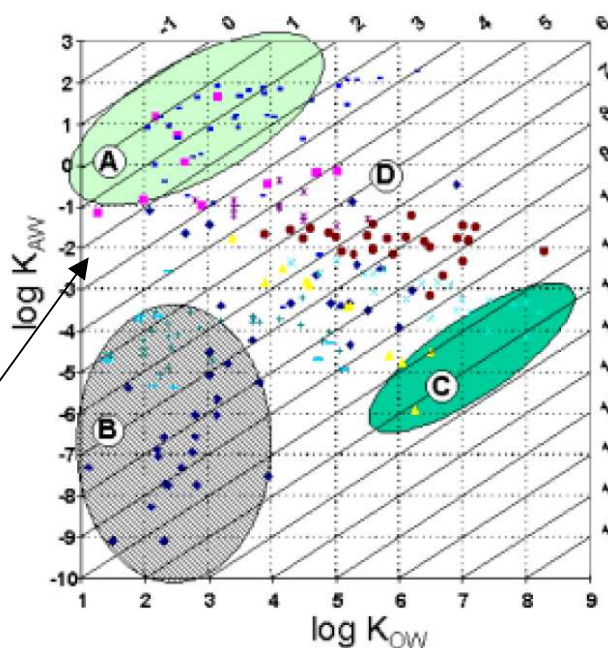
Removal of MITC in air by Deposition

Although there are many different factors, apart from the physico-chemical properties of the pesticide, that affect wet and dry deposition, it is clear that loss of pesticides from the air *via* deposition is an important removal process (FOCUS, 2008, and see Figure 1).

**Figure 1 Possible atmospheric partitioning pathways and deposition routes for pesticides in air**

However, no standard calculation frameworks for the estimation of removal rates *via* these processes is available. Nevertheless, it is possible to consider importance of these process in a qualitative manner.

On page 40 of the FOCUS_{AIR} document an approach is outlined which can help give an indication of the phases that a substance will likely equilibrate to ('environmental distribution'). A plot of logK_{OW} vs logK_{AW} (K_{AW} is the dimensionless Henrys Law Constant) is presented in Figure 2:



A: exists predominantly in air
B: exists predominantly in water
C: exists predominantly in soil
Others: multiple media chemicals
(van de Meent et al. 1998)

Figure 2 Distribution of substances between air sub-compartments according to physical properties (FOCUS, 2008, page 40)

The logK_{OW} for MITC is 1.05 (Flack, 1997), and the K_{AW} is given by:

$$K_{AW} = \frac{HLC}{RT}$$

Where HLC is the Henrys Law Constant, R is the universal gas constant (8.314) and T is the temperature (in °K).

The HLC for MITC is 14.2 Pa m³/mol (IIA 23.2-02), which gives a calculated K_{AW} of 5.829 x 10⁻³. Hence, logK_{AW} is -2.23. MITC's likely partitioning between the various air sub-compartments is indicated in Figure 2. It can be seen that MITC is likely to be found in air, but with a high affinity for water. Therefore, it is likely to be partitioned predominately between the air and atmospheric water (including aerosols). This implies that MITC is susceptible to both wet and dry deposition and that it will be readily scoured out of the air column by precipitation.

MITC Long Range Transport, potential contribution to global warming and ozone depletion

It can be seen from the considerations presented above that MITC has a transformational DT_{50} in air of between 4.8 and 6.3 days. In addition, this can be considered as an under estimation of the removal rate of MITC from air because it will also be subject to removal from the air by both wet and dry deposition.

Given this air DT_{50} range it is possible that MITC may be transported on a regional scale (up to 1000 km) via the constrained troposphere layer, but is unlikely to travel more widely because it is not persistent enough to move into the free moving troposphere layer (see section 1.1 above, and FOCUS, 2008). In addition, MITC is rapidly degraded in soil (DT_{50} 2.1 days), and is not unduly persistent in water (hydrolytic DT_{50} at pH 7 and 25°C of 50 days; Lowrie, 2005). MITC's relatively low LogP (1.05, Flack, 1997) also indicates that it will not bioaccumulate in the food chain. When all these factors are combined it is clear that MITC is not a threat to remote, pristine environments.

Ozone depletion potential of a substance depends on a number of factors (FOCUS, 2008). A main consideration is the persistence of the substance in the atmosphere being long enough so that significant quantities can reach the stratosphere. This requires an atmospheric residence time of >1 year. MITC clearly does not have such a long residence time in the atmosphere and was found to react only very slowly with ozone (Zetzsch, 1992b). As such, MITC cannot be considered as a candidate as an ozone depleting chemical.

Likewise, the global warming potential of a substance depends on the chemical's residence time in the atmosphere being >1 year (FOCUS, 2008, page 163). MITC clearly does not have such a long residence time in the atmosphere and so cannot be considered as a candidate as a contributor towards global warming.

Conclusions

MITC has been shown to have a worst case DT_{50} in air of between 4.8 and 6.3 days. Consideration of the removal from air of MITC via wet and dry deposition suggests that MITC's actual residence time in the atmosphere will be shorter than these determined transformational air DT_{50} values suggest. Although transport on a regional scale (up to 1000 km) cannot be ruled out, it is also clear that MITC will not be transported further than this, and together with MITC's non-persistence in soil and water, and its low bioaccumulation potential, mean that it is not a threat to remote, pristine environments. MITC's short atmospheric residence time (<<1 year) also means that it does not constitute a risk to the ozone layer, or contribute to global warming.

Conclusions of the RMS

It needs to be borne in mind that at this time there is no framework within Directive 91/414 to assess the risk arising from LRT, and particularly to the possibility of different sensitive species (FOCUS 2008).

The hazard potential to the atmosphere (long range transport) has been assessed according to the Focus guideline (2008). It depends strongly on the atmospheric residence time lifetime, which in turn depends on the rate by which removal processes (wet and dry deposition, chemical conversion) take place.

The estimation of the chemical conversion is based on the reassessment studies that have been submitted in the original dossier. MITC has been shown to have a DT_{50} in air of a few days (DT_{50} in troposphere (12 hr, days): 4.8-6.3 days), much less than 1 year. Even if the quality of studies and the accuracy of the results cannot be fully assessed by the RMS, similar estimations of degradation for other fumigants that have been performed by means of data proposed in the Guidance "Pesticides in air: considerations for Exposure assessment. SANCO/10553/2006 Rev 2 June 2008" indicate that the results are plausible (methylbromide, DT_{50} OH radicals: $5.5 \cdot 10^8$ days; 1-3 cis-dichloropropene, DT_{50} OH radicals and ozone: $1.9 \cdot 10^6$ days; chloropicrin, DT_{50} photolysis: 0.28 days; , methylisocyanate (degradate of MITC) DT_{50} photolysis: 2.39 days)

The estimation of removal of air by deposition has been performed on the basis of the physicochemical properties indicate that that MITC is likely to be found in air, but with a high affinity for water. Therefore, it is likely to be partitioned predominately between the air and atmospheric water (including aerosols). This implies that MITC is susceptible to both wet and dry deposition and that it will be readily removed of the air column by precipitation.

Short degradation rates of MITC in soil (DT_{50} 2.1 days) and in water (hydrolytic DT_{50} at pH 7 and 25°C of 50 days; Lowrie, 2005) as well as its low bioaccumulation potential (MITC's relatively low LogP: 1.05, Flack, 1997) indicate that the risk related to residues re-deposited in remote environments is negligible. MITC does not contain halogen atoms and has not been considered by Montreal convention as a compound responsible of ozone layer depletion.

B.8.9 Summary of behaviour in air and predicted environmental concentrations in air (PECa) (Annex IIIA 9.3)*Metam-sodium*

Atkinson calculation of the oxidative photodegradation of Metam-sodium: the hydroxyl rate constant obtained was $64.3 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$ and the half life was 1.997 hours based on 24h-day (assuming a hydroxyl radical concentration of $1.5 \times 10^6 \text{ OH}/\text{cm}^3$). The a.s. is not persistent in atmosphere.

Metam-sodium is moderately volatile (vapour pressure of $5.75 \cdot 10^{-2} \text{ Pa}$ at 25°C). It is very slightly volatile from water ($H = 1.28 \times 10^{-5} \text{ Pa}\cdot\text{m}^3/\text{mol}$ at 25°C).

MITC

As revealed by the various soil metabolism study and by the water/sediment studies, MITC is the most significant volatile compound that can potentially reach the air. MITC is considered to be a highly volatile substance (vapour pressure of 1739 Pa at 20°C , interpolated from measurements at 15°C and 25°C). MITC is moderately volatile from water ($H = 14.2 \text{ Pa}\cdot\text{m}^3/\text{mol}$ at 20°C)

The notifier submitted several field studies investigating the actual MITC concentrations in air. These studies were performed during the various steps of metam-sodium application (soil injection, seal breaking, soil injection in glasshouse) by professionals under the conditions of the practice (material, protective equipments, application period in autumn, realistic duration of the work). Data on the MITC concentrations in air at operator level (in the tractor) and at bystander level (at several meters of the field, outside the glasshouse) are available.

The rapporteur summarized the data in terms of MITC air concentrations expressed in mg/m^3

All the studies indicated that the largest amounts of MITC are released to air at soil injection and for a few days after application (1-5 days). The levels of MITC released afterwards and at seal breaking are much lower.

The levels of MITC at several meters from the field are low (in comparison with the levels released at application site) and transient (no detectable level after a few days)

A high variability of the MITC concentrations is observed for the various experiments. This variability cannot be explained in terms of application rate or material used.

Modelling simulations were provided by the notifier to evaluate the variability of MITC concentrations in air. The validity of these simulations is questionable.

Table B.8.9-1: Overview of the monitoring studies of MITC in air

Operation	Study location	Metam-sodium Application rate	MITC concentration in air at operator level	MITC concentration in air at bystander level	Reference
During soil-injection using tractor mounted equipment	15 fields, The Netherlands	153 kg a.s./ha	Inside the tractor: 0.012-0.169 mg MITC/m ³ levels after 2 minor incidents: contaminated gloves inside the cabin, contaminated soil on shoes: 0.189-0.592 mg MITC/m ³	outside the tractor: ND-0.054 mg MITC/m ³	(Mulder, A. et al, 1994)
During soil-injection using tractor mounted equipment (including tank filling)	11 fields, The Netherlands	214 to 357 kg a.s./ha	Inside the tractor: 0.006-0.187 mg MITC/m ³	-	(De Rooij, M. et al, 1993)
4-78 hours after soil-injection using tractor mounted equipment	2 fields, Wisconsin	166 kg a.s./ha.	-	Above the treated fields (samplings at 10-200 cm height, 4 to 78 hours after treatment): 0.0002-0.0074 mg MITC/m ³	(Saeed, I. et al., 2000)
1-5 days after soil-injection	2 fields, The Netherlands	153 kg a.s./ha.	-	at a distance of 0 to 214 m of the field : max level of 0.003 mg MITC/m ³ at day 1-5 after application	(van den Berg F., 1993)
During soil cultivation, 14-17 days after fumigation (seal breaking)	3 fields, The Netherlands	153 kg a.s./ha	Inside the tractor: ND-0.0046 mg MITC/m ³	-	(Schepel, E.G. and Dijksterhuis, A., 2003)
During soil cultivation, 3-4.5 weeks after fumigation (seal breaking)			Inside the tractor: ND	-	

Operation	Study location	Metam-sodium Application rate	MITC concentration in air at operator level	MITC concentration in air at bystander level	Reference
During soil-injection using self-propelled equipment	1 glasshouse, The Netherlands	994 kg a.s./ha	Inside the glasshouse (no operator present): maximum level of 65 mg MITC/ m ³ , 6 hours after treatment; Around 40 mg MITC/ m ³ , 0-3 days after treatment around 4.7 mg/m ³ at day 5	Outside the glasshouse (0-20 m distance): 0.15-0.25 mg MITC/ m ³ , 0-4 days after treatment; constant level of around 0.01 mg/m ³ for 4-8 days after application.	(den Tonkelaar and Heidema, 1988)
During soil-injection using self-propelled equipment	1 field, Germany	153 kg a.s./ha	Inside the tractor: 0.070-0.076 mg MITC/m ³	at a distance of 0 to 100 m of the field: highest residues levels found downwind of the field ; Levels of CS_2 <0.00004 (<LOD) to 0.036 mg MITC/m ³ at day 0-4 after application Levels of CS_2 <0.4 mg/m ³ (<LOD) at day 0-4 after application, for all samplings Levels of methylamine <0.027 mg/m ³ (<LOD) at day 0-4 after application, for all samplings Levels of MIC <0.004 mg/m ³ (<LOD) at day 0-4 after application, for all samplings	Links IHM, et al, 2006

The following MITC air concentrations are proposed for the operator/worker/ bystander exposure risk assessment.

Soil-injection using tractor mounted equipment (including tank filling)

- Exposure of the operator during soil-injection (including tank filling)

The level of 0.187 mg MITC/ m³ can be considered as a realistic worst case for operator exposure during soil injection. The max level is 0.592 mg MITC/m³ after minor incidents during application (contaminated gloves inside the cabin, contaminated soil on shoes)

- Exposure of the worker at seal removal (soil cultivation), cress test

The level of 0.0046 mg MITC/ m³ can be considered as a realistic worst case for worker exposure at seal removal and cress test.

- Exposure of the bystander during soil-injection

The level of 0.054 mg MITC/ m³ can be considered as a realistic worst case for bystander exposure during soil-injection of metam-sodium in field.

*Glasshouse use (drip irrigation system)**- Exposure of the operator*

The operator is not present in the glasshouse during application (closed system). Limited exposure can be expected during filling.

- Exposure of the worker at seal removal (soil cultivation), cress test

The level of 4.7 mg MITC/ m³ can be considered as a realistic worst case for worker exposure at seal removal and cress test.

- Exposure of the bystander

The level of 0.15-0.25 mg MITC/ m³, at 0-20 m distance, 0-4 days after treatment, can be considered as a realistic worst case for bystander exposure during the application of metam-sodium in glasshouse. Bystanders should not be allowed to stay near glasshouses (0-20 m) during treatments.

Exposure to CS₂, MIC, methylamine

Levels of CS₂, methylamine and MIC were respectively <0.4 mg/m³, <0.027 mg/m³, <0.004 mg/m³ (<LOD) at day 0-4 after soil injection. During this experiment, MITC has been recovered at level up to 0.036 mg/m³.

B.8.10 Definition of the residue (Annex IIA 7.3)*Soil*

Due to a rapid degradation of Metam-sodium in soil, the predominant metabolite methyl isothiocyanate (MITC) rather than the parent Metam-sodium is considered as the only relevant residue for quantitation in soil.

MITC was detected in amounts of up to 90% of the applied parent in the aerobic soil metabolism study and acts as soil fumigant against a variety of soil borne pests.

The aim of the risk assessment for this active substance is the establishment of the duration of the toxic effects to the soil organisms and of the duration of their recovery/recolonisation period.

Residue definition for risk assessment (soil): Metam-sodium, MITC

Residue definition for monitoring (soil): MITC

Water surface and sediment

Due to a pronounced instability of Metam-sodium in water and sediment (DT₅₀ whole system of 20 minutes), the predominant metabolite in water MITC rather than the parent Metam-sodium is considered as the only relevant residue in water and in sediment.

Other metabolites recovered in the water/sediment studies under aerobic and anaerobic conditions were lower than 5%AR after 8 hours.

Residue definition for risk assessment (surface water, sediment): MITC

Residue definition for monitoring (surface water, sediment): MITC

Ground water

Metam-sodium is rapidly degraded in the soil into MITC. The evaluation of possible groundwater contamination by the a.s. is not required.

Since the soil metabolite MITC was detected in soil in amounts greater than 5% of the applied parent, its relevance has to be checked according to the relevant guidance document (European Commission (2003): Guidance Document on the Assessment of the Relevance of Metabolites in Groundwater of Substances Regulated Under Council Directive 91/414/EEC, Sanco/221/2000-rev.10-final):

MITC is the major metabolite that is biologically active. This metabolite is toxicologically and ecotoxicologically relevant. This compound is fully assessed in the DAR.

Residue definition for risk assessment: MITC

Residue definition for monitoring : MITC

Air

Degradation of Metam-sodium in soil or water results in the rapid formation of volatile breakdown MITC that can enter the air, while metam-sodium itself is not volatile and therefore not supposed to reach the air.

Residue definition for risk assessment: MITC

Residue definition for monitoring : MITC

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.11 References relied on**B.8.11.1 Environmental fate and behaviour of the active substance (Annex IIA 7)**

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIA 7.1.1.1.1 /01	Burnett TJ	1987-05-08	VapamR aerobic soil metabolism Stauffer Chemical Company, PMS-226, MRC-87-21 GLP Not published	Y	USA TF
IIA 7.1.1.1.1 /02	Hall BE, Lowrie C, Morris A	2004-11-24	The degradation of [14C]-Metam Sodium and its Principal Degradation Product [14C]- MITC in Four Fresh Field Soils Inveresk, 24253 GLP Not published	Y	Taminco
IIA 7.1.1.1.2/ 01	Burnett TJ	1987-05-08	VapamR anaerobic soil metabolism Stauffer Chemical Company, PMS-194, MRC-87-22 GLP Not published	Y	USA TF
IIA 7.1.1.1.2 /02	Burnett TJ	1985-11-26	Photo-degradation of Vapam® on soil Stauffer Chemical Company, PMS – 166 MRC 85-07 Not GLP Not published	Y	USA TF
IIA 7.1.1.1.2 /03	Haag WR, Irwin K, Mill T	1989-01-12	Photolysis of Metam Sodium on Soil ICI Americas Inc., SRI 5915-3 GLP Not published	Y	USA TF
IIA 7.1.1.2.1 /01	Hall BE, Lowrie C, Morris A	2004-11-24	The degradation of [14C]-Metam Sodium and its Principal Degradation Product [14C]- MITC in Four Fresh Field Soils Inveresk, 24253 GLP Not published	Y	Taminco
IIA 7.1.1.2.1 /02	Burnett TJ	1987-05-08	VapamR aerobic soil metabolism Stauffer Chemical Company, PMS-226, MRC-87-21 GLP Not published	Y	USA TF
IIA 7.1.1.2.1/ 03	Völkel W.	2010-01-22	14C-N-N'-dimethylthiourea: Degradation and Metabolism in Four Soils Incubated under Aerobic Conditions Innovative Environmental Services Ltd. (IES), Witterswil, Switzerland Report No. 143 01 034 GLP: yes Not published	Y	Taminco

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIA 7.1.1.2.1/ 04	McMillan C.	2010-01-20	Determination of modelling endpoints for DMTU from laboratory degradation studies using ModelMaker4.0, according to Focus Kinetics. Cambridge Environmental Assessments, ADAS UK Ltd., Boxworth, Cambridge, United Kingdom Report No. CEA.525 GLP: yes Not published	Y	Taminco
IIA 7.1.1.2.1/ 05	Terry A.	2010-01-21	An Evaluation of the Fate in Soil of MITC under Aerobic Conditions Cambridge Environmental Assessments, ADAS, Boxworth, Cambridge, United Kingdom Report No. CEA.435 GLP: no Not published	Y	Taminco
IIA 7.1.1.2.1/ 06	McMillan C.	2010-01-20	Determination of modelling endpoints for MITC from laboratory degradation studies using ModelMaker4.0, according to Focus Kinetics. Cambridge Environmental Assessments, ADAS UK Ltd., Boxworth, Cambridge, United Kingdom Report No. CEA.526 GLP: no Not published	Y	Taminco
IIA 7.1.1.2.2 /01	Iwata Y	1989-11-28	Vapam®: Field Dissipation Study for Terrestrial Uses Leland, Mississippi, 1989 ICI Americas Inc. + Morse Laboratories, RR 89-064B GLP Not published	Y	USA TF
IIA 7.1.1.2.2 /02	Iwata Y	1989-11-28	Vapam: Field Dissipation Study for Terrestrial Uses Visalia, California, 1989 ICI Americas Inc. + Morse Laboratories, RR 89-065B GLP Not published	Y	USA TF
IIA 7.1.1.2.2 /03	Anonymous	1986-08-22	Metam sodium groundwater data call-in California field dissipation study Stauffer Chemical Company Not GLP Not published	Y	USA TF
IIA 7.1.1.2.2 /04	Anonymous	1986-03-07	Metam sodium groundwater data call-in Washington field dissipation studies Stauffer Chemical Company Not GLP Not published	Y	USA TF

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIA 7.1.1.2.2 /05	McKay JC	1987-10-15	Vapam® Field Dissipation study Stauffer Chemical Company, RRC 87-92 Not GLP Not published	Y	USA TF
IIA 7.1.2 /01	Dohn DR	1988-10-14	Stability of Metam-Sodium in Soil/Water Mixtures ICI WRC, PMS-317/WRC 88-61 Not GLP Not published	Y	USA TF
IIA 7.1.2 /02	Vonk JW, van den Hoven AM, van Osenbruggen WA	1985-12-9	Adsorption of metham-sodium on ditch-bottom sludge TNO, 85/03964/1306-14798/HV/GK R85/338 Not GLP Not published	N	Taminco
IIA 7.1.2 /03	Komatsu K	1990-03-23	Methyl Isothiocyanate: Adsorption in soil Japan Food Research Laboratories TM 82070013, BASF 90/10431 Not GLP Not published	Y	KST, Taminco
IIA 7.1.2/04	Völkel W.	2009-09-04	14C-N,N'-dimethylthiourea: adsorption/desorption on soil Innovative Environmental Services Ltd. (IES), Witterswil, Switzerland Report No. 143 01 011 GLP: yes Not published	Y	Taminco
IIA 7.1.2/05	Herrchen M.	2009-06-03	Determination of the Adsorption/Desorption of Methyl isothiocyanate (MITC) Fraunhofer Institute for Molecular Biology and Applied Ecology, Germany Report No. KST-008/7-13/1 GLP: yes Not published	Y	KST + Taminco
IIA 7.1.3.1 /01	Betteley J	2002-06-18	Metam Sodium – Soil Adsorption by HPLC Huntingdon Life Sciences Ltd., UCB 841/022456 GLP Not published	Y	Taminco, Buckman
IIA 7.1.3.3 /01	Fritsch HJ, Huber R	1995	Basamid granular – a halogen-free soil disinfectant BASF AG, Acta Hort. 382,76-85 Not GLP Published	N	public
IIA 7.2.1.3.1 /01	Hanstveit A.O.	2003-07-16	Biodegradation of metam sodium in an aerobic water/sediment system TNO, V4091/01 revised final report GLP Not published	Y	Taminco, Buckman, Cerexagri, FMC Foret, Lainco

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIA 7.2.1.3.2 /01	Cohen SP	1993-03-12	Potassium N-methyldithiocarbamate (PNMDC) Aerobic aquatic metabolism of PNMDC Center for Hazardous Materials Research, ME 9100132 GLP Not published	Y	USA TF
IIA 7.2.1.3.2 /02	Cohen SP	1992-09-21	Potassium N-methyldithiocarbamate (PNMDC) Anaerobic aquatic metabolism of PNMDC Center for Hazardous Materials Research, ME 9100133 GLP Not published	Y	USA TF
IIA 7.2.1.3.2 /03	Cohen SP	1993-03-12	Potassium N-methyldithiocarbamate (PNMDC) Supplemental report: Anaerobic aquatic metabolism of PNMDC. Isolation and identification of metabolites Center for Hazardous Materials Research, ME 9100133 GLP Not published	Y	USA TF
IIA 7.2.1.3.2 /04	Mason P., Terry A.	2010-22-01	ESTIMATION OF VOLATILISATION OF METHYL ISOTHIOCYANATE (MITC) FROM SEDIMENT/WATER SYSTEMS AT 12°C AND CONSEQUENCES FOR CHRONIC AQUATIC ECOTOXICOLOGY RISK Cambridge Environmental Assessments, ADAS, Boxworth, Cambridge, United Kingdom Report No. CEA.537 GLP: no Not published	Y	Taminco
IIA 7.4 /01	Notenboom J, Verschoor A, van der Linden A, van de Plassche E, Reuter C	1999-11-14	Pesticides in ground water: occurrence and ecological impacts RIVM, 601506002 Not GLP Published	N	public
IIA 7.4 /02	Anonymous	1984	The IPS Raw Water Monitoring and in depth analysis of the occurrence of the active ingredients of pesticides in drinking water resources IPS Not GLP Published	N	public

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIA 7.4 /03	Jüttner F	1992	Flavour compounds in weakly polluted rivers as a means to differentiate pollution sources Wat. Sci. Tech., Vol 25, No 2, pp 155-164 Not GLP Published	N	public
IIA 7.4 /04	Van den Berg F, Roos AH, Tuinstra LGMTh, Leistra M	1988-10	Concentrations of methyl isothiocyanate in the air near villages in the northeast of the Netherlands IOB + Rikilt Not GLP Not published	N	Taminco, KST, Cerexagri, Bayer

B.8.11.2 Environmental fate and behaviour of the formulations (Annex IIIA 9)

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIIA 9.2.1 /01	Jarvis T	2004-11-16	Predicted environmental concentrations of metam-sodium (as MITC) in groundwater in the EU using the FOCUS groundwater scenarios with the PRZM model Exponent International Ltd, TA 18804-1 Not published Not GLP	Y	Taminco
IIIA 9.2.1/02	Jarvis T	2007-06-29	Predicted environmental concentrations of metam-sodium (as MITC) in groundwater in the EU using the FOCUS groundwater scenarios with the PRZM and PEARL models Exponent International Ltd, TA 18804-1A Not published Not GLP	Y	Taminco
IIIA 9.2.1/03	Franey-Gardiner M., Terry A.	2010-01-22	PREDICTED ENVIRONMENTAL CONCENTRATIONS OF N,N'-DIMETHYLTHIOUREA (DMTU) IN GROUNDWATER IN THE EUROPEAN UNION USING THE FOCUS GROUNDWATER SCENARIOS Cambridge Environmental Assessments, ADAS, Boxworth, Cambridge, United Kingdom Report No. CEA.534 GLP: no Not published	Y	Taminco

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIIA 9.2.1/04	Terry A., Franey-Gardiner M., McMillan C.	2009-01-22	PREDICTED ENVIRONMENTAL CONCENTRATIONS OF METHYL ISOTHIOCYANATE (MITC) IN GROUNDWATER IN THE EUROPEAN UNION USING THE FOCUS GROUNDWATER SCENARIOS Cambridge Environmental Assessments, ADAS, Boxworth, Cambridge, United Kingdom Report No. CEA.532 GLP: no Not published	Y	Taminco
IIIA 9.3	Mulder A, Roosjen Js, Dijksterhuis A	1994	Blootstelling van de toepasser aan methylisothiocyanaat tijdens de grondontsmetting met metam-natrium in het fabrieksaardappelgebied (Exposure of the user to methylisothiocyanate during soil decontamination with Metam-sodium on industrial potato land) Hilbrands laboratorium voor bodemziekten, 9410 Not published Not GLP	Y	Taminco, Cerexagri
IIIA 9.3	de Rooij M, Dijksterhuis A, van Aartrijk J	1993-03	Blootstelling van de toepasser aan methylisothiocyanaat tijdens de grondontsmetting van bloembollenpercelen met metam-natrium (Exposure of the user to methylisothiocyanate during soil decontamination of bulb parcels with Metam-sodium) Stichting laboratorium voor bloembollen-onderzoek Lisse Not published Not GLP	Y	Taminco
IIIA 9.3	Links, IHM; Veldhof, RJG; Lurvink, MWM; Schouten, A; an Hemmen, G	2006-03-16	Operator exposure to methyl isothiocyanate (MITC) and methyl isocyanate (MIC), and air monitoring of MITC, MIC, carbon disulfide and methylamine following use of Metam-sodium TNO Zeist, V6654/01 GLP Not published	Y	Taminco
IIIA 9.3	Jarvis T.	2004-11-18	Predicted emission rates of MITC into air in the EU using the FOCUS Groundwater Scenarios with the PRZM model Exponent International Ltd, TA18804-3 Not published Not GLP	Y	Taminco

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIIA 9.2.3/03	Terry A., Franey-Gardiner M.	2010-01-25	Predicted environmental concentrations of methyl isothiocyanate (MITC) in surface waters in the European Union using the FOCUS Surface Water Scenarios. Cambridge Environmental Assessments ADAS Boxworth, Cambridge, United Kingdom Report No. CEA.533 GLP: no Not published	Y	Taminco
IIIA 9.2.3/04	Terry A., McMillan C.	2010-22-01	PREDICTION OF REDEPOSITION OF MITC TO SURFACE WATERS IN THE EU FOLLOWING APPLICATION OF METAM-SODIUM Cambridge Environmental Assessments ADAS, Boxworth, Cambridge, United Kingdom Report No. CEA.535 GLP: no Not published	Y	Taminco
IIIA 9.2.3/05	Hughes G.O.	2010-01-25	FOCUS Surface Water Scenario Contextualisation for Potatoes and Root Vegetables. Cambridge Environmental Assessments ADAS United Kingdom Report No. CEA.538 GLP ; no Not published.	Y	Taminco
IIIA 9.3/01	Terry A.	2010-22-01	FATE OF METHYL ISOTHIOCYANATE (MITC) IN AIR Cambridge Environmental Assessments, ADAS, Boxworth, Cambridge, United Kingdom Report No. CEA.536 GLP: no Not published	Y	Taminco
IIIA 9.3	Saeed IAM, Rouse DI, Harkin JM	2000	Methyl isothiocyanate volatilization from fields treated with metam-sodium Pest Manag Sci, 56:813-817 Not published GLP	N	public
IIIA 9.3	Van den Berg F	1993	Measured and computed concentrations of methyl isothiocyanate in the air around fumigated fields DLO Winand Staring Centre, Atmospheric Environment Vol 27A: 63-71 Not published GLP	N	public

Annex point / reference number	Author(s)	Date	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIIA 9.3	Schepel EG, Dijksterhuis A	2003	Operator and bystander inhalatory exposure to MITC during and after breaking of the seal after soil fumigation with Metam-sodium (including tunnel measurements) HLB, 193, project 2266 Published Not GLP	Y	Taminco
IIIA 9.3	den Tonkelaar WAM, Heidema LF	1988-11-21	Emissie en verspreiding van methylisothiocyanat bij grondontsmetting van kassen (Emission and spreading of methyl isothiocyanate with soil decontamination in glasshouses TNO, R 88/194A Not published Not GLP	N	Taminco, KST, Cerexagri, Bayer CS