

DATA EVALUATION RECORD

STUDY 2

CHEM 102001

Thiophanate-methyl

\$161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41482806

Soeda, Y., and H. Shiotani. 1990. Thiophanate-methyl - Photodegradation in water. Laboratory Project ID NISSO EC-74. Unpublished study performed by Nippon Soda Co., Ltd., Kanagawa, Japan, and submitted by Pennwalt Corporation, Philadelphia, PA.

STUDY ID 92186017

Soeda, Y. 1990. Phase 3 summary of existing study MRID 41482806; thiophanate-methyl - Photodegradation in water. Project EC-74. Prepared by Nippon Soda Co., Ltd., Kanagawa, Japan, and submitted by Pennwalt Corporation, Philadelphia, PA.

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study can be used to fulfill data requirements.
2. Thiophanate-methyl photodegraded with a half-life of 2.17 days in sterile aqueous pH 5 buffer solution that was irradiated with natural sunlight at 2.9-16.9 C for 5.5 days (sunlight quantum yield 5.97×10^{-3}). In the dark controls, thiophanate-methyl was relatively

stable. The degradates methyl 2-benzimidazolylcarbamate (MBC) and methyl N-[2-(N'-methoxycarbonylthioureido)phenyl-aminocarbonyl]-carbamate (DX-105) were isolated in both irradiated and dark control solutions. Dimethyl [(1,2-phenylene)bis(iminocarbonyl)]bis(carbamate) (FH-432) was isolated in the irradiated solution only.

3. This study is acceptable and fulfills EPA data requirements for Registering Pesticides by providing information on the photodegradation of phenyl ring-labeled [¹⁴C]thiophanate-methyl in sterile aqueous buffered pH 5 solution at 2.9-16.9 C.
4. No additional information on the photodegradation of thiophanate-methyl in water is required at this time.

METHODOLOGY:

Phenyl ring-labeled [¹⁴C]thiophanate-methyl (radiochemical purity >99%, specific activity 15 mCi/mmol, Amersham International) was added at 10 ppm to an aqueous buffered pH 5 solution (0.04 M acetate). The solution was filter-sterilized (0.2 um) and added to quartz tubes (11 x 130 mm) that were then sealed with glass stoppers. In order to serve as dark controls, half of the tubes were wrapped with aluminum foil. The tubes were placed on a black rubber sheet outdoors in Kanagawa, Japan (35 N, 139 11' E), oriented at a 30-degree angle with respect to the horizontal with the upper end pointing due north. The area was reported to be "free of shade and reflections of sunlight". To determine the sunlight quantum yield, a standard p-nitroacetophenone-pyridine actinometer was used. An aqueous solution containing 10⁻⁵ M p-nitroacetophenone plus 0.18 M pyridine was added to quartz tubes, which were placed outdoors along with the thiophanate-methyl test solutions. All solutions were irradiated with sunlight from December 8 (noon) to 15, 1986. Air temperatures, measured three times per day during the experiment, ranged from 2.9 to 16.3 C (Table 2). Duplicate tubes of the irradiated and dark control thiophanate-methyl solutions and the p-nitroacetophenone-pyridine solution were sampled at 0, 0.5, 1, 2, 4, and 5.5 days posttreatment.

Aliquots of the irradiated and dark control thiophanate-methyl solutions were analyzed for total radioactivity by LSC. Additional aliquots were analyzed for parent thiophanate-methyl directly by HPLC using a gradient of acetonitrile:water (1:1) and an unspecified method of detection; the detection limit was 5 ng. Aliquots of all irradiated thiophanate-methyl solutions and dark control solutions sampled at 2 and 5.5 days posttreatment were analyzed for thiophanate-methyl and its degradates by TLC. Aliquots of the solutions were extracted twice with methylene chloride. The extraction efficiencies ranged from 91.8 to 98.8%. The methylene chloride extracts were concentrated to dryness under reduced pressure. The residue was dissolved in methylene chloride and analyzed by one- and two-dimensional TLC on silica gel plates; one-

dimensional TLC was used for the basic quantitative analysis, and two-dimensional TLC was used to separate and quantify thiophanate-methyl and an unidentified degradate (Unknown 1). The solvent systems used were benzene:methanol:acetic acid (90:10:2, v:v:v) in the first direction and ethyl acetate:methylene chloride:acetic acid (50:50:2:1, v:v:v:v) in the second direction. Following development, radioactive areas were located by autoradiography, identified by comparison to R_f values of reference standards, and quantified by LSC. The method detection limit for TLC analysis was 0.004 ppm. The identities of major [^{14}C]compounds were confirmed by MS. The compounds were extracted from the TLC plates and purified by HPLC using methanol:methylene chloride (4:96, v:v) and an unspecified method of detection. Following purification, the identities of the [^{14}C]compounds were analyzed by MS in the EI mode.

The p-nitroacetophenone-pyridine actinometer solutions were analyzed for p-nitroacetophenone directly by HPLC with a gradient of acetonitrile:acetic acid:water (47.5:2.5:50, v:v:v) and an unspecified method of detection. The detection limit was not provided.

DATA SUMMARY:

Phenyl ring-labeled [^{14}C]thiophanate-methyl (radiochemical purity >99%), at 10 ppm, photodegraded with a registrant-calculated half-life of 2.17 days in sterile aqueous buffered pH 5 solutions that were irradiated with sunlight outdoors in Japan (Kanagawa; 35N and 139, 11'E) during December 1986. During the study, air temperatures ranged from 2.9 to 16.3 C. The sunlight quantum yield was determined to be 5.97×10^{-3} based on the results obtained from a standard p-nitroacetophenone-pyridine actinometer. Using TLC, [^{14}C]thiophanate-methyl in the irradiated solution accounted for 63.4% of the applied at 2 hours, 28.1% at 4 hours, and 12.5% at 5.5 hours (Table 4). The two major degradates,

methyl 2-benzimidazolylcarbamate (MBC) and

methyl N-[2-(N'-methoxycarbonylthioureido)phenyl-aminocarbonyl]-carbamate (DX-105),

reached maximum concentrations of 49.7 and 14.3% of the applied, respectively, at 5.5 days posttreatment.

Dimethyl [(1,2-phenylene)bis(iminocarbonyl)]bis(carbamate) (FH-432) and

two unidentified degradates (Unknowns 1 and 2) each reached maximum concentrations of 3.5-5.6% of the applied radioactivity, and at least six unidentified minor degradates ("Others") totaled up to 4.8% of the applied radioactivity. Unextracted radioactivity was a maximum of 7.3% of the applied at 5.5 days posttreatment.

In the dark control solution, thiophanate-methyl was relatively stable, and was present at 90.8% of the applied at 5.5 days posttreatment (Table 4). Based on TLC analysis of the 2- and 5.5-day dark control solutions, the degradates DX-105 and MBC were $\leq 2.0\%$ of the applied, and unidentified degradates ("Others") were $\leq 4.0\%$ of the applied. Unextracted radioactivity was a maximum of 1.8%.

Material balances for the irradiated and dark control solutions ranged from 98.8 to 101.9% of the applied.

COMMENTS:

1. The temperature was not maintained constant at 25 ± 1 C, as required by Subdivision N guidelines for photolysis studies. The study authors stated that the temperature was not controlled in order to determine the degradation patterns under "general practice".
2. Complete descriptions of the analytical methodology were not provided. For HPLC analysis, the method of detection that was used was not stated. For TLC analysis, it was not stated whether the [14 C]compounds were identified by comparison to the R_f values of reference standards that were chromatographed previously or to reference standards cochromatographed with the methylene chloride extracts. The R_f values of thiophanate-methyl and three degradates were provided in Table 1 of the original document.
3. The photodegradation half-life of thiophanate-methyl reported in the data summary of this review was calculated by linear regression. In addition, theoretical photodegradation half-lives of thiophanate-methyl were calculated using the quantum yield data obtained with the chemical actinometer; it was predicted that thiophanate-methyl photodegradation half-lives under clear skies would be 0.53 days for the summer, 0.66 days for the spring, and 2.48 days for the winter.
4. In the methods section of the document, the study authors incorrectly reported the final sampling interval as 7 days, rather than the correct interval of 5.5 days as indicated in the data tables.
5. The pH 5 buffered solution was selected for the definitive study since thiophanate-methyl is more hydrolytically stable at pH 5 than at pH 7 or 9.
6. The solubility of thiophanate-methyl in distilled water was reported to be 21.8 ppm at pH 5.2 and 25 C.
7. The absorbance spectrum of thiophanate-methyl in the pH 5 buffered solution is presented in Attachment 4. The spectrum shows maximum absorbance ca. 270 nm. Because the optical pathlength of the cell was not reported, the molar absorptivity for this chromophore could not be estimated.

8. Recovery efficiencies from fortified samples were not provided.
9. The study authors stated that volatile traps were not used in the study since results from a preliminary study indicated that there was no evidence that volatilization might occur. The material balances obtained for the definitive study show that volatilization was negligible.

Table 1 Rf values of thiophanate-methyl related compounds.

Compound	Rf in TLC*	
	A	B
TM	0.26	0.56
DX-105	0.20	0.46
FH-432	0.17	0.29
MBC	0.30	0.39

* TLC conditions

A : Merck Art. 5554,
Benzene : MeOH : AcOH (90:10:2)

B : Merck Art. 5554,
EtOAc : CH₂Cl₂ : acetone : AcOH (50:50:2:1)

Table 2 Weather conditions and photolysis time during sunlight photodegradation experiment of thiophanate-methyl.

Date (1986)	Sunrise	Sunset	Sunlight hours	Weather	Temp. (°C) at time		
					3:00	10:00	15:00
12/ 8	6:37	16:28	9.9	Sunny	-	10.3	12.8
9	6:38	16:28	9.8	Sunny	2.9	12.6	15.7
10	6:39	16:28	9.8	Sunny/cloud	3.3	13.0	16.2
11	6:40	16:28	9.8	Sunny	9.0	14.4	16.3
12	6:41	16:28	9.8	Sunny	6.4	13.1	14.7
13	6:41	16:28	9.8	Sunny	4.2	12.8	16.0
14	6:42	16:29	9.8	Cloudy/rain	9.7	10.7	13.6
15	6:43	16:29	9.8	Cloudy/rain	10.4	10.3	-

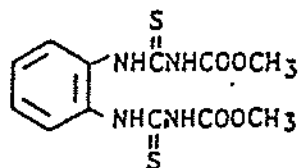
Date (1986)	Times photolyzed			Photolysis time for each date (day)
12/ 8	12:00	to 16:28	(4.5/9.9)	0.45
9	6:38	to 12:00	(5.4/9.8)	0.55
9	12:00	to 16:28	(4.4/9.8)	0.45
10	6:39	to 12:00	(5.4/9.8)	0.55
10	12:00	to 16:28	(4.4/9.8)	0.45
11	6:40	to 16:28	(9.8/9.8)	1.00
12	6:40	to 12:00	(5.4/9.8)	0.55
12	12:00	to 16:28	(4.4/9.8)	0.45
13	6:41	to 16:28	(9.8/9.8)	1.00
14	-	-	-	0.00
15	-	-	-	0.00
12/8-15	-	-	-	5.45

Table 4 The amount of ¹⁴C-thiophanate-methyl and its photo-products in water in sunlight and darkness.

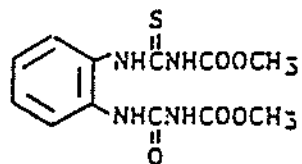
Fraction & compound	% of applied ¹⁴ C at exposure time (day)					
	0	0.5	1.0	2.0	4.0	5.5
Sunlight						
Extractable ¹⁴ C	98.8	98.9	100.0	97.0	93.9	91.8
TM	92.5	85.9	81.4	63.4	28.1	12.5
DX-105	2.0	3.2	6.3	8.5	11.5	14.3
FH-432	0.0	0.0	0.0	0.0	2.8	4.4
MBC	1.8	4.3	5.4	13.1	38.0	49.7
UK1	0.6	0.7	1.0	2.0	3.5	2.5
UK2	0.0	0.0	2.6	5.5	5.6	4.3
Others*	1.9	4.8	3.3	4.5	4.4	4.1
Aqueous ¹⁴ C	1.2	1.5	1.5	3.0	4.9	7.3
Total ¹⁴ C	100.0	100.4	101.5	100.0	98.8	99.1
Darkness						
Extractable ¹⁴ C	-	99.5	100.8	99.1	98.8	98.6
TM	-	-	-	91.9	-	90.8
DX-105	-	-	-	2.0	-	2.0
FH-432	-	-	-	0.0	-	0.0
MBC	-	-	-	1.8	-	1.8
Others	-	-	-	3.3	-	4.0
Aqueous ¹⁴ C	-	1.3	1.1	1.8	1.6	1.7
Total ¹⁴ C	-	100.8	101.9	100.9	100.4	100.3

* Consisted of at least six minor compounds including those remaining at the TLC origin.

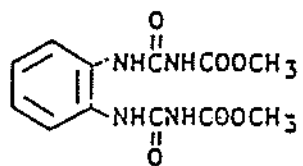
Dimethyl [(1,2-phenylene)bis(imino-carbonothioyl)]bis(carbamate)
(Thiophanate-methyl, TM)



Methyl N-[2-(N'-methoxycarbonylthioureido)phenylaminocarbonyl]-carbamate (DX-105)



Dimethyl [(1,2-phenylene)bis(imino-carbonyl)]bis(carbamate)
(FH-432)



Methyl 2-benzimidazolylcarbamate
(MBC)

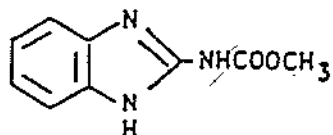
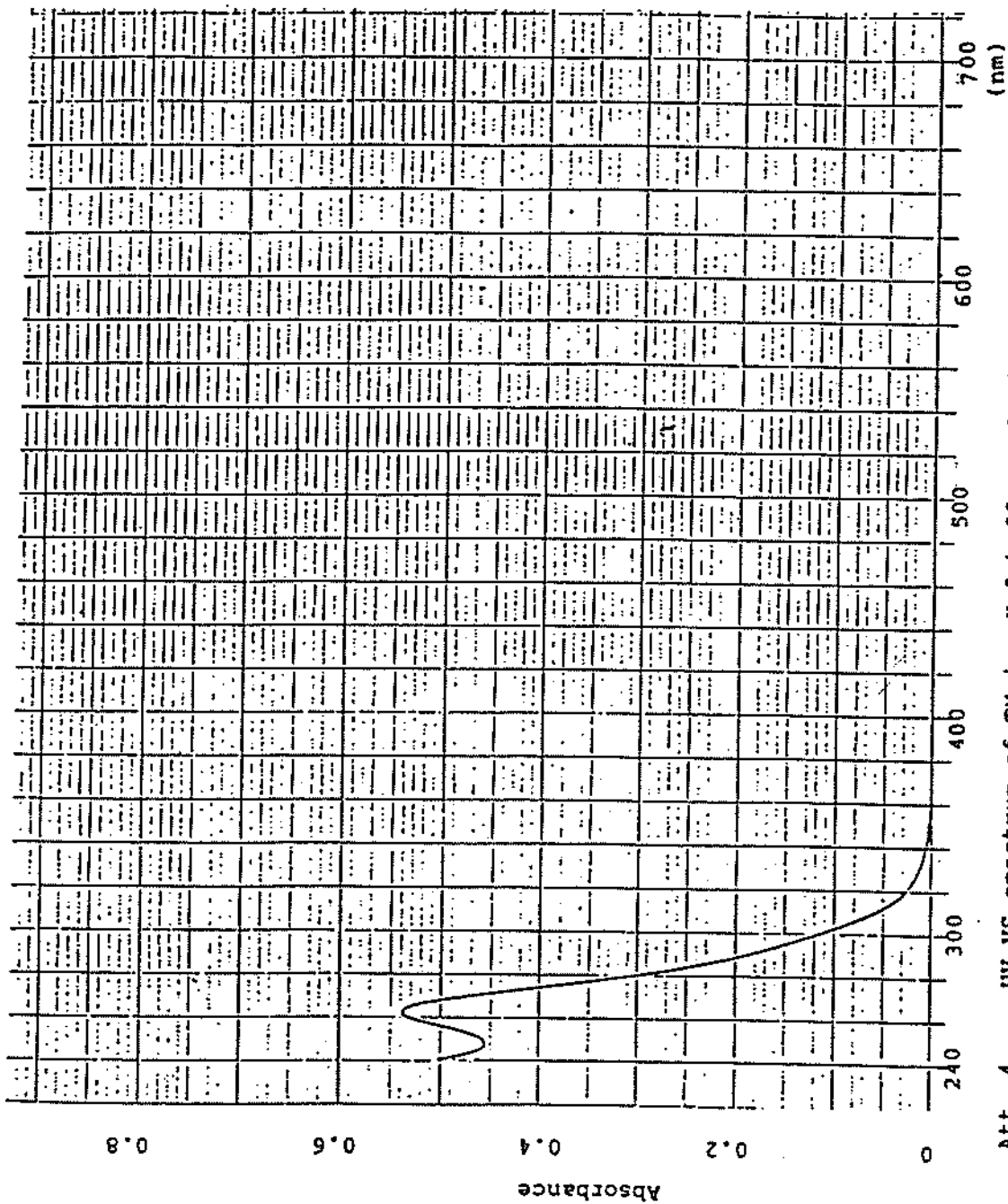


Fig. 1 Chemical names and structural formulas of TM and related compounds.



Att. 4 UV-VS spectrum of TM in pH 5 buffer solution(10ppm).