DYNAMAC
CORPORATION

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METHOMYL

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate Assessment

Contract No. 68-02-4250

SEPTEMBER 29,1987

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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INTRODUCTION

Methomyl is a broad-spectrum insecticide registered for use on a variety of terrestrial food crop, terrestrial nonfood (tobacco, ornamental plants, lawns, and turf), greenhouse food crop, greenhouse nonfood, aquatic food crop (watercress) and indoor sites. It is primarily used as a foliar spray, but may be used to treat soil or as a bait. Methomyl can be translocated within the plant. Single active ingredient formulations are: 2 and 5% D; 1-5% G; 2% P/T; 90% SC/S; 1.8 and 2.4 lb/gallon SC/L; and 1% RTU. It is applied at 0.042-1.0 lb/A, except to orchard (0.452-1.8 lb/A), lawn and turf (0.9-1.8 lb/A), and indoor (0.054-2.72 lb/A) sites. Multiple applications can be used. Methomyl may be formulated with (Z)-9-tricosene, cryolite, B. thuringiensis, maneb, and O,S-dimethyl acetylphosphoramidothioate. It may be applied using ground equipment or aircraft. Methomyl is a Restricted Use Pesticide. The vapor pressure of methomyl is 5.5×10^{-5} mm Hg.

CASE GS0028 METHOMYL STUDY 1 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00131249 CONTENT CAT 01

Friedman, P. 1983. Hydrolysis of 1-^{14}C-methomyl. Document No. AMR-109-83. Unpublished study received Oct. 3, 1983 under 352-366; submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE; CDL:251424-B.

SUBST. CLASS = S.

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CONCLUSIONS:

Degradation - Hydrolysis

1. This study is acceptable.

2. [1-^{14}C]Methomyl (radiochemical purity 95.5%), at 10 and 100 ppm, was relatively stable in pH 5 and 7 sterile aqueous buffered solutions incubated in the dark at 25°C for 30 days. In a pH 9 solution, [^{14}C]methomyl degraded with a half-life of ~30 days, at which time 50-54% of the applied radioactivity was methomyl. At 30 days, the degradate S-methyl-N-hydroxythioacetimidate was the only degradate in the pH 9 solution and accounted for 40-44% of the applied.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of methomyl in buffered solutions of pH 5, 7, and 9 at 25°C.

MATERIALS AND METHODS:

[1-^{14}C]Methomyl (radiochemical purity 95.5%, specific activity 16 μCi/mg, Du Pont de Nemours and Company) was added at 10 and 100 ppm to sterile

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aqueous buffered solutions (pH 5, 7, and 9) of 0.008 M. The solutions were incubated in stoppered flasks in the dark at 25°C, and sampled at intervals between 0 and 30 days posttreatment.

Aliquots of each sample were analyzed for total radioactivity by LSC. Additional aliquots were adjusted to between pH 3-4 with formic acid and were analyzed for methomyl and its degradates by HPLC with LSC.

REPORTED RESULTS:

[^{14}C]Methomyl was stable in the pH 5 and 7 solutions; an average of 93% of the applied was methomyl at all sampling intervals. In the pH 9 solution, [^{14}C]methomyl degraded with a half-life of 30 days (Table 1). The degradate S-methyl-N-hydroxythioacetimidate accounted for 41-44% of the applied radioactivity at 30 days posttreatment.

DISCUSSION:

1. The study author stated that [^{14}C]methomyl did not degrade (93% of the applied methomyl recovered at all sampling intervals) in pH 5 and 7 treated solutions at 1 and 10 ppm; however, no quantitative data were provided.

2. It appears that there was no replication of treatments or sampling.

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Table 1. Distribution of radioactivity (% of the applied) in pH 9 sterile aqueous buffered solutions treated with [^{14}C]methomyl (radiochemical purity 95.5%) at 10 and 100 ppm and incubated in the dark at 25 ± 1°C.[a]

Sampling interval (days)	Methomyl	S-methyl-N-hydroxy-thioacetimidate
	10 ppm	
0	90	2
0.17	89	1
1	90	3
2	87	6
3	86	8
6	80	11
9	80	16
14	67	27
21	60	34
30	50	44
	100 ppm	
0	94	2
0.17	94	2
1	92	3
2	90	5
3	89	6
6	84	11
9	79	17
14	71	24
21	64	32
30	54	41

[a] Data obtained from Table 1 in the original document.

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CASE GS0028 METHOMYL STUDY 2 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00161885 CONTENT CAT 01
Harvey, J. 1983. Photolysis of [1-^{14}C]methomyl. Document No. AMR-121-83. Unpublished study prepared by E.I. du Pont de Nemours and Company, Inc.

SUBST. CLASS = S.

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is acceptable.

2. [1-^{14}C]Methomyl (purity 95%), at 100 ppm, degraded with a half-life of 1 day in a sterile aqueous pH 5 buffered solution irradiated with artificial light at 25°C. At 15 days posttreatment, the degradates S-methyl-N-hydroxythioacetimidate and acetonitrile accounted for <1 and 66% of the applied radioactivity, respectively. In the dark control, methomyl comprised 91% of the applied at 14 days posttreatment.

3. This study fulfills EPA Data Requirements for Registering Pesticides.

MATERIALS AND METHODS:

[^{14}C]Methomyl (purity 95%, specific activity 14.1 µCi/mg, New England Nuclear) was added at 10 and 100 ppm to sterile aqueous buffered solutions adjusted to pH 5.

Aliquots (400-mL) of the treated solutions were placed in jacketed beakers and covered with flat quartz lids. The solutions were stirred constantly and maintained at 25°C by circulating water. The samples were irradiated continuously with six fluorescent sunlamps (FS 20, Westinghouse Co.) and six fluorescent blacklights (F20T 12/BL, General Electric Co.) arranged in an alternating pattern at a height of 6 inches above the surface of the solutions. The average intensity at peak wavelength (300-400 nm) was measured as 100 µW/cm^2 at the solution surface; the registrant stated that this was equivalent to approximately half of the intensity of typical summer sunshine at noon. One of the jars containing the 10 ppm methomyl solution was attached to a gas collection system (air-flow rate unspecified) containing 1 N sodium hydroxide solution. For dark controls, similar solutions were placed in stoppered flasks and incubated in the dark at 25°C. The irradiated and dark control solutions were sampled at various intervals between 0 and 15 days posttreatment. The trapping solution was changed at 2, 4, 7, and 10 days posttreatment.

An aliquot of each treated solution was analyzed for total radioactivity by LSC. Additional aliquots of each treated solution were adjusted to pH 3-4 with dilute formic acid and analyzed by HPLC. The HPLC elutions were collected at 1-minute intervals and quantified by LSC. Methomyl and S-methyl-N-hydroxy thioacetimidate were identified by comparison to reference standards. The degradate acetonitrile was identified by GC-MS. Aliquots of each trapping solution were analyzed for total radioactivity by LSC; the remaining solutions were titrated with saturated barium chloride to determine evolved $^{14}CO_2$.

REPORTED RESULTS:

Methomyl degraded with a half-life of 1 day in the irradiated solution treated at 10 ppm (Table 1). Acetonitrile was the major degradate, comprising 39-66% of the applied at 15 days posttreatment. Acidic volatiles accounted for 1% of the applied radioactivity; no $^{14}CO_2$ was trapped. In the dark controls 91-92% of the applied radioactivity remained undegraded at 14 days posttreatment.

DISCUSSION:

1. Data for the 10 ppm treatment were too variable to accurately assess the dissipation of methomyl in solution. The concentration of methomyl increased from 89 to 105% of the applied during the first two days of the study, then began to decrease in a pattern similar to the 100 ppm treatment.

2. The artificial light source was not adequately characterized; a continuous spectrum graphing wavelength vs intensity and comparing the artificial light to sunlight was not provided. The study author stated

that the intensity of the light source is equivalent to approximately half of the intensity of typical summer sunshine at noon; however, no data to support this claim was provided.

3. By day 7, >30% of the applied radioactivity was not accounted for. The study authors suggested that this radioactivity had volatilized, but only 1% of the radioactivity was trapped by sodium hydroxide.

4. Recoveries from fortified samples and detection limits were not reported.

Table 1. Distribution of radioactivity (% of the applied) in pH 5 aqueous solutions treated with [^{14}C]methomyl (purity 95%) at 10 and 100 ppm and irradiated under artificial light at 25°C.[a]

Sampling interval (days)	Methomyl	S-Methyl-N-hydroxytnio-acetimidate	Aceto-nitrile	Total [^{14}C][b]
		10 ppm		
0	89	3	6	100
1	83	2	22	108
2	105	1	30	138
3	67	1	41	112
7	31	1	29	64
15	13	1	39	55
		100 ppm		
0	90	3	5	100
1	50	1	39	93
2	42	1	55	100
3	35	1	68	106
7	9	<1	56	67
15	3	<1	66	74

[a] Data obtained from Table I in the original document.

[b] By LSC prior to HPLC analysis.

CASE GS -- METHOMYL STUDY 3 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00163745 CONTENT CAT 01

Swanson, M.B. 1986. Photodegradation of [1-^{14}C]methomyl on soil. Document No. AMR-611-86. Prepared and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is acceptable.

2. [1-^{14}C]Methomyl (radiochemical purity 98%), at ~1 lb ai/A, degraded with a half-life of 34 days (registrant-calculated) on silty clay loam soil irradiated with natural sunlight at 24-28°C. After 30 days of irradiation, 53% of the applied methomyl remained undegraded. All extractable radioactivity was identified as [^{14}C]methomyl using HPLC and TLC. [^{14}C]Acetonitrile, which was the only volatile compound, totaled 40% of the applied radioactivity in irradiated samples at 30 days posttreatment. In the dark controls, [1-^{14}C]methomyl was stable for the duration of the study.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of methomyl on soil irradiated with natural sunlight.

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MATERIALS AND METHODS:

A slurry of air-dried Keyport silty clay loam soil (5% sand, 67.5% silt, 28.0% clay, 1.4% organic matter, pH 6.8, CEC 6.25 meq/100 g) and water was spread on glass microscope slides to a thickness of 1-mm using a TLC spreader and allowed to air dry for several days. [1-^{14}C]Methomyl (radiochemical purity 98%, specific activity 19.3 µCi/mg, 4.28 x 10^4 dpm/mg, New England Nuclear) dissolved in N,N-dimethylformamide was applied evenly by syringe to the soil layer at 161 µg/slide (~1 lb ai/A). The soil slides were placed on two stainless steel heat exchangers, each of which was contained inside a water-tight Lucite box (Figure 1). The temperature of the slides was controlled by pumping 25°C water through the heat exchanger at a flow rate of 1 L/minute using a refrigerated circulating water bath. The top of each photolysis apparatus had a quartz window through which samples were irradiated. The photolysis apparatus containing the dark control samples was covered with aluminum foil to exclude light. Each photolysis apparatus was equipped with vents which allowed a 10 mL/minute stream of air to be drawn through a gas washing bottle containing anhydrous calcium sulfate, through the apparatus itself, and then through two charcoal tubes, one containing 2-ethoxyethanol, and one bottle containing 1.0 M sodium hydroxide. Both photolysis apparatus were placed on a platform on the roof of a building at the E.I. du Pont de Nemours Co., Inc., Experimental Station in Wilmington, DE (39°40'N latitude) from July 31 to August 30, 1986. Soil temperature was maintained between 24-28°C. A pyranometer was used to continuously monitor the solar radiation striking the soil samples (Table 1). Irradiated soil slides were removed from the photolysis apparatus at 2, 5, 8, 15, and 30 days posttreatment. Soil slides were removed from the dark control apparatus at 8, 15, 22, and 30 days posttreatment. At each sampling interval, all gas trap solutions were removed for analysis and replaced with fresh solutions. If soil samples could not be analyzed on the day they were taken, the soil was wrapped in aluminum foil and placed in a freezer at -20°C until analysis. Charcoal tubes were replaced every day.

Each soil sample was scraped off of the slide and extracted three times by shaking for 20 minutes with methanol. Each extraction mixture was centrifuged, the supernatant was decanted, and all three extracts were combined. The radioactivity of the combined extract was determined by LSC. Degradates were identified by HPLC and TLC using silica gel plates developed in ethyl acetate. Plates were visualized using autoradiography and quantitated using a linear analyzer. Radioactive compounds were identified by cochromatography with standards, which were visualized with UV light. Volatiles collected in the charcoal tubes were extracted by mixing the charcoal with N,N-dimethylformamide and agitating the mixture overnight. The mixture was centrifuged and aliquots of the supernatant were fractionated by HPLC. The compounds in the fractions were identified according to retention time and were quantified by LSC.

REPORTED RESULTS:

[1-^{14}C]Methomyl degraded with a registrant-calculated half-life of 34 days when irradiated by natural sunlight. After 30 days of irradiation, 53% of the applied methomyl remained undegraded (Table 2). All extractable

radioactivity was identified as [1-^{14}C]methomyl. [^{14}C]Acetonitrile, which was the only volatile compound, totaled 40% of the applied radioactivity in irradiated samples at 30 days posttreatment.

[1-^{14}C]Methomyl in the dark controls ranged from 96% of the applied at day 0 to 99% at day 30. [^{14}C]Acetonitrile (volatile) totaled 4% of the applied radioactivity at day 30.

DISCUSSION:

1. The registrant called the test soil a silt loam, but it was a silty clay loam according to the USDA Soil Textural Classification System and was referred to as such.

2. Raw data were not provided.

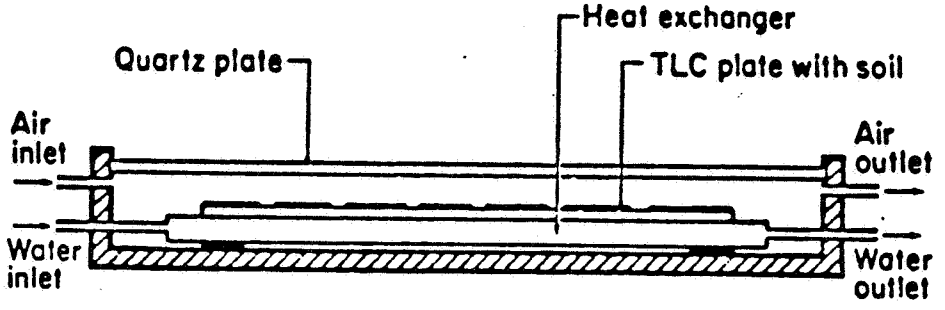

Figure 1. Photolysis apparatus.

Table 1. Solar radiation (Watt-hours/m^2) measured by pyranometer at the E.I. du Pont de Nemours Co., Inc., Experimental Station in Wilmington, DE (39°40'N latitude; July 31, 1986-August 30, 1986).

Sampling interval (days)	Total energy per day	Cumulative energy	Cumulative energy at sampling[a]
0	1708	1708	
1	4933	6641	
2	4020	10661	10293
3	3596	14257	
4	7298	21555	
5	5908	27463	26135
6	5665	33128	
7	3448	36576	
8	3979	40555	39757
9	6560	47115	
10	5792	52907	
11	4917	57824	
12	4486	62310	
13	6075	68385	
14	6499	74884	
15	6404	81288	79457
16	3878	85166	
17	3257	88423	
18	5301	93724	
19	3511	97235	
20	3161	100396	
21	897	101293	
22	6361	107654	106038
23	5861	113515	
24	6911	120426	
25	6547	126973	
26	6092	133065	
27	3654	136719	
28	3185	139904	
29	6986	146890	
30	5064	151954	151954

[a] Cumulative energy up to time of sampling (~3:00 p.m.).

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Table 2. Distribution of radioactivity (% of the applied) in silty clay loam soil treated with [^{14}C]methomyl (radiochemical purity 95%) at ~1 lb ai/A and irradiated with natural sunlight.[a]

Sampling interval (days)	Methomyl[b]	Unextractable	Acetonitrile (volatile)[c]	Total
		Irradiated		
0	96	--	--	--
2[c]	91	3	12	106
5	84	2	15	101
8	80	3	20	103
15	64	3	38	105
22	54	4	39	97
30[d]	53	4	40	97
		Dark controls		
0	96	2	0	98
8	103	3	2	108
15	100	2	3	105
22	99	4	4	107
30[c]	99	4	4	107

[a] Data obtained from Table 3 of the original document.

[b] Methomyl accounted for 100% of the extractable radioactivity.

[c] Acetonitrile accounted for 100% of the volatile radioactivity.

[d] Values represent the average of duplicate samples.

CASE GS0028 METHOMYL STUDY 4 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00009325 CONTENT CAT 01

Harvey, J., Jr. 19??. Decomposition of ^{14}C-methomyl in a high organic matter soil in the laboratory. Unpublished study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE.

SUBST. CLASS = S.

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CONCLUSIONS:

Metabolism - Aerobic Soil

This study is unacceptable because the sampling protocol (one sampling interval, 45 days posttreatment) was inadequate to accurately assess the pattern of degradation of [^{14}C]methomyl. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the analytical methodology (extraction of soil samples) was inadequate, the test substance was uncharacterized, the test soil was incompletely characterized, and incubation conditions (soil moisture and incubation temperature) were not reported.

MATERIALS AND METHODS:

Peat soil (52% organic matter, pH 5.45) was treated with [^{14}C]methomyl (test substance uncharacterized) at 4 lb ai/A and the soil was placed in a glass metabolism apparatus connected to a series of sodium hydroxide traps and an oxidizing furnace (Figure 1). A stream of air was drawn continuously through the apparatus for 45 days. Sodium hydroxide traps were samples at 10, 17, 24, 31, 38, and 45 days after treatment. The soil was sampled at 45 days posttreatment. Aliquots of the sodium

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hydroxide trapping solutions were analyzed for total radioactivity using LSC. Following LSC, $^{14}CO_2$ trapped in the sodium hydroxide solution was precipitated with barium chloride and analyzed for total radioactivity by LSC. The soil was extracted three times with 400 mL of water. The extracts were analyzed for total radioactivity by LSC and then combined and concentrated in a rotary evaporator. The extracted soil was air-dried and ball-milled for 16 hours; aliquots of the mixture were then analyzed by combustion in a Tri-Carb Sample Oxidizer. Additional aliquots of the concentrated extracts were analyzed for [^{14}C]methomyl and its degradates using TLC on silica gel plates developed in ethyl acetate and visualized with a TLC radioscanner. Reference compounds that were cochromatographed with the sample extracts were located by fluorescence quenching. The bands were scraped off the TLC plates, added to scintillation solution, and analyzed for total radioactivity by LSC.

REPORTED RESULTS:

[^{14}C]Methomyl accounted for 7.7% of the applied radioactivity at 45 days posttreatment. Unextractable [^{14}C]residues and $^{14}CO_2$ comprised 46 and 47% of the applied, respectively. S-methyl-N-hydroxythioacetinidate and an unidentified polar derivative accounted for 0.2 and 0.1% of the applied, respectively.

DISCUSSION:

1. One sampling interval, at 45 days posttreatment, is inadequate to accurately assess the pattern of degradation for methomyl.

2. The extraction procedure may have been inadequate to separate [^{14}C]-residues since 46% of the applied was unextractable at 45 days posttreatment.

3. The purity and source of the test substance and position of the radiolabel were not reported.

4. Complete soil characteristics, including textural analysis and CEC, were not reported.

5. The incubation temperature was not reported.

6. The soil moisture content was not reported.

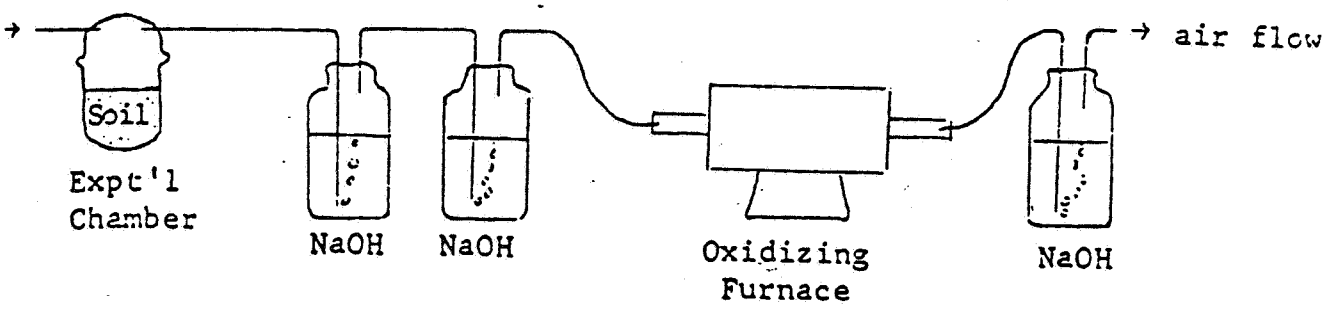

Figure 1. Aerobic soil metabolism apparatus.

CASE GS0028 METHOMYL STUDY 5 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00155756 CONTENT CAT 01

Harvey, J., and H. Pease. 1973. Decomposition of methomyl in soil. J. Agric. Food Chem. 21(5):10-12. Unpublished study prepared by E.I. du Pont de Nemours and Company, Wilmington, DE.

FICHE/MASTER ID 00133187 CONTENT CAT 01

E.I. du Pont de Nemours and Company. 1964. Disappearance of S-methyl 1-C14-N-(methylcarbamoyl)oxy-thio-acetimidate in three soils in the laboratory. Unpublished study received June 29, 1977 under 352-342; CDL:115397-D.

SUBST. CLASS = S.

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CONCLUSIONS:

Metabolism - Aerobic Soil

This study is unacceptable because the sampling protocol was inadequate (only one sampling date) to accurately assess the dissipation of methomyl in aerobic soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was uncharacterized, the test soils were incompletely characterized, the incubation temperature and the soil moisture content were not reported.

MATERIALS AND METHODS:

Moist Keyport silt loam (one sample at pH 4.7 and a second limed to pH 7.9) and a soil from San Joaquin, California (pH 7.9); test soils not further characterized) were placed in glass containers and treated with [^{14}C]methomyl (test substance uncharacterized) at approximately

4-5 lb/A. The containers were sealed and attached to a continuous air-flow system; moistened air was drawn through the incubation flasks (flow rate not reported) and then sequentially through two 1 N sodium hydroxide solution traps, an oxidizing furnace containing cupric oxide trap, and a third sodium hydroxide trap for 42 days. Samples of the soil and trapping solutions were taken only at 42 days posttreatment.

The soil samples were extracted twice with methanol and four times with water by shaking for 20 minutes each time. The supernatants were filtered through a celite filter bed. All extracts were analyzed for total radioactivity by LSC. The combined methanol and aqueous extracts were concentrated by evaporation on a water bath. Aliquots of the reduced methanol and aqueous extracts were analyzed by a one-hundred transfer counter-current distribution system using benzene:water (ratio unspecified); aliquots of all fractions were analyzed by LSC. Also, additional aliquots from fractions 10-25 and 30-55, which contained most [^{14}C]residues, were analyzed by TLC on silica gel plates developed in ethyl acetate for S-methyl-N-hydroxythioacetimidate and methomyl. Nonlabeled references standards were cochromatographed with the samples. Radioactive residues were located by autoradiography. Unextractable radioactivity in the soil was determined by wet combustion. The trapping solutions were analyzed for total radioactivity by LSC; aliquots were titrated with barium chloride to determine $^{14}CO_2$.

REPORTED RESULTS:

[^{14}C]Methomyl declined to 31-48% of the applied radioactivity during 42 days of aerobic incubation (Table 1). The major degradate was carbon dioxide (31-45% of the applied); 97-99% of the total volatiles were $^{14}CO_2$. S-Methyl-N-hydroxythioacetimidate (1-2% of the applied) and a polar fraction (1%) were also isolated. Unextractables totaled 12-18% of the applied at 42 days posttreatment.

DISCUSSION:

1. The sampling protocol was inadequate; samples were taken only at 42 days posttreatment at which time only 31-48% of the applied radioactivity remained undegraded in the soil.

2. The test substance was not characterized.

3. Soil characteristics, including textural analysis, organic matter content, and CEC, were not reported.

4. The soil moisture content was not reported.

5. The incubation temperature was not reported.

6. Data on run-off studies included in the original document were not reviewed because the experimental design is not pertinent to current environmental fate data requirements. Data of field dissipation are reviewed in Study 12 of this report.

Table 1. Distribution of radioactivity (% of the applied) in three soils treated with [^{14}C]methomyl and incubated for 42 days posttreatment.[a]

[^{14}C]-Compounds	Keyport silt loam soil (pH 4.7)	Keyport silt loam soil (pH 7.9)[b]	California soil (pH 7.9)
Methomyl	48	44	31
S-Methyl-N-hydroxy-thioacetimidate	1	2	1
Unknown (polar fraction)	1	1	1
Unextractable	14	18	12
Volatiles (mainly CO_2)	39	31	45
Total [^{14}C]	103	90	90

[a] Data were obtained from Table 1 in the original document.

[b] pH adjusted to 7.9 by liming.

CASE GS0028 METHOMYL STUDY 6 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00008844 CONTENT CAT 01

Harvey, J. 1964a. Disappearance of the S-methyl N-[(methylcarbamoyl)oxy]-thioacetimidate. In Exposure of S-methyl N-(methylcarbamoyl)oxy-thioacetimidate in sunlight, water, and soil. Unpublished study received Dec. 28, 1968 under 8F0671. Submitted by E.I. du Pont de Nemours and Company, Inc.. Wilmington, DE; CDL:091179-V.

SUBST. CLASS = S.

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CONCLUSIONS:

Metabolism - Aerobic Soil

This study is unacceptable because there was no material balance, therefore it could not be determined if methomyl degraded, leached, or was volatilized from the samples. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the pattern of formation and decline of degradates was not addressed, the test substance and soil were not characterized, and the incubation conditions were not reported.

MATERIALS AND METHODS:

Unsterilized Keyport silt loam soil (soil not further characterized) was placed in twelve plastic pots (500 g/pot). The soil in nine pots was treated with 25 mL of a 0.40% aqueous solution of methomyl (test substance uncharacterized), equivalent to approximately 200 lb ai/A; one additional pot was treated with [^{14}C]methomyl at 100 lb ai/A. The two remaining pots were treated with 25 mL of water and served as controls. The single pot treated at 100 lb ai/A and one of the pots

treated at 200 lb ai/A were allowed to stand for two hours, then analyzed to determine recovery efficiency. Four of the pots treated at 200 lb ai/A and one control pot were placed in saucers on a laboratory windowsill where they were exposed to sunlight, chilling at night, and a heat radiator. Six pots were placed on a laboratory shelf under "milder environmental conditions". Pots kept on the laboratory windowsill were watered on a more regular basis than those kept on the laboratory shelf. Pots were incubated for 15, 25, 36, or 42 days prior to analysis.

Soil from each pot was spread onto a sheet of polyethylene, allowed to air-dry, and sieved through a 10-mesh sieve. The dry, sieved soil was used to fill a chromatographic column (540 mm length). The soil was moistened, then eluted with methanol. The eluate was evaporated to dryness on a rotary evaporator at 40°C. The residues were dissolved in either a water:chloroform or ethyl acetate:water mixture and filtered. The first 10 mL of filtrate were fractioned with a 20-tube countercurrent fractionator. The tubes were then removed from the fractionator, and the upper phase of the water:chloroform filtrate was diluted with methanol and analyzed on a recording spectrophotometer. The upper phase of the ethyl acetate:water filtrate was evaporated to dryness with a stream of nitrogen, diluted with methanol, and analyzed on a recording spectrophotometer. Recovery efficiencies were reported to be 88-89%.

REPORTED RESULTS:

Methomyl dissipated with a half-life of approximately 30 days in silt loam soil (Figure 1).

DISCUSSION:

1. There was no material balance. Samples were analyzed only for methomyl. The formation and decline of degradates was not addressed.

2. Volatilization was neither measured nor controlled.

3. The study was conducted in pots which were set in saucers, suggesting it was possible for water (and methomyl residues) to leach out of the pots.

4. The test substance was uncharacterized.

5. Soil characteristics, including textural analysis, organic matter content, pH and CEC were not reported.

6. Incubation conditions, such as temperature and soil moisture, were not reported.

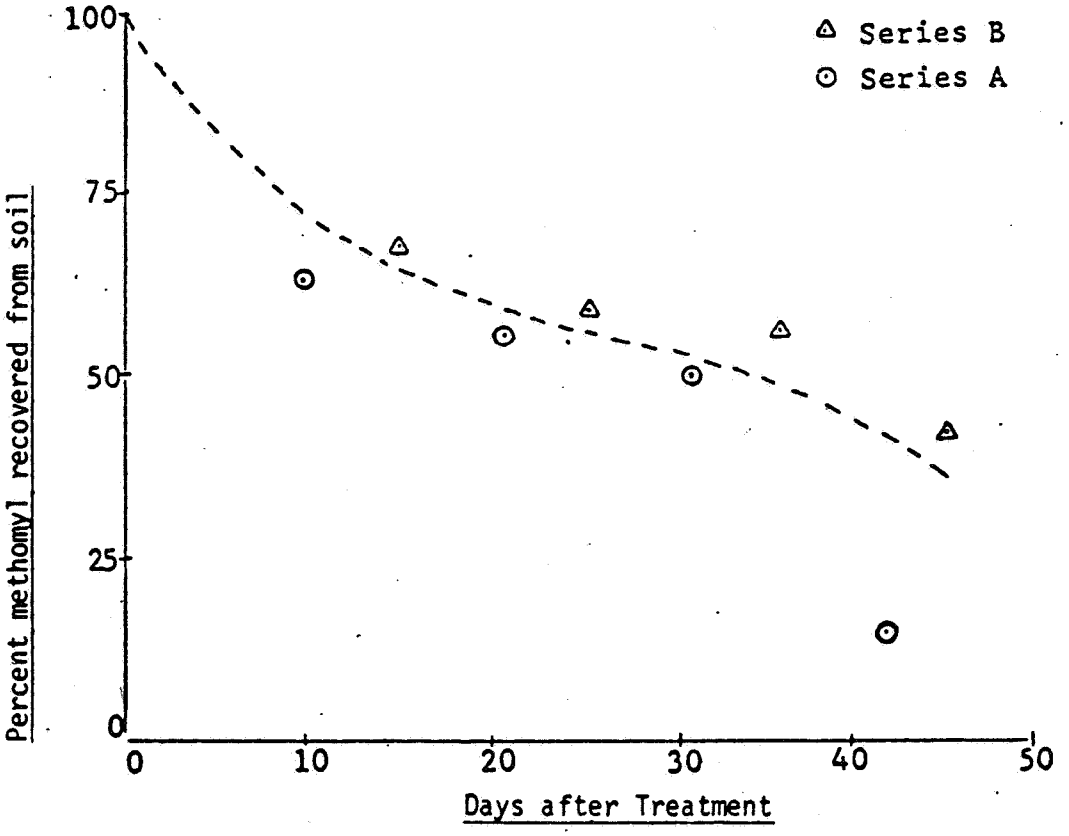

Figure 1. Dissipation of methomyl ~~in a soil~~ loam soil in the laboratory. Series A was incubated on the laboratory windowsill; Series B was incubated on the laboratory shelf.

CASE GS0028 METHOMYL STUDY 7 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00008567 CONTENT CAT 01

Harvey, J. Jr. 1977b. Decomposition of ^{14}C-methomyl in a sandy loam soil in the greenhouse. Unpublished study received February 28, 1977 under 352-342. Prepared in cooperation with University of Delaware, Soil Testing Laboratory and Submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL: 096026-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically sound and provides supplemental information towards the registration of methomyl.

2. [^{14}C]Methomyl (test substance uncharacterized), at 4 lb ai/A, decreased from 91% of the the applied immediately after treatment to 55% at 15 days posttreatment and 33% at 30 days posttreatment in a sandy loam soil maintained under unspecified conditions in a greenhouse. Minor amounts of S-methyl-N-hydroxythioacetimidate (0.3-0.4% of the applied) and polar compounds (0.6-1.7%) were detected throughout the study. Nonextractable [^{14}C]residues increased during incubation to 20% of the applied at 45 days posttreatment.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the material balance was incomplete (volatiles were not quantified), the test substance was uncharacterized, and incubation conditions (soil moisture and incubation temperature) were not reported.

MATERIALS AND METHODS:

Sandy loam soil (74% sand, 19.5% silt, 6.5% clay, 0.73% organic matter, pH 5.9, CEC 3.17 meq/100 g) was added to a depth of 5 inches to six glass beakers. [^{14}C]Methomyl (test substance uncharacterized) was applied at 4 lb ai/A to the surface of each soil, then each beaker was watered with ~0.25 inches (50 mL) of water. One beaker was set aside immediately for analysis. The remaining beakers were placed in a greenhouse and maintained under "moist conditions". Soil samples were taken at 3, 7, 15, 30, and 45 days posttreatment.

The soil samples were extracted twice with methanol and four times with water. Total radioactivity in the extracts was determined by LSC. The extracts were combined and concentrated on a rotary evaporator in a water bath at 40°C. Aliquots of the extracts were mixed with unlabeled reference standards of methomyl and S-methyl-N-hydroxythioacetimidate and analyzed by TLC on silica gel plates developed in ethyl acetate. Unlabeled reference compounds were visualized with UV light. Radioactive areas were visualized with a TLC linearscanner. Radioactivity was quantified by scraping bands of silica gel from the plates and analyzing them by LSC. Reported recovery efficiencies averaged 98 ±5%. Following extraction, the soil was air-dried and analyzed for residual radioactivity by LSC following combustion. A sample of the air-dried soil taken from the 45-day treatment was further analyzed by fractionating the soil organic matter into fulvic acid, humic acid, and humin.

REPORTED RESULTS:

Methomyl declined from 91% of the applied at 0 days posttreatment to 21% at 45 days posttreatment in the sandy loam soil (Table 1). Minor amounts of S-methyl-N-hydroxythioacetimidate (0.3-0.4% of the applied) and polar compounds (0.6-1.7%) were detected throughout the study. Nonextractable [^{14}C]residues increased to 20% of the applied at 45 days posttreatment.

DISCUSSION:

1. The material balance was incomplete. Total [^{14}C]residues in the system were only 52.9% of the recovered on day 30.

2. Volatilization was neither measured nor controlled.

3. The test substance was incompletely characterized.

4. Incubation conditions were not described. The incubation temperature was not reported. The soil moisture content was not provided. It was not stated whether the flasks were maintained in the dark or under greenhouse lighting conditions.

Table 1. Distribution of radioactivity (% of the applied) in sandy loam soil treated with [^{14}C]methomyl (test substance uncharacterized) at 4 lb ai/a and incubated in a greenhouse under "moist conditions".[a]

Sampling interval (days)	Methomyl	S-Methyl-N-hydroxythio-acetimidate	Polar fraction	Non-extractable	Total [^{14}C] residues
0	91	0.3	0.8	3	95.1
3	80	0.4	0.6	8	89.0
7	72	0.3	1.7	7	81.0
15	55	0.3	1.5	14	70.8
30	33	0.4	1.5	18	52.9
45	21	0.3	1.5	20	42.8

[a] Data obtained from Table II of the original document.

CASE GS0028 METHOMYL STUDY 8 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00008568 CONTENT CAT 01

Harvey, J. Jr. 1977c. Degradation of 14-C methomyl in Flanagan silt loam in biometer flasks. Unpublished study received February 28, 1977 under 352-342; Prepared in cooperation with University of Delaware, Soil Testing Laboratory, Submitted by E.I. du Pont de Nemours and Company, Wilmington, DE; CDL:096026-B.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is acceptable.

2. [^{14}C]Methomyl (test substance uncharacterized), at 4 ppm, degraded with a half-life of 30-45 days in silt loam soil incubated in the dark at 25°C and 70% of water holding capacity. The major degradate was $^{14}CO_2$, which totaled 22.5% of the recovered by day 45. Minor quantities of S-methyl-N-hydroxythioacetimidate (0.5-2.0% of the recovered) and polar compounds (1.2-3.1%) were identified at all sampling intervals. Nonextractable [^{14}C]residues were 26.2% of the recovered at day 45. ←

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of methomyl in aerobic silt loam soil.

MATERIALS AND METHODS:

[^{14}C]Methomyl (test substance uncharacterized) was added at 4 ppm to

six biometer flasks containing nonsterile Flanagan silt loam (19% sand, 70% silt, 11% clay, 8.26% organic matter, pH 6.5, CEC 31.6 meq/100 g) that had been inoculated with fresh soil and to one flask containing sterile soil. The soil was adusted to 70% of the water holding capacity and sodium hydroxide was placed in the sidearm of the biometer flasks. The flasks were closed with rubber stoppers fitted with ascarite filters and stopcocks, and were incubated in the dark at 25°C. Nonsterile soil and trapping solution samples were taken at intervals up to 45 days posttreatment. Sterile soil samples were taken at 45 days posttreatment. Trapped $^{14}CO_2$ in the sodium hydroxide solutions was precipitated with barium chloride and quantified by LSC. Soil samples were extracted twice with methanol and four times with water. Total radioactivity in the extracts was analyzed by LSC. The extracts were combined and concentrated on a rotary evaporator in a water bath maintained at 40°C. Aliquots of the extracts were mixed with unlabeled references standards of methomyl and S-methyl-N-hydroxythioacetimidate and were analyzed by TLC on silica gel plates developed in ethyl acetate. Unlabeled reference compounds were visualized with UV light. Radioactive areas were visualized with a TLC linearscanner. Radioactive zones were quantified by scraping bands of silica gel from the plates and analyzing by LSC. Reported recovery efficiencies averaged 92±1%. Following extraction, the soil was air-dried and analyzed for residual radioactivity by LSC following combustion. A sample of air-dried soil taken from the 45-day treatment was further analyzed by fractionating the soil organic matter into humic acid, fulvic acid, and humin.

REPORTED RESULTS:

[^{14}C]Methomyl degraded with a half-life of 30-45 days in silt loam soil (Table 1). The major degradate was $^{14}CO_2$, which comprised 22.5% of the recovered by day 45. Nonextractable [^{14}C]residues were 26.6% of the recovered at day 45. Also identified in minor quantities were S-methyl-N-hydroxythioacetimidate (0.5-2.0% of the recovered) and polar compounds (1.2-3.1% of the recovered).

In the sterile soil, 89.3% of the methomyl remained undegraded at 45 days posttreatment (Table 1).

DISCUSSION:

1. The degradate characterization data were presented as percent of recovered rather than percent of applied; however, the registrant stated that reported recovery efficiencies averaged 92%.

2. The purity and source of the test substance and position of the radiolabel were not reported.

Table 1. Distribution of radioactivity (% of the recovered) in Flanagan silt loam soil treated with [^{14}C]methomyl at 4 ppm and incubated at 25°C in the dark.[a]

Sampling interval (days)	Methomyl	S-Methyl-N-hydroxythio-acetimidate	Polar fraction	Unextract-able	$^{14}CO_2$
		Nonsterilized			
0	96.7	1.1	1.3	0.9	0.0
3	85.3	1.7	2.0	7.5	3.5
7	78.5	1.0	1.2	13.2	6.1
15	70.0	2.0	2.6	13.8	11.6
30	57.2	0.5	3.1	21.1	18.1
45	47.0	1.4	2.9	26.2	22.5
		Sterilized			
45	89.3	0.5	0.5	8.0	1.4

[a] Data obtained from Table II of the original document.

CASE GS0028 METHOMYL STUDY 9 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00073214 CONTENT CAT 01

Harvey, J. Jr. 1977d. Decomposition of ^{14}C-methomyl in flooded anaerobic soils. Unpublished study received Mar. 27, 1979 under 352-342. Submitted by E.I. du Pont de Nemours & Company, Wilmington, DE; CDL:237906-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Anaerobic Soil

1. This study is acceptable.

2. Although acetonitrile is the major degradate of methomyl in the early stages, $^{14}CO_2$ is the end product under flooded conditions. Total conversion of methomyl to CO_2 would likely occur in about 8 days. ←

3. This study fulfills EPA Data Requirements for Registering Pesticides.

MATERIALS AND METHODS:

Samples of moist sediment (soil not further characterized) taken from a Maine backwater were filtered, weighed (100 g), and added with 100 mL of the filtrate to centrifuge bottles. Also, separate samples of air-dried Fallsington silt loam and Flanagan silt loam soils (soils not further characterized) were each pre-mixed with powdered dry alfalfa and added to centrifuge bottles with distilled water and water from the Maine creek. Polyethylene-lined screw caps were loosely fitted onto the three sets of centrifuge bottles, which were then purged with nitrogen three times. The caps were tightened and the bottles were incubated at room temperature in the dark for at least 30 days. At the end of the incubation per-

iod, each bottle was briefly opened and an aqueous solution of [^{14}C]methomyl (radiochemical purity >99%, specific activity 1.42 μCi/mL, source unspecified) was added to the bottles at 0.409 mg/bottle. The caps were secured, and the bottles were again purged with nitrogen and again incubated at room temperature in the dark. Soil samples were taken at 0, 2, 7, and 14 days posttreatment.

Soil samples were extracted several times with water to obtain four aqueous and two methanolic extracts. The aqueous extracts were combined and extracted three times with ethyl acetate. A portion of the ethyl acetate extract was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator and a stream of nitrogen. Radioactivity in the liquid fractions was quantified by LSC. The ethyl acetate concentrates were analyzed for methomyl and its degradates using HPLC. The soil solids remaining after the extractions were air-dried, and the unextractable radioactivity was quantified by LSC following combustion.

In order to determine the amount of $^{14}CO_2$ that was trapped in the flood water, an additional bottle sealed with a septum cap was filled to the shoulder with Maine sediment and water. The atmosphere in the bottle was evacuated and replaced with nitrogen. An aqueous solution of [^{14}C]methomyl was added at 0.4 mg/mL to the bottle and it was incubated in the dark under anaerobic conditions. At various intervals (unspecified) the supernatant liquid was removed, and total radioactivity was analyzed by LSC before and after the precipitation of carbonate by barium chloride.

In order to determine the amount of acetonitrile produced by the soil: water system, additional bottles containing sediment and water were incubated as previously described. At various sampling intervals, aliquots of the headspace were analyzed for acetonitrile by GC/MS. The amount of $^{14}CO_2$ in the flood water was determined by precipitation with barium chloride.

REPORTED RESULTS:

Methomyl was not detected in any of the soils at the 0-day sampling interval. Almost all of the radioactivity volatilized; [^{14}C]acetonitrile was identified as the initial degradation product and $^{14}CO_2$ was the final degradation product. Greater than 90% of the applied radioactivity was $^{14}CO_2$ at 8 days posttreatment (0.6, 4.8, 16.9, 45, 77, 94 and 96% of the radioactivity was detected as $^{14}CO_2$ at 30 min, 1 hr, 24 hr, 4 days, 6 days, 7 days and 8 days, respectively).

DISCUSSION:

1. Methomyl was not detected at any sampling interval.

2. Soil and sediment characteristics, such as textural analysis, organic matter content, pH and CEC were not provided.

3. A material balance was not provided. The author stated that total recoveries of radioactivity were low, ranging from 60 ± 4% to 81 ± 2%.

CASE GS0028 METHOMYL STUDY 10 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00044306 CONTENT CAT 01

Khasawinah, A.M. and G.C. Holsing. 1976. UC 51762 Pesticide: Mobility on soil thin layer chromatograms. File No. 22754. Unpublished study received September 10, 1980 under 264-341; submitted by Union Carbide Agricultural Products Co., Ambler, PA, CDL:099602-J.

SUBST. CLASS = S.

DIRECT RVW TIME = 2 (MH) START-DATE END DATE

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is acceptable.

2. [^{14}C]Methomyl and S-methyl-N-hydroxythioacetimidate (radiochemical purities 98%) were very mobile on sandy loam, silty clay loam, and silt loam soil TLC plates, with R_f values ranging from 0.64 to 0.93.

3. This study contributes towards to the fulfillment of EPA Data Requirements for Registering Pesticides by providing information on the mobility (soil TLC) of methomyl in sandy loam, silt loam, and silty clay loam soils.

MATERIALS AND METHODS:

A silty clay loam, a silt loam, and two sandy loam soils (Table 1) were air-dried, sieved to either 500 µm (both sandy loam soils) or 250 µm (silty clay loam and silty loam soil) and mixed with water to form slurries. The slurries were spread on glass TLC plates (20 x 20-cm;

two plates per soil type) to a thickness between 500 and 1000 µm, then air-dried and stored until use.

Unaged [^{14}C]methomyl, its degradate [^{14}C]S-methyl-N-hydroxythioacetimidate (radiochemical purity of methomyl and its degradate was 98%, specific activities 6.5 µCi/mMole, Pathfinder Laboratories), and three reference compounds (diquat, 2,4,5-T, and 2,4-D) were applied at 1 µg/spot 3.0 cm from one edge of each plate. The plates were then developed in solvent (unspecified), air-dried, and autoradiographed.

REPORTED RESULTS:

[^{14}C]Methomyl and S-methyl-N-hydroxythioacetimidate were very mobile in all four soils with R_f values ranging from 0.64-0.79 and 0.86-0.93, respectively (Table 1).

DISCUSSION:

1. The methomyl and S-methyl-N-hydroxythioacetimidate spots ranged from 16-43 mm in width. Depending on where the spot was measured, the pesticides could be considered mobile or very mobile.

2. Sieving the soils through 250 or 500 µm mesh screens would remove the coarse sand fraction and tend to make the pesticide less mobile than in an unsieved or "normally" sieved soil (a 200 µm mesh screen is used in the majority of soil textural analyses).

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)	R_f values[a]	
	%						Methomyl	Methomyl oxime[b]
Norfolk sandy loam[c]	83	15	2	0.8	5.8	2.9	0.77	0.89
(California) silty clay loam[d]	25	42	33	1.3	8.1	21.6	0.64	0.86
(Texas) sandy loam[c]	65	17	18	1.0	7.8	11.7	0.79	0.93
Muskingum silt loam[d]	38	42	20	1.3	5.4	5.6	0.73	0.88

[a] R_f value measured from the leading edge of the spot.

[b] S-Methyl-N-hydroxythioacetimidate.

[c] Sieved through 500 µm screen.

[d] Sieved through 250 µm screen.

CASE GS0028 METHOMYL STUDY 11 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00161884 CONTENT CAT 01

Priester, T. 1984. Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with methomyl: Document No. AMR-174-84. Unpublished study prepared by E.I. du Pont de Nemours and Co., Inc.

SUBST. CLASS = S.

DIRECT RVW TIME = 3 (MH) START-DATE END DATE

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is acceptable.

2. Based on batch equilibrium studies, [1-^{14}C]methomyl (radiochemical purity 98.2%), at 0.2-6.0 ppm, was very mobile in two sandy loams, a silt loam, and a silt soil with Freundlich K_{ads} values ranging from 0.86 to 0.90 and K_{des} values ranging from 0.5 to 2.8. Based on soil TLC studies, [^{14}C]methomyl was very mobile in sandy loam, silt loam, and silt soils with R_f values ranging from 0.46 to 0.82.

3. This study contributes towards the fulfillment of EPA Data Requirements for Registering Pesticides by providing information on the mobility of methomyl in four soils (two sandy loam, one silt loam, and one silt soil).

MATERIALS AND METHODS:

Adsorption/Desorption

Two sandy loam, a silt, and a silt loam soil (20-g samples, Table 1)

were mixed with 20-mL aliquots of aqueous solutions containing [1-^{14}C]-methomyl (radiochemical purity >98%, specific activity 19.3 µCi/mg, New England Nuclear) at 0.2, 0.5, 1.0, 2.5, or 6.0 ppm. The soil:water slurries were shaken for 24 hours in a temperature bath maintained at 25°C. The slurries were centrifuged (2000 rpm, 10 minutes) and aliquots of the supernatant were analyzed by LSC.

To determine desorption, the slurries treated at 6.0 ppm that were used in the adsorption phase of the study were resuspended in 20 mL of pesticide-free distilled water and shaken for 24 hours in a water bath maintained at 25°C. Aliquots of the supernatant were sampled and replaced with pesticide-free solution. The soils were desorbed a total of five times. Samples of the supernatant were analyzed by LSC.

Soil TLC

The four soils were hammer-milled to 1-5 µm particle size and used to prepare soil TLC plates (400 µm thickness, 20 x 20-cm). The soils were spotted with [^{14}C]methomyl at 1 µg/spot at a distance 3-cm from the bottom edge of each plate. The plates were developed in water to a distance of 10-cm. After development, the plates were air-dried for 24 hours and visualized by autoradiography.

REPORTED RESULTS:

Adsorption/Desorption

[^{14}C]Methomyl was very mobile in all four soils; Freundlich K_{ads} values ranged from 0.23-1.4 (Table 2). The slopes of the adsorption isotherms (1/n) ranged from 0.86 to 0.90. Freundlich K_{des} values for the four soils ranged from 0.5 to 2.8; the slopes of desorption isotherms ranged from 0.09 to 0.55.

Soil TLC

[^{14}C]Methomyl was very mobile in all four soils with R_f values ranging from 0.46 to 0.82 (Table 1).

DISCUSSION:

The Keyport silt loam soil was misclassified in the study. The soil was determined to be a silt soil according to the USDA Textural Classification system and is described as such in this report.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)	R_f values
	%						
Cecil sandy loam	61	21	18	2.1	6.5	6.6	0.53
Flanagan silt loam	2	81	17	4.3	5.4	21.1	0.82
Silt[a]	12	83	5	7.5	5.2	15.5	0.52
Woodstown sandy loam	60	33	7	1.1	6.6	5.3	0.46

[a] This soil was described as a Keyport silt loam by the registrant.

Table 2. Freundlich K and 1/n values for the adsorption and desorption of [^{14}C]methomyl and two reference pesticides.

Soil type	Adsorption			Desorption		
	K_{ads}	K_{oc}	$1/n_{ads}$	K_{des}	K_{oc}	$1/n_{des}$
Cecil sandy loam	0.72	34	0.86	1.0	48	0.55
Flanagan silt loam	1.0	23	0.88	1.6	37	0.50
Silt	1.4	19	0.86	2.8	37	0.09
Woodstown sandy loam	0.23	21	0.90	0.5	45	0.46

40

CASE GS0028 METHOMYL STUDY 12 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00133188 CONTENT CAT 01

Harvey, J. 1964b. Disappearance of S-methyl 1-C14-(methylcarbamoyl)oxy-thioacetimidate in field soil. Unpublished study received June 29, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Company, Wilmington, DE; CDL:115397-E.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Terrrestrial

This study is unacceptable because the sampling protocol was inadequate (first sampling at 1 month posttreatment) to accurately assess the dissipation of methomyl in soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was uncharacterized, pretreatment samples were not analyzed, immediate posttreatment samples were not analyzed, the test soil was uncharacterized, field test data were not provided, and the pattern of formation and decline of degradates was not addressed.

MATERIALS AND METHODS:

[^{14}C]Methomyl (test substance uncharacterized) was applied at 4.5 lb ai/A (8.9µC/cylinder) to the surface of soil (uncharacterized) inside stainless steel cylinders (4-inch diameter x 15-inch length, 1/2-inch above soil surface) that had been driven into field plots at Stein Farm (location incomplete, date of application not provided). The treated surface was then covered with 1.5 inches of soil and an 8-mesh screen.

Soil samples (0- to 1.5-, 1.5- to 3-, 3- to 4.5-, 4.5- to 6-, 6- to 8-, 8- to 10-, 10- to 12.5-, 12.5- to 15-inch depths) were collected from entire cylinders at 1, 3, and 12 months posttreatment.

Soil samples were mixed with water and/or methanol and subsamples of the extracted soil were analyzed for unextractable radioactivity by wet combustion. Aliquots of the soil extracts were analyzed by TLC; the remainder were analyzed by a one hundred transfer counter-current distribution system using benzene:water. Aliquots of selected fractions (10-30 and 30-60) were analyzed by LSC and TLC (developed in an ethyl acetate solvent system). The TLC plates were analyzed by autoradiography.

REPORTED RESULTS:

Methomyl degraded with a half-life of <1 month in the treated soil; only 1.8% (0.161 µCi) of the methomyl applied to the cylinders was recovered at 1 month posttreatment (Table 1). S-Methyl-N-hydroxythioacetimidate was 0.16 µC at 1 month posttreatment and decreased to 0.012 µC by 3 months posttreatment. The majority of the [^{14}C]residues were recovered in the 0- to 1.5-inch soil depth; [^{14}C]residues were detected as deep as 8 inches (Table 2).

DISCUSSION:

1. The sampling protocol was inadequate to accurately establish the dissipation of methomyl in soil. The first sampling was not until 1 month posttreatment, at which time only 2.61µC of the 8.9µC applied were recovered.

2. The test substance was not characterized.

3. The test soils were not characterized.

4. Field test data such as meteorological data, location of the field, and slope of the field, were not reported.

5. Extraction techniques may have been inadequate; >90% of the [^{14}C]residues were not extracted.

6. The detection limit and recovery from fortified samples were not reported.

Table 1. Distribution of radioactivity(μCi) in soil from cylinders in the field that were treated with [^{14}C]methomyl (test substance uncharacterized) at 4.5 lb/A(8.9μCi).[a]

[^{14}C]Residues	Sampling interval (months) 1	3	12
Total	2.61	1.72	1.34
Extractable	0.26	0.10	0.03
Methomyl	0.161	0.025	ND[b]
S-Methyl-N-hydroxy-thioacetimidate	0.16	0.012	ND
Polar fraction	0.083	0.063	0.03

[a] Data are from Table VIII in the original document.

[b] Not detected; the detection limit was not reported.

Table 2. Distribution of radioactivity (μCi) through columns of soil in the field that were treated with [^{14}C]methomyl (test substance uncharacterized) at 4.5 lb/A (8.9 μCi).[a]

Sampling depth (inches)	Sampling interval (months)		
	1	3	5
0-1.5	1.55	1.39	0.95
1.5-3	0.95	0.29	0.33
3-4.5	0.08	0.03	0.04
4.5-6	0.02	0.01	0.01
6-8	0.01	<0.01	0.01
8-10	ND[b]	ND	ND
10-12.5	ND	ND	ND
12.5-15	ND	ND	ND

[a] Data are from Table VII in the original document.

[b] Not detected, the detection limit was not reported.

CASE GS0028 METHOMYL STUDY 13 PM --

CHEM 0903201 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00009326 CONTENT CAT 01

E.I. du Pont de Nemours and Company. 1971. Methomyl decomposition in muck soil - a field study. Unpublished study received May 5, 1977 under 352-342; CDL:229711-F.

SUBST. CLASS = S.

DIRECT RVW TIME = 1 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Terrestrial

This study is unacceptable because the sampling protocol (first sample at 7 days posttreatment contained no methomyl) was inadequate to accurately assess the dissipation of methomyl in soil, and no analytical methodology was provided. In addition, this study does not fulfill EPA Data Requirements for Registering Pesticides because no pretreatment or immediate posttreatment samples were analyzed, the test substance was not characterized, the test soil was incompletely characterized, and field test data were not provided.

MATERIALS AND METHODS:

A field plot (10 x 40 feet) of muck soil (52% organic matter, pH 5.4, soil not further characterized) located in Excelsior, Minnesota, was sprayed with methomyl (test substance uncharacterized) at 1 or 2 lb ai/A on August 23, 1971. Soil samples (0- to 8-inch depth) were taken at 7, 14, and 32 days posttreatment.

The analytical methodology was referenced and was not provided for review.

REPORTED RESULTS:

No methomyl was detected (<0.02 ppm) in any of the soil extracts.

DISICUSSION:

1. The sampling protocol was inadequate to accurately assess the dissipation of methomyl. No pretreatment or immediate posttreatment samples were taken to confirm the application rate. At the first sampliny interval, methomyl was not detected in the soil.

2. The analytical methodology was referenced and was not provided for review; hence, it could not be determined if the methods were adequate to accurately determine the concentration of methomyl in soil.

3. The test substance was not characterized.

4. Soil characteristics, including textural analysis and CEC, were not provided.

5. Meteorological data, including soil and air temperatures, were not provided. Field test data, including slope of the field, depth to the water table, and soil temperatures, were not provided.

6. Raw data were not provided.

7. Recoveries of methomyl from fortified samples were 65 and 74% at fortification levels of 0.08 and 0.2 ppm, respectively.

CASE GS0028 METHOMYL STUDY 14 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00019947 CONTENT CAT 01

Harvey, J., Jr. 1977a. Crop rotation study with 14C-methomyl in the greenhouse. Unpublished study received Jan. 19, 1978 under 352-342; submitted by E.I. du Pont de Nemours and Company, Wilmington, DE; CDL:232720-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 10 (MH) START-DATE END DATE

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CONCLUSIONS:

Confined Accumulation - Rotational Crops

1. This study is acceptable.

2. Total radioactivity in the beets (leaves and roots) and cabbage (whole) planted 30 and 120 days posttreatment ranged from 0.04 to 0.15 ppm; total [^{14}C]residues in the sunflower seeds ranged from 1.5 to 2.0 ppm (table 1). Ethyl acetate-soluble residues in all crops from both planting intervals were ≤0.01 ppm. The application rate was 4 lb. ai/A which is four times the maximum single use rate (multiple applications are permitted).

3. This study would not fulfill EPA Data Requirements for Registering Pesticides because residues in the crops were not characterized, soils were not analyzed at the time of harvest of the rotational crops, and the test substance was uncharacterized.

MATERIALS AND METHODS:

Six metal flats (12 x 12 x 12 inches) lined with polyethylene were firmly packed with sandy loam soil (74% sand, 19.5% silt, 6.5% clay, 0.73% organic matter, pH 5.9, CEC 3.17 meq/100 g). The flats were treated with an aqueous solution of [^{14}C]methomyl (test substance uncharacterized) at 4 lb ai/A (42 mg/flat). The flats were placed in a greenhouse and maintained in a "moist condition".

At 30 days posttreatment, three flats were randomly selected, two soil core samples were taken (0.75-inch diameter x 12-inch length) and sectioned into 0- to 4-, 4- to 8-, and 8- to 12-inch depths, and the flats were planted with beets, cabbage, and sunflowers. At 120 days posttreatment, the remaining three flats were sampled and planted as described above. The flats were kept in the greenhouse until the crops matured and were harvested.

Beet leaves and roots and whole cabbages were "exhaustively" extracted with methanol in a blender. The methanol extracts from each sample were combined and concentrated on a rotary evaporator. The concentrate was diluted with hexane, then partitioned three times with hexane and three times with ethyl acetate. Radioactivity in the aqueous, hexane, and ethyl acetate fractions was determined by LSC, and radioactivity remaining in the extracted plant tissue was determined by LSC following combustion. Sunflower seeds were extracted in a blender sequentially three times with hexane, three times with ethyl acetate, and three times with methanol. Extracts and extracted tissues were analyzed by LSC as described. The soil samples taken at planting were extracted twice with methanol and four times with water by shaking for 20 minutes each time. The supernatants were filtered through a celite filter bed. All extracts were analyzed for total radioactivity by LSC. The combined methanol and aqueous extracts were concentrated by evaporation on a water bath. Aliquots of the reduced methanol and aqueous extracts were analyzed by a one-hundred transfer counter-current distribution system using benzene:water (ratio unspecified); aliquots of all fractions were analyzed by LSC. Also, additional aliquots from fractions that contained the most [^{14}C]residues were analyzed by TLC on silica gel plates developed in ethyl acetate for S-methyl-N-hydroxythioacetimidate and methomyl. Nonlabeled reference standards were cochromatographed with the samples. Radioactive residues were located by autoradiography. Unextractable radioactivity in the soil was determined by wet combustion.

REPORTED RESULTS:

Total radioactivity in the beets (leaves and roots) and cabbage (whole) planted 30 and 120 days posttreatment ranged from 0.04 to 0.15 ppm; total [^{14}C]residues in the sunflower seeds ranged from 1.5 to 2.0 ppm (Table 1). Ethyl acetate-soluble residues in all crops from both planting intervals were $\leq$0.01 ppm. In the soil, 42.4% of the applied methomyl remained undegraded at the 30-day planting and 26.9% remained undegraded at the 120-day planting (Table 2). S-Methyl-N-hydroxythioacetimidate and polar compounds were <1.5% of the applied. Unextractable [^{14}C]residues ranged from 15-18% of the applied. The study concluded that radiocarbon from the degraded methomyl residues were significantly reincorporated into natural products.

DICUSSION:

1. The soils were not analyzed immediately after treatment to confirm the application rate. At the first sampling, <60% of the theoretically applied radioactivity remained in the soil.

2. [14C]Residues in the crops were not characterized. The registrant assumed that only the ethyl acetate-soluble fraction of the extractable

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able residues totaled 0.04-0.2 ppm and no attempt was made to characterize these residues.

3. The test substance was not characterized.

4. The "moist conditions" under which the treated soils were held were not described.

Table 1. Distribution of radioactivity (ppm methomyl equivalents) in crops grown in sandy loam soil treated with [^{14}C]methomyl at 4 lb ai/A 30 or 120 days prior to planting.[a]

Plant part	Total [^{14}C]	Methanol-extractable	Ethyl acetate-soluble
	30-day-Treatment-to-planting interval		
Beet leaves	0.09	0.05	<0.01
Beet roots	0.10	0.05	0.01
Cabbage head	0.15	0.10	0.01
Sunflower seed	2.0	0.2	--[b]
	120-day-Treatment-to-planting interval		
Beet leaves	0.05	0.04	<0.01
Beet roots	0.06	0.04	<0.01
Cabbage head	0.04	0.02	<0.01
Sunflower seed	1.5	0.1	<0.01

[a] Data obtained from Table 3 in the original document.

[b] Not tested; the study author reported insufficient radioactivity remained in the sample to analyze.

Table 2. Distribution of radioactivity (% of the applied) in sandy loam soil treated with [^{14}C]methomyl at 4 lb ai/A.[a]

Sampling interval (days)	Methomyl	S-Methyl-N-hydroxythio-acetimidate	Polar compounds	Unextractable
30	42.4	0.3	1.1	15
120	26.9	0.1	0.8	18

[a] Data obtained from Table 2 in the original document.

CASE GS0028 METHOMYL STUDY 15 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 01 - TECHNICAL CHEMICAL

FICHE/MASTER ID 00131251 CONTENT CAT 01

E.I. du Pont de Nemours and Company, Inc. 1972. Residues: Lannate in rainbow trout (Salmo gairdneri). Compilation; unpublished study received October 31, 1983 under 352-366; CDL:251424-E. Prepared by Bionomics, Inc., and submitted by E.I. du Pont de Nemours & Co., Wilmington, DE, CDL:229712-N.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

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CONCLUSIONS:

Laboratory Accumulation - Fish

This study is unacceptable because residues in the water were not characterized; therefore, it could not be determined if the fish were exposed only to undegraded methomyl. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because residues in the water and fish tissue (carcass) were not completely characterized, whole fish and visceral tissue were not analyzed, an inappropriate species of fish was used and because the analytical methods were not provided.

MATERIALS AND METHODS:

Rainbow trout (Salmo gairdneri; average length and weight of 160 mm and 42 g, respectively) were held in hatchery facilities for ≥ 30 days prior to the study initiation. Flow-through aquatic exposure systems were prepared using six 150-gallon aquaria. Aerated well water (pH 7.3, dissolved oxygen 5.0 mg/L, hardness 25 µg/L $CaCO_3$, 18±0.5°C) was provided to each aquarium at a rate of 250 L/hour (~10 turnovers per day).

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Rainbow trout (100) were placed in each aquarium. Four aquaria were treated with 90% technical methomyl at 0.075 and 0.75 ppm (two aquaria/treatment) and the remaining two aquaria served as untreated controls. Following a 28-day exposure period, fish remaining in the aquaria treated at 0.075 ppm were transferred to aquaria containing untreated water for a 21-day depuration period (fish remaining in the aquaria treated at 0.75 ppm had been transferred to untreated water after 21 days due to evidence of toxic poisoning). Treated water and untreated and treated fish (12) were sampled on days 3, 7, 14, 21, and 28 of the exposure period. During the depuration period, water samples and untreated and treated fish (3) were sampled on days 3, 7, 14, and 21.

Fish were dissected into viscera and carcasses, and the samples were frozen until analysis. Prior to analysis, the head, tail, and fins were removed from the carcass, and only the remaining carcass tissue was analyzed. The water and fish carcasses were analyzed for methomyl using the "standard methomyl residue method" (details not provided). Reported recoveries from fish tissues fortified with 0.02-2.0 ppm of methomyl ranged from 66 to 110%. The detection limit in fish tissue was 0.02 ppm; the detection limit in water was not reported.

REPORTED RESULTS:

During the exposure period, total methomyl residues ranged from 0.07 to 0.10 ppm in the 0.075 ppm treatment water and 0.75 to 1.1 ppm in the 0.75 ppm treatment water (Table 1).

During exposure, residues in fish from the 0.075 ppm-treated aquaria ranged from 0.04 to 0.07 ppm and in fish from the 0.75 ppm treatment ranged from 0.36 to 0.45 ppm (Table 1). Methomyl residues were <0.02 ppm (detection limit) in all fish during depuration. No mortality of the fish was observed in the untreated or 0.075 ppm treatment aquaria. Fish mortality in two aquaria treated at 0.75 ppm totaled 10 and 11 fish at the end of the exposure period.

DISCUSSION:

1. The analytical methodology was not provided to review.

2. Residues in the water and fish were not characterized.

3. Total residues based on whole-body fish samples and residues in the viscera were not determined.

4. An inappropriate species of fish (Salmo gairdneri) was used. Bluegill sunfish or channel catfish are preferred species.

5. Bioconcentration factors were not reported by the registrant.

Table 1. Residues (ppm) in water and carcass tissue[a] of rainbow trout treated with methomyl during a 21- or 28-day exposure period and a 21-day depuration period.[b,c]

Sampling interval (days)		0.075 ppm		0.75 ppm	
		Water	Carcass	Water	Carcass
Exposure	3	0.09	0.07	0.90	0.43
	7	0.09	0.05	0.90	0.44
	14	0.10	0.05	0.75	0.45
	21	0.07	0.05	1.00	0.36
	28	0.09	0.04	1.10	0.43
Depuration	3	--[d]	ND[e]	--	ND
	7	--	ND	--	ND
	14	--	ND	--	ND
	21	--	ND	--	ND

[a] Viscera, head, tail, and fins removed.

[b] Fish in the higher treatment (0.75 ppm) were exposed for 21 days, and fish in the lower treatment (0.075 ppm) were exposed for 28 days.

[c] Data obtained from pages 2 and 3 of an addendum attached to the study that was bound with the study in the original document.

[d] Residues in the water during the depuration were not reported.

[e] Not detected; the detection limit was 0.02 ppm.

CASE GS0028 METHOMYL STUDY 16 PM --

CHEM 090301 Methomyl

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00157991 CONTENT CAT 01

Collins, R. and F. Kenny. 1986. Octanol-water partition coefficient of Nudrin insecticide. Code 5-8-0-0: RIR-25-009-86. Unpublished study prepared by Shell Development Co.

SUBST. CLASS = S.

DIRECT RVW TIME = 2 (MH) START-DATE END DATE

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CONCLUSIONS:

Ancillary Study - Octanol/Water Partition Coefficients

1. This study is acceptable.

2. The octanol/water partition coefficient (K_{OW}) values for [^{14}C]methomyl (purity 99.8%) ranged from 1.29 to 1.33 in water-saturated octanol solutions containing 0.005 to 0.05 M methomyl.

MATERIALS AND METHODS:

Prior to use, octanol was cosaturated with distilled, deionized water.

[^{14}C]Methomyl (purity 99.8%, test substance not further characterized) was dissolved at 0.005, 0.01, 0.025, and 0.05 M in octanol-saturated octanol.

The test solutions were combined with octanol at ratios of 8:1 (octanol:water) and 7:2. The octanol:water solutions were mixed on a wrist action shaker for one hour at 20 ±1°C, and centrifuged (2500 rpm,

30 minutes). and the phases were separated. The water and octanol phases were diluted with water and methanol, respectively, and analyzed by reverse-phase HPLC using UV detection at 237 nm.

REPORTED RESULTS:

The K_{ow} values for methomyl ranged from 1.29 to 1.33.

DISCUSSION:

1. Characteristics of the water, including pH, dissolved oxygen content, hardness, and alkalinity, were not provided.

2. The specific activity and source of the test substance were not reported.

Table 1. Octanol/water partition coefficients (K_{ow}) and total radioactivity recovered for methomyl.[a]

Concentration (molarity)	Concentration in octanol (µg/mL)	Concentration in water (µg/mL)	K_{ow}	Total [^{14}C] (%)
0.05	949	725	1.31	103
0.025	967	749	1.29	102
0.01	193	148	1.30	104
0.005	199	150	1.33	105

[a] Data obtained from Table 1 in the original document.

EXECUTIVE SUMMARY

The following findings are derived from those reviewed studies which have met the requirements of 40 CFR Part 158.130 and the guidance of Subdivision N and were also deemed acceptable.

[1-^{14}C]Methomyl (radiochemical purity 95.5%), at 10 and 100 ppm, was relatively stable in pH 5 and 7 sterile aqueous buffered solutions incubated in the dark at 25°C for 30 days. In a pH 9 solution, [^{14}C]methomyl degraded with a half-life of about 30 days, at which time 50-54% of the applied radioactivity was methomyl. At 30 days, the degradate S-methyl-N-hydroxythioacetimidate was the only degradate in the pH 9 solution and accounted for 40-44% of the applied.

[1-^{14}C]Methomyl (purity 95%), at 100 ppm, degraded with a half-life of 1 day in a sterile aqueous pH 5 buffered solution irradiated with artificial light at 25°C. At 15 days posttreatment, the degradates S-methyl-N-hydroxythioacetimidate and acetonitrile accounted for <1 and 66% of the applied radioactivity, respectively. In the dark control, methomyl comprised 91% of the applied at 14 days posttreatment.

[1-^{14}C]Methomyl (radiochemical purity 98%), at about 1 lb ai/A, degraded with a half-life of 34 days (registrant-calculated) on silty clay loam soil irradiated with natural sunlight at 24-28°C. After 30 days of irradiation, 53% of the applied methomyl remained undegraded. All extractable radioactivity was identified as [^{14}C]methomyl using HPLC and TLC. [^{14}C]Acetonitrile, which was the only volatile compound, totaled 40% of the applied radioactivity in irradiated samples at 30 days posttreatment. In the dark controls, [1-^{14}C]methomyl was stable for the duration of the study.

[^{14}C]Methomyl (test substance uncharacterized), at 4 ppm, degraded with a half-life of 30-45 days in silt loam soil incubated under aerobic conditions in the dark at 25°C and 70% of water holding capacity. The major degradate was $^{14}CO_2$, which totaled 22.5% of the recovered by day 45. Minor quantities of S-methyl-N-hydroxythioacetimidate (0.5-2.0% of the recovered) and polar compounds (1.2-3.1%) were identified at all sampling intervals. Nonextractable [^{14}C]residues were 26.2% of the recovered at day 45.

Although acetonitrile is the major degradate of methomyl in the early stages (less than 5 hrs), $^{14}CO_2$ is the end product under anaerobic conditions. Total conversion of methomyl to CO_2 would likely occur in about 8 days.

[^{14}C]Methomyl and S-methyl-N-hydroxythioacetimidate (radiochemical purities 98%) were very mobile on sandy loam, silty clay loam, and silt loam soil TLC plates, with R_f values ranging from 0.64 to 0.93.

Based on batch equilibrium studies, [1-^{14}C]methomyl (radiochemical purity 98.2%), at 0.2-6.0 ppm, was very mobile in two sandy loams, a silt loam, and a silt soil with Freundlich K_{ads} values ranging from 0.86 to 0.90 and K_{des} values ranging from 0.5 to 2.8. Based on soil TLC studies, [^{14}C]methomyl was very mobile in sandy loam, silt loam, and silt soils with R_f values ranging from 0.46 to 0.82.

Total radioactivity in the beets (leaves and roots) and cabbage (whole) planted 30 and 120 days posttreatment ranged from 0.04 to 0.15 ppm; total [^{14}C]residues in the sunflower seeds ranged from 1.5 to 0.15 ppm. Ethyl acetate-soluble residues in all crops from both planting intervals were less than 0.01 ppm. The application rate was 4 lb ai/A, which is four times the maximum use rate.

The octanol/water partition coefficient (K_{ow}) values for [^{14}C]methomyl (purity 99.8%) ranged from 1.29 to 1.33 in water-saturated octanol solutions containing 0.005 to 0.05 M methomyl.

The following findings are derived from those reviewed studies which have not met the requirements of 40 CFR 158.130 and/or the guidance of Subdivision N., but have been deemed studies following generally sound scientific practice. They thereby provide <u>supplemental</u> information on the fate of methomyl.

[^{14}C]Methomyl (test substance uncharacterized), at 4 lb ai/A, decreased from 91% of the applied immediately after treatment to 55% at 15 days posttreatment and 33% at 30 days posttreatment in a sandy loam soil maintained under unspecified conditions in a greenhouse. Minor amounts of S-methyl-N-hydroxythioacetimidate (0.3-0.4% of the applied) and polar compounds (0.6-1.7%) were detected throughout the study. Nonextractable [^{14}C]residues increased during incubation to 20% of the applied at 45 days posttreatment.

<u>RECOMMENDATIONS</u>

Available data are insufficient to fully assess the environmental fate of methomyl. The submission of data required for full registration for terrestrial food crop terrestrial nonfood, aquatic food crop (watercress), greenhouse food crop, greenhouse nonfood, forestry, and indoor use sites is summerized below:

The following data are required:

<u>Anaerobic aquatic metabolism studies</u>: No data were reviewed.

<u>Aerobic aquatic metabolism studies</u>: No data were reviewed.

Laboratory volatility studies: No data were reviewed.

Aquatic dissipation studies: No data were reviewed.

Accumulation studies on irrigation crops: No data were reviewed.

Groundwater monitoring: Based on results of the laboratory studies on mobility, additional data are necessary to determine the impact of methomyl on ground water. Therefore, small scale retrospective groundwater field monitoring studies are being required. This type of study evaluates the impact of past (and current) use of a pesticide on ground water beneath, and if appropriate downgradient of fields with known histories of usage and hydrogeologic vulnerability. A minimum of three field sites will be required. For each site, the study will encompass at least one set of soil samples (to characterize the soil down to the water table and to locate contaminate plumes from recent applications) and several water samples from wells installed for the study. Existing wells may also be used for sampling if properly constructed and tapping appropriate portions of the aquifer. A protocol should be submitted to the Agency for review prior to the initiation of this study. This protocol should also propose geographic areas (preferably counties) in which appropriate sites will be located. These areas should be typical of the use sites of methomyl and should be hydrogeologically vulnerable. The proposal should include justification of the proposed area: hydrogeologic vulnerability as evidenced by sandy soils, shallow aquifers and use patterns as evidenced by sales data. In addition, suggested sampling and laboratory methodology (including analytical recovery data) should be included for parent methomyl and degradates.

Reentry: Reentry intervals of 1 to 7 days are required as well as further data for mint, roses and chrysanthemums. See attached review by James Adams.

Spray drift: The Agency is requiring Droplet Spectrum and Spray Drift Field Evaluation tests due to the toxicity of the chemical, its methods of application, and the likely exposure of off-site people to the pesticide. The droplet spectrum study is to be performed to reflect the nozzle and other equipment types to be used in the application of methomyl where mist blowers and aircraft are used. The spray drift field evaluation is to be performed to reflect the application equipment, use pattern, and typcial locations of use, which includes different weather factors, in the application of methomyl for these uses.

The following data requirements are fulfilled:

Hydrolysis studies: One study (Friedman, 1983) was reviewed and fulfills data requirements by providing information on the hydrolysis of methomyl in buffered solutions of pH 5, 7, and 9 at 25°C.

Photodegradation studies on soil: One study (Swanson, 00163745) was reviewed and fulfills data requirements by providing information on the photodegradation of methomyl on soil irradiated with natural sunlight.

Photodegradation studies in water: One study (Harvey, 00161885) was reviewed which fulfills data requirements.

Aerobic soil metabolism studies: Five studies were reviewed. Three of these studies (Harvey, 00009325; Harvey, 00008844; and Harvey and Pease, 00155756) were unacceptable and one of these studies (Harvey, 00008567) was scientifically sound but did not fulfill data requirements. One study (Harvey, 00008568) fulfills data requirements by providing information on the metabolism of methomyl in aerobic silt loam soil.

Anaerobic soil metabolism studies: One study (Harvey, 00073214) was reviewed which fulfills data requirements.

Leaching and adsorption/desorption studies: Two studies (Khasawinah and Holsing, 00044306; Priester, 00161884) were reviewed and provide information on the mobility (soil TLC and batch equilibrium) of methomyl in sandy loam, silt loam, silt, and silty clay loam soils.

Terrestrial field dissipation studies: Two studies were reviewed. One study (Harvey, 00133188 and E.I. du Pont de Nemours and Company, 00009326) which in addition with Harvey and Pease, 00009324, fulfills data requirements for this FRSTR. Groundwater concerns will be addressed in the requested monitoring studies.

Confined accumulation studies on rotational crops: One study (Harvey, 00019947) was reviewed. Combined with the results of the aerobic metabolism study and the finding of the Residue Chemistry Branch that no significant additional metabolites were found in treated crops, this rotational crop study fulfills data requirements for this FRSTR. Residues did not accumulate even at the 30 day rotation interval.

Laboratory studies of pesticide accumulation in fish: One fish accumulation study (E.I. du Pont de Nemours and Company, 00131251) and one octanol/water partitioning study were reviewed. The fish study was unacceptable because methomyl residues in the water were not characterized; however, no bioaccumulation of the uncharacterized residues occurred. The octanol/water partition coefficients of 1.29-1.33 suggest methomyl is unlikely to bioaccumulate.

The following data requirements are deferred or are not required for currently registered uses:

Photodegradation studies in air: No data were reviewed. The data requirement is deferred pending the results of the laboratory volatility study.

Field volatility studies: No data were reviewed. The data requirement is deferred pending the results of the laboratory volatility study.

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Forestry dissipation studies: No data were reviewed; however no data are required since there are no forestry uses for methomyl.

Dissipation studies for combination products and tank mix uses: No data were reviewed; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed; however, no data are required because less than 50% of methomyl residues remained upon subsequent application.

Field accumulation studies on rotational crops: No data were reviewed; however, no data are required.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed.

Protective clothing: This will be addressed in the label improvement program.

REFERENCES

The following studies were reviewed:

Collins, R. and F. Kenny. 1986. Octanol-water partition coefficient of Nudrin insecticide. Code 5-8-0-0: RIR-25-009-86. Unpublished study prepared by Shell Development Co. (00157991)

E.I. du Pont de Nemours and Company. 1964. Disappearance of S-methyl 1-C14-N-(methylcarbamoyl)oxy-thio-acetimidate in three soils in the laboratory. Unpublished study received June 29, 1977 under 352-342; CDL:115397-D. (00133187)

E.I. du Pont de Nemours and Company. 1971. Methomyl decomposition in muck soil - a field study. Unpublished study received May 5, 1977 under 352-342; CDL:229711-F. (00009326)

E. I. du Pont de Nemours and Company, Inc. 1972. Residues: Lannate in rainbow trout (Salmo gairdneri). Compilation; unpublished study received October 31, 1983 under 352-366; CDL:251424-E. Prepared by Bionomics, Inc., and submitted by E.I. du Pont de Nemours & Co., Wilmington, DE, CDL:229712-N. (00131251)

Friedman, P. 1983. Hydrolysis of 1-^{14}C-methomyl. Document No. AMR-109-83. Unpublished study received Oct. 3, 1983 under 352-366; submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE; CDL:251424-B. (00131249)

Harvey, J., Jr. 19??. Decomposition of ^{14}C-methomyl in a high organic matter soil in the laboratory. Unpublished study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE. (00009325)

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Harvey, J. 1964a. Disappearance of the S-methyl N-[(methylcarbamoyl)oxy]-thioacetimidate. In Exposure of S-methyl N-(methylcarbamoyl)oxy-thioacetimidate in sunlight, water, and soil. Unpublished study received Dec. 28, 1968 under 8F0671. Submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE; CDL:091179-V. (00008844)

Harvey, J. 1964b. Disappearance of S-methyl 1-C14-(methylcarbamoyl)oxy-thioacetimidate in field soil. Unpublished study received June 29, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Company, Wilmington, DE; CDL:115397-E. (00133188)

Harvey, J., Jr. 1977a. Crop rotation study with 14C-methomyl in the greenhouse. Unpublished study received Jan. 19, 1978 under 352-342; submitted by E.I. du Pont de Nemours and Company, Wilmington, DE; CDL:232720-A. (00019947)

Harvey, J. Jr. 1977b. Decomposition of ^{14}C-methomyl in a sandy loam soil in the greenhouse. Unpublished study received February 28, 1977 under 352-342. Prepared in cooperation with University of Delaware, Soil Testing Laboratory and submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL: 096026-A. (00008567)

Harvey, J. Jr. 1977c. Degradation of 14-C methomyl in Flanagan silt loam in biometer flasks. Unpublished study received February 28, 1977 under 352-342; Prepared in cooperation with University of Delaware, Soil Testing Laboratory and submitted by E.I. du Pont de Nemours and Company, Wilmington, DE; CDL: 096026-B. (00008568)

Harvey, J. Jr. 1977d. Decomposition of ^{14}C-methomyl in flooded anaerobic soils. Unpublished study received Mar. 27, 1979 under 352-342. Submitted by E.I. du Pont de Nemours & Company, Wilmington, DE; CDL:237906-A. (00073214)

Harvey, J. 1983. Photolysis of [1-^{14}C]methomyl. Document No. AMR-121-83. Unpublished study prepared by E.I. du Pont de Nemours and Company, Inc. (00161885)

Harvey, J., and H. Pease. 1973. Decomposition of methomyl in soil. J. Agric. Food Chem. 21(5):10-12. Unpublished study prepared by E.I. du Pont de Nemours and Company, Wilmington, DE. (00155756)

Khasawinah, A.M. and G.C. Holsing. 1976. UC 51762 Pesticide: Mobility on soil thin layer chromatograms. File No. 22754. Unpublished study received September 10, 1980 under 264-341; submitted by Union Carbide Agricultural Products Co., Ambler, PA, CDL:099602-J. (00044306)

Priester, T. 1984. Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with methomyl: Document No. AMR-174-84. Unpublished study prepared by E.I. du Pont de Nemours and Co., Inc. (00161884)

Swanson, M.B. 1986. Photodegradation of [1-^{14}C]methomyl on soil. Document No. AMR-611-86. Prepared and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE. (00163745)

The following studies were not reviewed because they contain summary data only:

E.I. du Pont de Nemours and Company. 1971. Environmental safety of Lannate methomyl insecticide. Summary of studies 095024-B through 095024-K. Unpublisned study received Apr. 9, 1971 under 1F1021; CDL:095024-A. (00008259)

E.I. du Pont de Nemours and Company, Inc. 1979. Ecosystem residue study: spruce/fir forest and cedar swamp, Princeton, Maine, 1978. Compilation; unpublished study received Oct. 3, 1983 under 352-366; CDL:251424-D. (00131250)

Harvey, J., Jr. 1975. Metabolism of aldicarb and methomyl. Pages 389-393, In Pesticides: International Union of Pure and Applied Chemistry Third International Congress; July 3-9, 1974, Helsinki, Finland. Edited by F. Coulston and F. Korte. Stuttgart, West Germany: George Thieme. Environmental quality and safety supplement, vol. III. (05010818)

The following studies were not reviewed because they do not contain data on methomyl:

Allen, C. 1980. Dissipation of azodrin and trimethyl phosphate (TMPO) nondislogables (cotton leaf disc) and dislogables (water rinses) following one aerial application of azodrin to cotton plants, a Texas study. Project No. RIR-24-169-80; 01761518. Unpublished study prepared by Shell Chemical Co. (00155663)

Burkhardt, C.C. and M.L. Fairchild. 1967. Bioassay of field-treated soils to determine bioactivity and movement of insecticides. J. Economic Entom. 60(6): 1602-1610. Also In unpublished submission by American Cyanamid Co., Princeton, NJ; CDL:120350-C. (00092960)

Union Carbide Agricultural Products Company, Incorporated. 1980. Thiodicarb in the environment: Environmental chemistry, environmental fate. Summary of studies 099602-B through 099602-P. Unpublished study received Sept. 10, 1980 under 264-341; CDL:099602-A. (00044299)

The following studies were not reviewed because they contain product chemistry data only:

E.I. du Pont de Nemours and Company. 19??. Calculation of maximum methomyl vapor. Unpublished study received July 29, 1976 under 352-342; CDL:224800-R. (00009188)

Harvey, J. 19??. Stability of S-metnyl N-(methylcarbamoyl)oxy-thioacetimidate in sunlight. Unpublished study received June 29, 1977 under 352-342; submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE; CDL:115397-A. (00133184)

The following studies were not reviewed because they contain reentry data only:

E.I. du Pont de Nemours and Company, Inc. 1981. Proposed reentry intervals for methomyl-treated crops. Compilation; unpublisned study received Oct. 3, 1983 under 352-366; CDL:251425-A. (00131252)

McEwen, F.; G. Ritcey; H. Braun; et al. 1980. Foliar pesticide residues in relation to worker reentry. Pestic. Sci. 11:643-650. (00144442)

The following studies were not reviewed because they contain human exposure data only:

E.I. du Pont de Nemours and Company. 19??. Measurement of cholinesterase of field workers exposed to methomyl residues. Unpublished study received Jul. 29, 1976 under 352-342; CDL:224800-U. (00009190)

E.I. du Pont de Nemours and Company. 19??. Reentry experience in Lannate treated fields. Unpublished study received July 29, 1976 under 352-342; CDL:224800-T. (00009189)

E.I. du Pont de Nemours and Company. 1975. Reentry of workers. Summary of studies 224800-L through 224800-U. Unpublished study received July 29, 1976 under 352-342; CDL:224800-J (00009185)

Guthrie, F.E; J.J. Domanski; A.R. Main; D.G.Sanders; and R.R. Monroe. 1974. Use of mice for initial approximation of reentry intervals into pesticide-treated fields. Arch. Environ. Contam. Toxic. 2(3):233-242. (05013771)

Maddy, K.T. 1976. Current considerations on the relative importance of conducting additional studies on hazards of field worker exposure to pesticide residues as compared to studying other occupational safety hazards on the farm. Pages 125-142, In Pesticide Residue Hazards to Farm Workers - Proceedings of a Workshop; Feb. 9-10, 1976, Salt Lake City, UT. Washington DC.: U.S. Government Printing Office. HEW publication No. (NIOSH) 76-191. (05001833)

Owens, C.B.; E.W. Owens, and D. Zahn. 1978. The extent of exposure of migrant workers to pesticide and pesticide residues abstract. Int. J. Chronobiology 5(2):428-429. (05009824).

The following study was not reviewed because it is a literature review and contains no original data:

Karickhoff, S. and D. Brown. 1979. Determination of octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients for hydrophobic organic pollutants. Prepared by U.S. Environmental Protection Agency, Environmental Research Laboratory; available from the National Technical Information Service, PB80-103591. (00163150)

The following study was not reviewed because it contains residue chemistry data only:

E.I. du Pont de Nemours and Company, Inc. 1983. Results of tests on the amount of residue remaining on treated crops: methomyl. Unpublished study received Feb. 28, 1983 under 352-370; CDL:071432-A. (00125813)

The following studies were not reviewed because they contain ecological effects data only:

E.I. du Pont de Nemours and Company. 1979. Ecosystem study. Unpublisned study received Mar. 27, 1979 under 352-342; CDL:237906-B. (00073215)

E.I. du Pont de Nemours and Company. 1978. Environmental and wildlife information relating to the use of Lannate methomyl insecticide in pineapple in Hawaii. Reports by various sources; unpublished study including published data received Jan. 6, 1981 under 352-EX-106; CDL:099858-A. (00050459)

The following study was not reviewed because the experimental design is not pertinent to current environmental fate data requirements (mobility study done in field with natural rain):

Harvey, J. Jr., 1976. Letter sent to D.D. Drake date Jul. 28, 1976: Methomyl in soil. Unpublished study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL:229725-A. (00051134)

The following study was not reviewed because the experimental design is not pertinent to current enviromental fate data requirements (photodegradation in river water study):

Harvey, J. Jr. 1979. Decomposition of ^{14}C-methomyl in aerated river water exposed to sunlight. Unpublished study received May 6, 1976 under 352-342; submitted by E.I. du Pont de Nemours and Company, Wilmington, DE; CDL:224073-AJ. (00022439, 00038327)

The following study was not reviewed because the experimental design is not pertinent to current environmental fate data requirements (run-off studies):

Pease, H.L. 1970. Letter sent to H.M. Baker dated Aug. 19, 1970: run-off studies with methomyl. Unpublished study received Apr. 9, 1971 under 1F1021; submitted by E.I. du Pont de Nemours & Co., Inc., Wilmington, DE; CDL:095024-E. (00051093)

The following studies were not reviewed because they contain toxicity data only:

McCann, J.A. 1979. Study of the degradation rate of aqueous solutions of methomyl. U.S. Environmental Protection Agency, Chemical and Biological Investigations Branch, unpublished study. (00073256)

Sleight, B.H. III. 1971. Research report: Continuous exposure of rainbow trout (Salmo gairdneri) to Lannate in water. Unpublished study received May 6, 1976 under 352-342; prepared by Bionomics, Inc., submitted by E.I. du Pont de Nemours and Company, Wilmington, DE; CDL:224073-AH. (00009133; 00038325)

The following study was not reviewed because insufficient details about the experimental design were provided in the report to allow an accurate critique:

E.I. du Pont de Nemours. 1983. Volatility data for "Lannate": L and LV. Unpublished study. 4 p. (00156945)

The following study was not reviewed because it is a partial duplicate of 00155756:

Harvey, J., Jr. and H.L. Pease. 1971?. Decomposition of methomyl in soil. Unpublished study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL:229711-D. (00009324)

Harvey, J. and H. Pease. 1973. Decomposition of methomyl in soil. J. Agric. Food Chem. 21(5):784-786. (00158694)

The following study was not reviewed because it is a partial duplicate of 00008844:

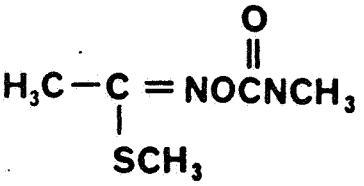
Harvey, J. 19??. Disappearance of the S-methyl N-(methylcarbamoyl)oxy-thioacetimidate from soil in the laboratory. Unpublished study received June 29, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL:115397-C. (00133186)

The following study was not reviewed because it is a partial duplicate of 00131251:

Holt, R.F. 1972. Letter sent to H.M. Baker dated Jan. 10, 1972: lannate (R) fish exposure study - rainbow trout. Unpublisned study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL:229711-C. (00051137)

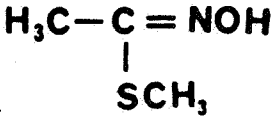
APPENDIX

METHOMYL AND ITS DEGRADATES



Methomyl

S-Methyl-N-[(methylcarbamoyl)oxy]thioacetimidate



S-Methyl-N-hydroxythioacetimidate

Acetonitrile

REVIEW OF METHOMYL REENTRY DATA SUBMITTED BY DUPONT IN RESPONSE TO A REGISTRATION STANDARD

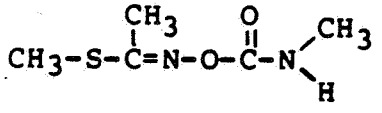
1.0 INTRODUCTION

EPA requires in 40 CFR § 158.140 that registrants must submit data for evaluation of a pesticide's hazard to fieldworkers if the pesticide meets certain criteria. Among the criteria are: 1) acute toxicity of the pesticide is such that the pesticide would be classified in Toxicity Category I, or the pesticide has been implicated in fieldworker poisonings; and 2) the pesticide is used on crops in which agricultural practice requires human tasks that involve substantial contact with residues of the pesticide. Methomyl meets both the toxicity and exposure criteria of 40 CFR § 158.140; and data were, therefore, required under a Registration Standard for Methomyl. In response to that Standard, DuPont has submitted data. This is a review of that data.

Methomyl has been implicated in fieldworker poisoning episodes in California. In response to these complaints, the California Department of Food and Agriculture [CDFA] has established reentry intervals for methomyl ranging from 24 hours to 4 days depending on the crops.

2.0 PESTICIDE STRUCTURE/NOMENCLATURE

Methomyl: Acetimidothioc acid, methyl-, N-(methylcarbamoyl) ester



Other names are: Lannate; Nudrin; DuPont 1179; S-methyl N-[(methylcarbamoyl)oxy]thioacetimidate; and 3-thiabutan-2-one, O-(methylcarbamoyl)oxime.

Molecular Formula: $C_5H_{10}N_2O_2S$ Molecular Weight: 162.2 Daltons

3.0 DISCUSSION

Under the Registration Standard (Task 2. pp. 19-20) and Subdivision K of the Guidelines, the registrant is allowed three major options for the estimation of reentry intervals. Du Pont has chosen the second option by submitting dislodgeable-residue-data dissipation-curves for methomyl applied to a number of crops and even varieties of some crops. It appears that all of this data was previously submitted to the CDFA and was gathered in that environment. Since it is recognized that California's meteorological conditions are generally the least conducive to dissipation of dislodgeable residues in the United States, data gathered

in California are acceptable for establishment of reentry intervals for other environmental conditions in the United States.

Their approach to the calculation of reentry intervals from the dislodgeable residue data is to use Dr. J. Knaak's [CDFA] method and his calculation of a reentry level for methomyl. Knaak's method for the calculation of a reentry interval has been shown to yield essentially the same reentry intervals as the Agency model/method detailed in Subdivision K of the Pesticide Assessment guidelines. Therefore, Du Pont's approach here is valid.

Knaak's method involves calculation of a reentry level from a known allowable reentry level for a standard pesticide in conjunction with the dermal-dose erythrocyte-acetylcholinesterase response data obtained with rats by Knaak's method. [It should be noted here that Knaak's data indicates significant acetylcholinesterase reduction from dermal doses of methomyl even though Du Pont maintains that there is no dermal hazard for the pesticide because of a low acute dermal toxicity (>5000 mg/kg).] Knaak has determined experimentally that an allowable reentry level for methomyl on citrus foliage is 1.55 ug/cm^2. This level is based on the inhibitory effect of dermal doses of methomyl on acetylcholinesterase. It is not relevant if animals, and therefore people, are more sensitive to methomyl through some other mode of toxic effect.

The Registration Standard required that the Registrant submit data and propose reentry intervals for several crops [Task 2. p. 20] that are listed in the first column of Table 1 of this DER. The Registrant is submitting dislodgeable residue data for the crops listed in the second column of Table 1. The Registrant is not submitting data for all of the crops listed in the registration standard. However, this approach is acceptable because residue data from the most hazardous crops are included, and the data can be used for other crops on a worst case basis.

Data are required for those crops which have agricultural practices such as harvesting, thinning, etc. that involve substantial human contact with foliage or soil subsequent to methomyl application. Requirement of data does not necessarily mean that reentry intervals will be required for the pesticide for all or any of its registrations; but if the data do show an unreasonable risk, reentry protection statement/interval(s) will be required for placement on the pesticide's labeling.

Except for the summaries, this submission consists of 12 Exhibits. Exhibits 1, 2, 7, 8, 9, and 11 consist of published papers and CDFA reports or reports submitted to CDFA.

Exhibit 3 contains a summary of methomyl dislodgeable-residue recoveries from recovery studies conducted at the Du Pont and Stoner (contractor) laboratories. Exhibit 3 also contains summaries of the dislodgeable residue dissipation data.

Exhibit 4 contains dislodgeable residue data and dissipation curves for methomyl applied to grape, orange, peach, and nectarine foliage. The primary thrust of this exhibit was to petition for the CDFA reentry interval of 4 days to be reduced to 24 hours. Exhibits 5 and 6 consist of methomyl dislodgeable residue studies on ornamentals and corn, bean, and cabbage plants, respectively.

They also submit fieldworker health data to support their contention that methomyl is not a significant hazard to fieldworkers. Those data are contained in: 1) Exhibit 9 which is a sort of epidemiology study of people working in fields treated with methomyl; 2) Exhibit 12 which is a copy of the 1981 PIMS report; 3) Exhibit 10 which is a report of cholinesterase activity levels in workers sampling foliage for dislodgeable residue determination; and 4) Exhibit 11 which contains a melange of toxicity and metabolism studies, several graphs of methomyl dissipation, a published paper on dissipation of insecticides from cotton, a 1975 reentry paper by Spear et al., calculations for estimation of methomyl inhalation exposure, and a report that industrial exposure to methomyl has not caused symptoms in their workers.

(1) Evaluation of the foliar residue data

Except for the published papers included in the exhibits the experimental procedures for methomyl residues collection, extraction, and quantitation contained in this submission are cursory. There is a short, but valid, estimate of surface residues that can be easily removed by their procedure and a statement that "Methomyl is soluble in water to the extent of 5.8 grams per 100 grams of water." That implies that the extraction was done with water without detergents. This does not coincide with the methodology suggested in Subdivision K but appears to be adequate. The recovery data for rose, chrysanthemum, and carnation foliage reported in their Exhibit 5 indicates that it is minimally adequate. They have submitted a table (Table I of Exhibit 3) of recovery data to support their submitted dissipation data.

The submission also contains data as "dislodgeable residue data". The use of the term "Dislodgeable Residues" is usually taken to mean employment of the procedure of that name developed by Drs. F. A. Gunther and Y. Iwata, but it is questionable that that was the procedure that was used to gather the data. They do not cite the appropriate methodology papers, and they did not originally use leaf punches for foliar sampling as is done in the Dislodgeable Residue procedure (although they later used leaf punches to estimate leaf weight to surface ratios). Much if not all of the submitted data were gathered before 3/31/1976 which could be before the Dislodgeable Residue method came to their attention.

Much of the dislodgeable residue data that Du Pont submits was gathered on whole leaves rather than on a known foliar surface area. That is, their original data was expressed in parts per

million of leaf weight. [N.B.: In this case, the reports in ppm do not mean that the penetrated residues were quantified as well as dislodgeable residues.]

(2) Ratios of Foliar Weight to Surface Area

For implementation of either the CDFA's or the EPA's methods for calculation of reentry intervals, the dislodgeable residue data must be expressed in weight of residue per cm^2 of leaf surface. For that reason, the registrant had to convert the whole-leaf residue values in parts per million to leaf-surface values in ug/cm^2. This has been done in the data submitted, but the reporting of how the conversion factors were determined and calculated is cursory.

The data that they have submitted for estimation of foliar weights per unit surface-area are important here because those ratios are used to convert their whole-leaf residue data from parts per million to weights per unit area, i.e. ug/cm^2. The residue data in ug/cm^2 are then used to estimate exposure levels. Thus, the weight to area ratios affect the estimated worker-exposure rates and the estimated reentry intervals.

In Table XXI of their Exhibit 3, they report data and the calculations for estimation of the surface to weight ratios for nine types of foliage. Their calculations are based on two sides of the leaves. [Some investigators have based their work on one side of the leaf, and this must be recognized when surrogate exposure data are used.] They report replicates of the total weight of 50 leaf-disk samples. Generally they cut 2.54 cm (1 inch) disks, but in the case of carnations they cut 0.317 cm^2 disks. They have 3 leaf-disk weight-replicates for grape, rose, carnation, and pinto-bean foliage; 4 replicates for nectarine, orange, cabbage, and cotton foliage, but only one replicate for chrysanthemum foliage.

The table below presents a summary of their ratios and similar ratios for two types of grass from other studies for comparison.

REPORTED LEAF WEIGHT TO AREA RATIOS

Type of Plant Foliage	Weight/Area Ratio (Two Sides: mg/cm^2)
Grapes	10.92
Nectarines	12.70
Oranges	13.12
Roses	8.68
Carnations	10.41
Chrysanthemums	22.50
Pinto Beans	6.97
Cabbage	29.95
Cotton	8.60
Grass, California	6.83
Grass, North Carolina	10.09

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(3) Calculation of an allowable exposure level

The following calculation is according to methodology presented in Subdivision K of the Pesticide Assessment Guidelines. It is based on: a) Dermal Penetration (DP) factor of 1 since appropriate dermal penetration data are not available; b) a No Observed Effect Level (NOEL) of 2.5 mg/kg/day from a 2-year chronic feeding study in which prostate and kidney effects were observed at higher doses; and c) on a 100 Safety Factor which is used for chronic effects of this type. The calculation is also based on an 8-hour work day and a 70 kg body weight for a fieldworker.

$$AEL = \frac{(NOEL)(BODY\ WEIGHT)}{(SF)(DP)(8\ hr/d)} = \frac{(2.5\ mg/kg/d)(70\ kg)}{(100)(1)(8\ hr/d)}$$

$$= 220\ ug/hr$$

(4) Estimation of the reentry level

The corresponding reentry level is 50 ng/cm^2 [from Popendorf's correlation]. This is 30 times less than the ChE reentry level determined by Knaak (1.55 ug/cm^2).

(5) Estimation of reentry intervals for methomyl

The dislodgeable residue and application rate data contained in this submission are summarized in Table 2. The foliar residue data reported for corn were not converted from ppm to weight per area values in the submission nor is there a weight to area ratio reported. For that reason, it is not possible convert the data to a useable form, and the corn data is not considered here. The foliar residue data in this submission show the high variability commonly reported in such studies. For that reason, I have averaged data points to increase reliability wherever possible. Wherever the dislodgeable residue level was not reported for a period, I have taken the previous date's datum as a surrogate in order to calculate an average (mean) for that period.

REENTRY INTERVAL FOR ORANGE/CITRUS

The means of dislodgeable residue data for orange foliage at 33 ng/cm^2 indicate that a 3-day reentry interval is appropriate.

REENTRY INTERVAL FOR GRAPES

The reported dislodgeable residue levels for grape foliage are higher than for orange foliage even though the pesticide usage rates are the same. The data indicate that methomyl tends to be more persistent on grape foliage under conditions of the test. Even though the data is highly variable, the dissipation rate is clearly lower for grape foliage than for orange foliage. The data reported are based on application of 1.8 lbs of active ingredient per acre (a.i.a.) even though they state that the maximum usage is now 0.9 lbs a.i.a. The use of data from the 1.8 lb a.i.a.

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applications can be used for this review because residues from application of 0.9 lb a.i.a. would be less and the exposure would be less.

There are graphs of grape foliar residue dissipation presented in Exhibit 4 that are not presented as data in Exhibit 3. In order to track the data in Exhibit 4 with that in Exhibit 3, note that data in their Table II (1st and 3rd sprays) correspond to "exhibits 3A and 3B, but "4th spray" does not correspond to "exhibit 3C". Their Table III (1st and 3rd spray) correspond to "exhibit 5A" and "exhibit 5B" in Exhibit 4; but data in their Table III (5th spray) do not represent "exhibit 5C". Their Table IV (1st and 3rd spray) correspond to "exhibit 4A" and "exhibit 4B" in Exhibit 4; but data in their Table III (5th spray) do not represent their "exhibit 4C". Their Table V (1st and 3rd spray) correspond to "exhibit 6A" and "exhibit 6B" in Exhibit 4; but data in their Table V (5th spray) do not represent their "exhibit 6C". The differences in residue levels coincide with a change of analytical laboratory. These differences should be resolved.

The means of dislodgeable residue data for grape foliage are not less than 50 ng/cm^2 until the 7th day after application (when they are 16 ng/cm^2). This indicates that a 7-day reentry interval is appropriate. Interpolation of the data is not possible until there is a resolution of the discrepancy between the data and graphs.

REENTRY INTERVAL FOR PEACHES

The means of dislodgeable residue data for peach foliage are not less than 50 ng/cm^2 until the 4th day after application (when they are 38 ng/cm^2). This indicates that a 4-day reentry interval is appropriate.

REENTRY INTERVAL FOR NECTARINES

The means of dislodgeable residue data for nectarine foliage are not less than 50 ng/cm^2 until the 3rd day after application (when they are 19 ng/cm^2). This indicates that a 3-day reentry interval is appropriate.

REENTRY INTERVAL FOR COTTON

The dislodgeable residue data for cotton foliage are not less than 50 ng/cm^2 through the 3rd day after application when they are 55 ng/cm^2. A 3-day reentry interval appears to be appropriate.

REENTRY INTERVAL FOR MINT

Data have been submitted for residues on mint foliage after application of 0.9 and of 1.8 lb a.i.a. In neither case do the residues dissipate to the 50 ng/cm^2 level at any of the sample dates. Thus it is not possible to establish a reentry interval for mint with the submitted data.

REENTRY INTERVAL FOR ROSES

Dissipation data have been submitted for indoor and outdoor use of methomyl on roses, chrysanthemums, and carnations. The data were taken at short intervals with the last samples taken 24 hours after application.

The means of dislodgeable residue data for rose foliage outdoors are less than 50 ng/cm^2 after 24 hours application (when they are 20 ng/cm^2). This indicates that a 1-day reentry interval is appropriate for roses when grown out of doors. However, the data indicate that methomyl dissipation in the greenhouse is slower than out of doors. When the crop is grown in a greenhouse, the means of dislodgeable residue data for rose foliage is not less than 50 ng/cm^2 after 24 hours application (when they are 286 ng/cm^2). This indicates that a 1-day reentry interval is not adequate for that situation. No data at later sampling dates were reported so it is not possible to establish a rose-greenhouse reentry interval for methomyl with the available data.

REENTRY INTERVAL FOR CHRYSANTHEMUMS

Again the methomyl dissipation rate in the greenhouse is slower than out of doors, but in no case do the foliar residues dissipate to or less than the reentry level at 24 hours after application. Thus, it is not possible to set reentry intervals with the available data.

REENTRY INTERVAL FOR CARNATIONS

In both indoors and outdoors data, the foliar residue levels have dissipated to less than 50 ng/cm^2 at 24 hours after application. Therefore, a one day reentry interval is appropriate for work in carnations either outdoors or in a greenhouse.

REENTRY INTERVAL FOR BEANS AND CABBAGES

Foliar residue levels for both beans (at 31 ng/cm^2) and cabbage (at 13 ng/cm^2) have dissipated to less than the reentry level within 6 hours after application. Therefore, a 24 hour reentry interval is appropriate.

4.0 CONCLUSIONS

The submitted data in concert with toxicological information indicate the following reentry intervals are appropriate: one day for beans, cabbages, roses grown outdoors, and carnations whether grown outdoors or in a greenhouse; three days for cotton, nectarines, and oranges/citrus; four days for peaches; and 7 days for grapes. Although there is limited dissipation data for several other crops, it is not possible to determine an appropriate reentry interval for them either because the foliar sampling was not

conducted long enough [e.g. mint, roses in greenhouses, and chrysanthemums in greenhouses or outdoors] or because the data could not be converted to weight-per-area values for lack of a conversion factor [e.g. corn, celery, lettuce, spinach].

Because of similarity in crops and the work tasks performed in those crops, I believe that a 3 day reentry interval would be adequate for work in apple orchards and that a 1 day reentry interval would be adequate for alfalfa, asparagus, brocoli, brussel sprouts, carrots, cauliflower, celery, collards, cucumbers, lettuce, melons, onions, peanuts, peas, peppers, potatoes, sorhgum, soybeans, summer squash, spinach, sugar beets, tobacco, and tomatoes.

5.0 RECOMMENDATIONS

The Registrant should be required to submit further data for mint, roses in greenhouses, and chrysanthemums in greenhouses or outdoors and to submit weight/area conversion factors for corn foliage (for reentry protection of detasselers). The Registrant should also be required to place the above reentry intervals on his labels.

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TABLE 1

LIST OF FOLIAR DISLODGEABLE RESIDUE DATA BY PLANT/CROP

DATA REQUIRED BY THE REGISTRATION STANDARD	DATA CONTAINED IN DU PONT SUBMISSION
1. citrus	orange
2. grapes	grapes
3. peaches	peaches
4. nectarines	nectarines
5. alfalfa	
6. apples	
7. asparagus	
8. beans	beans
9. brocoli	
10. brussel sprouts	
11. cabbage	cabbage
12. carrots	
13. cauliflower	
14. celery	
15. collards	
16. corn	corn
17. cotton	cotton
18. cucumbers	
19. lettuce	
20. melons	
21. mint	mint
22. onions	
23. peanuts	
24. peas	
25. peppers	
26. potatoes	
27. sorhgum	
28. soybeans	
29. summer squash	
30. spinach	
31. sugar beets	
32. tobacco	
33. tomatoes	
34. trees, forest	
35. ornamentals	ornamentals rose chrysanthemum carnation

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TABLE 2

SUMMARY OF DISLODGEABLE RESIDUE DATA SUBMITTED

Type of foliage	Dislodgeable Residue Data, ng/cm² at an Interval After Application						Pesticide Treatment Level
	4 hr	1 d	2 d	3 d	4 d	7 d	
ORANGE							
Navel	5	<3	<3	<3			1.8 lb a.i.a.
	315	84	123	76			"
	236	92	42	13			"
Valencia	10	<3	3	<3			"
	102	81	197	87			"
	171	126	31	16			"
averages	140	65	67	33			
GRAPE							
Thompson IIa	15	142	70	39	2	< 2	1.8 lb a.i.a.
" IIb	1267	415	70	153	87	15	"
" IIc	633	197	44	22	39	31	"
IIIa	131	120	65	28	28#	13*	"
IIIb	458	79	100	46	92	44*	"
IIIc	74	100	26	4	4#	24*	"
Palomino IVa	764	186	131	142	33	13	"
IVb	786	306	218	218	349	20	"
IVc	306	142	41	9	4	6	"
Cabernet Va	349	197	120	85	85#	2*	"
Vb	480	284	262	131	240	20	"
Vc	197	131	33	11	11#	4*	"
averages	455	192	98	74	82	16	
PEACH	229	94	99	81	28		1.8 lb a.i.a.
	241	178	96	-	-		"
	51	178	107	53	38		"
averages	174	150	101	67	38		
NECTARINE	140	70	58	15			1.8 lb a.i.a.
	203	86	46	23			"
averages	172	78	52	19			
COTTON	5930	1220	115	55			0.5 lb a.i.a.
MINT	1520	707	333				0.9 lb a.i.a.
	2297	1233	627				~~1.8 lb a.i.a.~~

= datum taken from previous date's to replace missing datum

* = residues at 6 days

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TABLE 2 [continued]

SUMMARY OF DISLODGEABLE RESIDUE DATA SUBMITTED

Type of foliage	Dislodgeable Residue Data, ng/cm² at an Interval After Application					Pesticide Treatment Level
	1 hr	2 hr	4 hr	8 hr	24 hr	
ORNAMENTAL						
rose;						
outdoors	564	460	451	234	18	0.45 lb a.i.a
	712	651	556	503	21	"
averages	638	556	504	369	20	
greenhouse	755	738	955	825	286	0.45 lb a.i.a
	781	1160	868	668	373	"
averages	768	949	912	747	330	
chrysanthemum						
outdoors	1845	2003	1463	1125	27	0.45 lb a.i.a
	1240	1890	1485	990	248	
averages	1543	1947	1474	1058	138	
greenhouse	755	738	955	825	286	0.45 lb a.i.a
	781	1160	868	668	373	"
averages	768	949	912	747	330	
carnation						
outdoors	489	271	208	148	17	0.45 lb a.i.a
	354	343	115	104	19	
averages						
greenhouse	115	146	146	72	11	0.45 lb a.i.a
	115	167	135	82	4	"
averages	115	157	141	77	8	
	0 hr	2 hr	6 hr	12 hr	24 hr	
BEAN	153	118	31	15	11	0.5 lb a.i.a.
CABBAGE	51	45	13	15	7	0.5 lb a.i.a.

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