METHOMYL

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-5830

Final Report

May 21, 1981

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

Enviro Control, Inc.
One Central Plaza
11300 Rockville Pike
Rockville, Maryland 20852

METHOMYL

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CASE GS0028 METHOMYL STUDY 1 PM 20C 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 30 TOPIC 051515 GUIDELINE 40 CFR 163.62-7c

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00CC8844 CONTENT CAT C1

Harvey, J. (1964?) Exposure of S-Methyl N-ø(methylcarbamcyl)oxy]-thioacetimidate in Sunlight, Water, and Soil. (Unpublished study received Dec 28, 1968 under 8F0671; submitted by E.I. du Pont de Nemours & Co., Inc., Wilmington, Del.; CDL:091179-V)

DIRECT RVW TIME = 33½ (MH) START-DATE END DATE

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: Apr. 22, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Physico-Chemical Transformations - Hydrolysis

This section of the study is scientifically invalid because there is no indication that it was performed in the dark. Also, controls and blanks were not run and the samples were not run in duplicate.

Physico-Chemical Transformations - Photolysis

This section of the study is scientifically invalid because dark controls were not run and hours of exposure of methomyl to sunlight were not stated.

Metabolism - Aerobic Soil

1. This section of the study is scientifically valid.

2. Methomyl exhibited a half-life of 30-40 days in a silt loam soil.

3. At 6 weeks after treatment of a silt loam soil with [^{14}C]methomyl, 31-39% of the parent compound was degraded to CO_2 and 44-48% remained as undegraded parent compound.

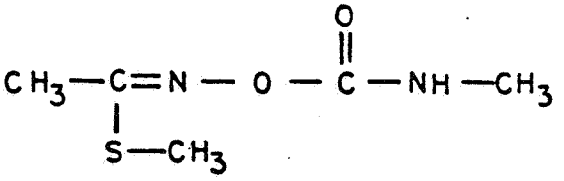
Field Dissipation - Terrestrial

1. This section of the study is scientifically valid.

2. At 1 month after treatment 71% of the radioactivity and 98% of the methomyl had dissipated from a silt loam soil, and at 1 year after treatment methomyl residues were not detected.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Hydrolysis

A 3.0% solution of methomyl (E.I. du Pont de Nemours and Co.; purity not reported) in distilled water was stored in a glass-stoppered vessel in the laboratory for 168 days. A 10-ml sample of the solution was fractionated with a benzene/water solution on a 100-tube counter-current fractionator.

Aliquots (1.0 ml) of the aqueous phase were diluted with methanol, and the absorbance was determined at 220-260 nm on a recording spectrophotometer.

Photolysis

The surfaces of five glass plates were coated with 1.0 ml of a 5% solution of methomyl (E.I. du Pont de Nemours and Co.) in chloroform. After the solvent evaporated, each plate containing crystalline methomyl was covered with a $^{1}/_{16}$-inch-thick sheet of polished quartz, and the edges were sealed with silicone rubber clear-seal. The clear-seal was allowed to dry overnight and the edges were then covered with black electrical tape.

Four of the glass plates were placed on the roof with the quartz side up. The fifth sample was opened immediately and the methomyl crystals were scraped from the plate. The sample was analyzed by IR spectroscopy using a cesium iodide disc technique (not described).

The samples were removed from the roof at 20, 50, 80, and 120 days and analyzed with the IR spectrophotometer.

Soil Metabolism

Each of 12 plastic pots was filled with 500 g of unsterilized Keyport silt loam soil. The soil in nine of the pots was treated with methomyl at 200 lb ai/A (25 ml of a 0.40% aqueous solution; E.I. du Pont de Nemours and Co., purity not reported). The soil in one pot was treated at 100 lb ai/A with the same solution, and the soil in the two control pots was treated with 25 ml of water.

One of the pots treated at 200 lb ai/A and the pot treated at 100 lb ai/A were allowed to stand for 2 hours prior to analysis. Four of the treated pots and one control were placed on the laboratory windowsill (series A). One treated pot was removed from the windowsill and analyzed at 10, 21, 31, or 42 days after treatment. The remaining pots were placed on a shelf in the laboratory (series B) and allowed to stand for 15, 25, 36, or 46 days prior to analysis. The pots were watered as necessary (as if plants were growing in the soil).

After standing for the specified period of time, the soil was spread out on a sheet of polyethylene, allowed to air dry, and sieved through a 10-mesh sieve. The dry soil (<10 mesh) was added to a chromatographic column (540 mm long) that contained 0.5 inches of Florisil. The column was eluted with 1.2 liters of methanol. The eluate was evaporated to dryness on a rotary evaporator. The residue was dissolved in either a water/chloroform or an ethyl acetate/water mixture and filtered. The first 10 ml of filtrate was fractionated with a 20-tube counter-current fractionator.

The tubes were removed from the fractionator, and the upper phase of the water/chloroform filtrate was diluted to 10 ml 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 spectrophotometrically.

Soil Metabolism of [^{14}C]Methomyl

A glass metabolism chamber consisting of two parts attached with an O-ring seal and a pressure clamp was connected to three NaOH traps and an oxidizing furnace with Tygon tubing. The oxidizing furnace was between traps 2 and 3.

Three metabolism chambers (Figure 1) were each filled with 400 g of moist soil (either Keyport silt loam, pH 4.7; Keyport silt loam, limed to pH 7.9; or a soil from the San Joaquin Valley, California, pH 7.9) and treated with an aqueous solution of [1-^{14}C]methomyl (E.I. du Pont de Nemours and Co.; purity not reported) at 4.0, 4.3, and 5.5 lb ai/A, respectively. A stream of air was circulated through the apparatus continuously.

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After a 42-day incubation period, 1.0-ml aliquots from the NaOH traps were added to a scintillation vial filled with 15 ml of scintillation solution (3.4 g PPO [2,5-diphenyl oxazole], 9.0 mg dimethyl POPOP [1,4-bis-2-(4-methyl-5-phenyloxazolyl)benzene], 600 ml toluene, and 378 ml absolute ethanol) and counted on a liquid scintillation counter (LSC). Counting efficiency was determined by internal standardization with labeled toluene.

An aqueous solution of $BaCl_2$ (to precipitate $^{14}CO_2$) was added to the solution remaining in the first NaOH trap until formation of a precipitate ceased. Individual traps were examined, although the $BaCl_2$ precipitate proved that 97-99% of the original ^{14}C was caught in the first trap. Aliquots of the clear supernatant liquid were counted by LSC. This was done to determine what portion of the radioactivity in the trap can be attributed to $^{14}CO_2$.

After the incubation period the soil was removed from the metabolism chamber and divided into four parts. Each part was added to a centrifuge bottle filled with methanol, capped, and shaken for 20 minutes. The slurry was centrifuged and the supernatant was removed. The soil was extracted twice with methanol and four times with water by shaking and centrifugation. The extracts were filtered, and 50-µl aliquots of the filtrate were added to 15-ml portions of scintillation solution (12 volumes spectro-grade p-dioxane; 2 volumes anhydrous ethyleneglycol dimethylether; 1 volume anisole; 0.32 g PPO; 2.1 mg POPOP/100 ml solvent; and 8 g naphthalene/100 ml solvent) and analyzed by LSC.

The remainder of the filtered extracts were combined and concentrated to 10-25 ml under reduced pressure. An aliquot of the concentrate was fractionated in a benzene/water system in a counter-current fractionator. Aliquots (50 µl) of the soil extract fractions were counted in 15 ml of the scintillation solution.

After extraction the soil was air dried and sieved through a 20-mesh sieve. Aliquots of the extracted soil were analyzed by wet combustion.

Thin-layer chromatography (TLC) was used to confirm the presence of methomyl and [^{14}C]S-methyl-N-hydroxythioacetimidate (a hydrolysis product). The TLC plates were developed for 15 minutes in ethyl acetate and exposed to X-ray film.

Field Dissipation

Three stainless steel cylinders (4-inch diameter and 15 inches long) were driven into a silt loam soil so that 0.5 inches of the cylinder remained above the soil surface. The top 1.5 inches of the silt loam soil was removed from the cylinders and a ring with a 3-inch outer diameter and 1-inch wide was placed on the exposed soil surface. The

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soil surface inside the ring was treated with the equivalent of 4.5 lb ai/A of 1-[^{14}C]methomyl (E.I. du Pont de Nemours and Co.). The 1.5 inches of soil that had been removed was placed back in the cylinder on top of the rings and 60 ml of water was added. The plot was covered with an 8-mesh screen to minimize the splashing of raindrops.

Two weeks after treatment, the 3-inch-diameter rings were dug up and washed with water. The water was allowed to fall in the cylinders. Weeds that grew in the cylinders were cut prior to the first leaf stage and left to decompose on the soil surface.

Cylinders were dug up at 1, 3, and 12 months after treatment and returned to the laboratory where the soil was extruded, sectioned (four 1.5-inch layers, followed by two 2-inch layers and two 2.5-inch layers) and analyzed. Individual sections from the 1-month sample were slurried with water, ball-milled, air dried, sieved through a 10 and a 20-mesh sieve, and further sampled for a wet-combustion analysis. Results were compared with those from longer term exposures.

Sections from the 3-month core were handled in two ways: the upper three layers were extracted first five times with methanol and then four times with H_2O. Radioactivity in the extracts was determined by scintillation counting, and the extracted soil was dried, sieved, and analyzed by wet-combustion as mentioned for the 1-month sample. The remaining lower layers were analyzed by wet combustion as described.

Each section of the 12-month samples was mixed with water and subjected to ball-milling for 1 hour. The mixtures from the top four layers were centrifuged and analyzed by LSC as described. The extracted soil and the slurries from the remaining sections were dried, sieved, and analyzed by the methods used on the 1-month samples.

Methomyl and S-methyl-N-hydroxythioacetimidate were confirmed by shaking the dried top layer of the soil cores four times with water, centrifuging, and combining the extracts. The combined extracts were concentrated to 10 ml under reduced pressure and fractionated as described in the soil metabolism section. The extract and standard fractions were analyzed by TLC followed by X-ray film exposure.

REPORTED RESULTS:

Hydrolysis

After 168 days, all of the methomyl applied was found to be present as either methomyl (90%) or the hydrolysis product S-methyl-N-hydroxythioacetimidate (9%).

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Photolysis

When methomyl was exposed to sunlight for periods up to 120 days, no decomposition was observed.

Soil Metabolism

The recovery rates for methomyl were 88-89%. The half-life of methomyl in a silt loam soil was approximately 30 days (Figure 2).

Soil Metabolism of [^{14}C]Methomyl

Under laboratory conditions, the results for all three soils were similar. In all three soils, 31-45% of the [^{14}C]methomyl applied was degraded to $^{14}CO_2$ over the 42-day period. Methomyl was the primary compound extracted from the soil. Small amounts of S-methyl-N-hydroxythioacetimidate and an unidentified polar fraction (<2%) were determined (Table 1).

Field Dissipation

One month after treatment 29% of the applied radioactivity remained in the soil, and 1 year after treatment 15% of the applied radioactivity remained. Methomyl residues declined over the course of the experiment, with none detectable 1 year after treatment. S-methyl-N-hydroxythioacetimidate could not be detected 1 year after treatment. The remaining residues were unextractable.

All of the radioactivity recovered from the soil was present in the top 8 inches. Approximately 28, 19, and 14% of the applied radioactivity was recovered in the upper 3 inches of soil at 1, 3, and 12 months, respectively, after treatment. These recoveries represented 97-98% of the total amount recovered in the upper 15 inches of soil (Table 2).

DISCUSSION:

Hydrolysis

1. The description of the materials and methods was vague. There is no indication that controls were run or that the experiment was performed in the dark to prevent photolysis. The amount of 3% aqueous methomyl solution used was not stated. The temperature and pH of the solution were not stated.

2. There is no indication that a reagent blank was analyzed or that the samples were run in duplicate.

Photolysis

The experiment location, cloud cover, and average daily temperature during the experiment were not given. Also, hours of sunlight exposure were not reported and dark controls were not run.

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Soil Metabolism

1. Plastic pots were used in the experiment. Some of the methomyl may have adsorbed to the plastic pots. Glass containers should have been used.

2. The incubation temperature and soil moisture content were not included. Also, the method sensitivity was not presented.

3. Methomyl dissipated at a slightly faster rate in the samples incubated on the windowsill than in the samples incubated on a shelf in the laboratory. This was presumed to have resulted from a less uniform environment (temperature and light fluctuations) at that location.

4. Sterile controls were not run; therefore, the amount of methomyl actually degraded by microorganisms cannot be determined.

Soil Metabolism of [^{14}C]Methomyl

1. The texture of the California soil and the pH, CEC, organic matter content, and particle size analysis of both soils were not given. Also, the incubation temperature, moisture content, and method sensitivity were not given.

2. Sterile controls were not run; therefore, the amount of methomyl actually degraded by microorganisms cannot be determined.

Field Dissipation

1. More than 44% of the radioactivity recovered from the soil was found in the top 1.5 inches of soil. Although some radioactivity would have been expected in the top 1.5 inches of soil because of upward percolation of water and dissolved methomyl, the amount present was excessive because the top 1.5-inch soil layer was untreated. When the top 1.5 inches of soil was disturbed by removing the stainless steel ring, some of the ^{14}C methomyl-treated soil may have become mixed with the untreated soil, thus explaining the residues.

2. The method sensitivity was not given.

3. Soil characteristics such as particle size analysis, pH, and organic matter content were not included for the silt loam soil.

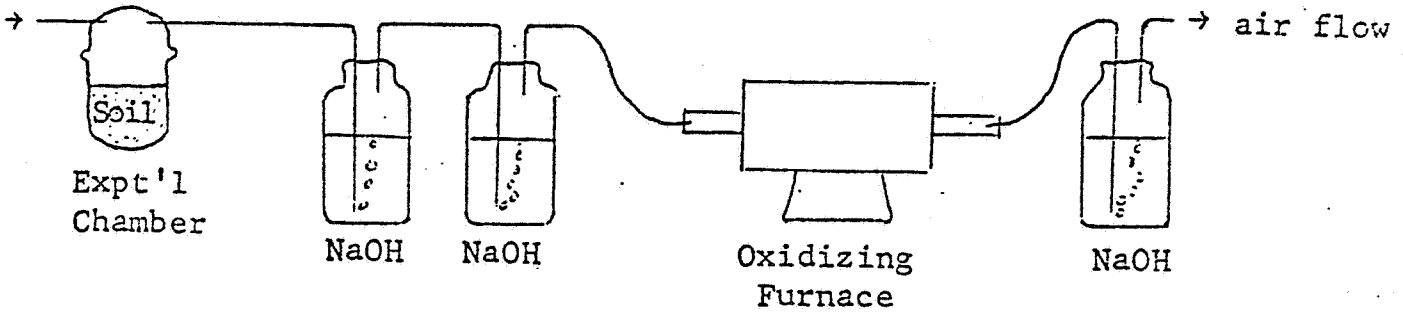


Figure 1. Primary trapping system - laboratory study of soils treated with methomyl.

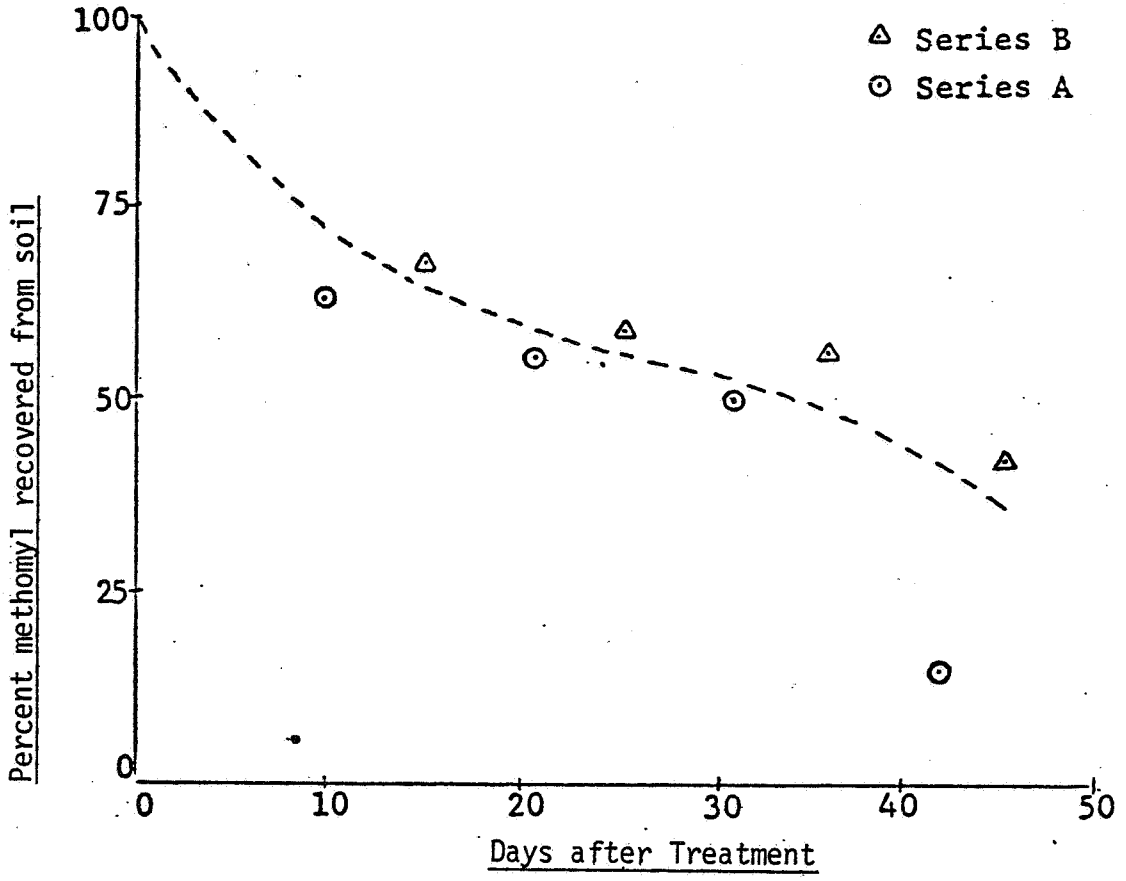


Figure 2. Dissipation of methomyl in a silt loam soil in the laboratory.

Series A incubated on laboratory windowsill.

Series B incubated on laboratory shelf.

Table 1. Decomposition of [^{14}C]methomyl in soil over a 42-day period.

Soil	pH	Treatment (lb ai/A)	Recovery of radioactivity (%)[a]			Composition of soil extractable radioactivity (%)[a]		
			$^{14}CO_2$	Soil extractable	Soil residue	Methomyl	Compound A[b]	Compound B[c]
Keyport silt loam	4.7	4.0	39	51	14	48	1	1
Keyport silt loam	7.9	4.3	31	47	18	44	2	1
California	7.9	5.5	45	33	12	31	1	1

[a] Percent of original treatment.

[b] Compound A - S-methyl-N-hydroxythioacetimidate.

[c] Unidentified polar fraction.

Table 2. 1-[^{14}C]Methomyl residues recovered from a silt loam soil treated at 4.5 lb ai/A.

Depth (inches)	Radioactivity recovered after treatment (% of applied)		
	1 month	3 months	12 months
0-1.5	17.4	15.6	10.7
1.5-3.0	10.7	3.3	3.7
3.0-4.5	0.9	0.3	0.4
4.5-6.0	0.2	0.1	0.1
6.0-8.0	0.1	ND	0.1
8.0-10.0	ND[a]	ND	ND
10.0-12.5	ND	ND	ND
12.5-15.0	ND	ND	ND
Total	29.3	19.3	15.0

[a]ND nondetectable.

CASE GS0028 METHOMYL STUDY 2 PM 200 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION CC - ACTIVE INGREDIENT

FICHE/MASTER ID 00CC9325 CONTENT CAT 01

Harvey, J., Jr. (19??) Decomposition of 14C-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, Del.; CDL:229711-E)

SUBST. CLASS = S.

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

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: Apr. 23, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

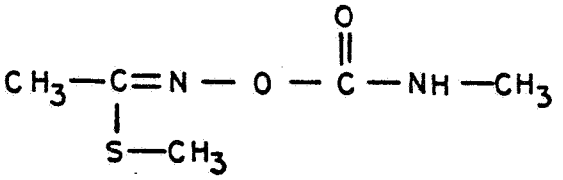
Metabolism - Aerobic Soil

1. The metabolism data in this study are scientifically valid. However, the method used in the soil extraction portion of this study was scientifically invalid because it did not effectively remove methomyl from soil.

2. Over a 45-day period 47% of the applied methomyl was degraded to CO_2, indicating that methomyl has a half-life of approximately 45 days in soil.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

A Minnesota muck soil (52% organic matter; pH 5.5) was treated at 4.0 lb ai/A with [^{14}C]methomyl (E.I. du Pont de Nemours and Co., Inc.). The treated soil was placed in a metabolism chamber described in Study 1 (MRID 00008844) and incubated for 45 days.

The NaOH traps were changed at 10, 17, 24, 31, 38, and 45 days after treatment. Aliquots (1.0 ml) of the NaOH solution were added to a scintillation vial containing 15 ml of scintillation solution and analyzed by liquid scintillation counting (LSC).

After LSC, $BaCl_2$ was added to the first trap and the solution was analyzed as described in Study 1 (MRID 00008844).

At 45 days posttreatment the soil was removed and extracted three times with a total of 400 ml of water. The extracts were analyzed by LSC and then combined. The combined extracts were concentrated in a rotary evaporator.

The concentrated extracts were spotted on silica gel thin-layer chromatography (TLC) plates, developed for 15 minutes in ethyl acetate, compared with spots of possible metabolites, and scanned for radioactivity. The bands were scraped off of the TLC plates, added to scintillation solution, and analyzed by LSC.

The extracted soil was air dried and ball-milled for 16 hours. Aliquots of the mixture were analyzed by combustion in a Tri-Carb Sample Oxidizer.

REPORTED RESULTS:

At 45 days after treatment, 7.7% of the applied radioactivity was recovered as methomyl, 46% was unextracted, and 47% had degraded to $^{14}CO_2$ (Table 1).

DISCUSSION:

1. The author extracted the soil with 400 ml of water. This was an insufficient amount of water for the extraction of 400 g of muck soil, as was evidenced by the fact that 46% of the applied radioactivity was unextractable. A much larger volume of water or a different solvent should have been used. Recovery data were not presented for the extraction procedure.

2. The fact that the soil had a high organic matter content (52%) would indicate the possibility of adsorption of methomyl to the organic fraction of the soil. This could be the reason for the high amount of unextractable residues found by the author.

Table 1. Degradation of [^{14}C]methomyl in a muck soil.

Radioactivity recovered	Percent of treatment
$^{14}CO_2$	47
Unextractable soil residues	46
Extractable soil residues identified by TLC	8
Methomyl (7.7%) S-methyl-N-hydroxythioacetimidate (0.2%) Unidentified polar derivative (0.1%)	

CASE GS0028 METHOMYL STUDY 3 PM 200 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION CC - ACTIVE INGREDIENT

FICHE/MASTER ID 00008567 CONTENT CAT C1

Harvey, J., Jr. (1977) Decomposition of 14C-Methomyl in a Sandy Loam Soil in the Greenhouse. (Unpublished study received Feb 28, 1977 under 352-342; prepared in cooperation with Univ. of Delaware, Soil Testing Laboratory, submitted by E.I. du Pont de Nemours & Co., Wilmington, Del.; CDL:C5C026-A)

SUBST. CLASS = S.

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich DATE: May 5, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

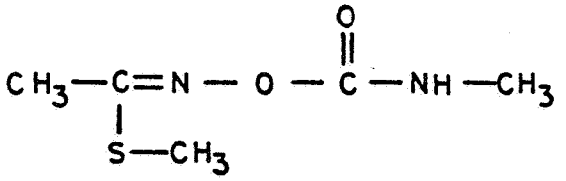
Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Methomyl decomposed in a sandy loam soil in the greenhouse with a half-life of less than 30 days, although the cause of decomposition, microbial or physico-chemical, could not be determined from this study.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Six 1,000-ml glass beakers were filled to a 5-inch depth (1,400 g air-dried soil) with a sandy loam soil from New Castle, Delaware (74% sand; 19.5% silt; 6.5% clay; 0.73% organic matter; pH 5.9; cation exchange capacity 3.17 meq/100 g). An aqueous solution of 3.34 mg S-methyl[1-^{14}C]N-[(methylcarbamoyl)oxy]thioacetimidate (methomyl; E.I. du Pont de Nemours & Co., purity not reported) was pipetted onto the soil surface (equivalent of 4 lb ai/A) and 50 ml of water was added (soil moisture content not given). The beakers were placed in a greenhouse (temperature not reported) and maintained in a moist condition. Soil was harvested at 0, 3, 7, 15, 30, and 45 days after treatment.

At harvest, each entire soil sample was extracted two times with methanol (500 ml per extraction) and four times with water (500 ml per extraction). Radioactivity in the extracts was determined by liquid scintillation counting. The six extracts were then combined and concentrated. Aliquots were mixed with nonradioactive methomyl and an oximino compound (hydrolysis product) and streaked on silica gel GF thin-layer chromatography (TLC) plates, which were developed with ethyl acetate. Bands corresponding to methomyl, oximino compound, and origin (polar fraction) were scraped off the TLC plates and counted in scintillation solution.

The soil was dried after extraction and analyzed for residual radioactivity after combustion. A 50-g sample of air-dried soil from the 45-day treatment was further analyzed by fractionating the soil organic matter components and measuring radioactivity in each fraction. The cited fractionation procedure involved a hot alkali extraction yielding the insoluble humic acid and the soluble fraction, which was acidified (α-humus insoluble), treated with dilute NaOH (β-humus insoluble), and then extracted with ethyl acetate to separate the methomyl and/or oximino compound from the water-soluble fulvic acid fraction. TLC plates were utilized as described previously for compound identification of the ethyl acetate extract (only oximino compound could be present, as methomyl would be hydrolyzed during the procedure).

REPORTED RESULTS:

Results given in Table 1 show that extractable methomyl decomposed rapidly in this soil, with a half-life of less than 30 days. Only trace amounts of the oximino compound or polar fraction were extracted, whereas steadily increasing amounts of radioactivity were found in the unextracted residue. Presumably, the radioactivity lost was volatilized as CO_2 (not measured).

Fractionation of the "unextractable residue" at day 45 showed 32% of the residual radioactivity was insoluble in hot alkali. Some radioactivity was found distributed in each fraction, ranging from 3 to 24% of the "unextractable radioactivity." The ethyl acetate fraction had 14% of the "unextractable radioactivity" (3% of the total radioactivity), which was identified as oximino compound with no polar fraction present.

DISCUSSION:

1. Microbial effects could not be separated from physico-chemical effects in this study because there was no sterile control soil and no measurement of $^{14}CO_2$, and the incubation was presumably in the light in the greenhouse.

2. Neither the temperature nor the moisture content of the soil is reported, further compounding limitations of the usefulness of the data.

3. About 3% of the applied label was reincorporated into the soil organic matter during the 45 days. The ^{14}C was found in all fractions of the organic matter and thus the authors implied that methomyl had degraded to $^{14}CO_2$ and the $^{14}CO_2$ had been reincorporated. However, it is also likely that methomyl or some of its metabolites were adsorbed by the various fractions of soil organic matter.

Table 1. Decomposition of [^{14}C]methomyl in a sandy loam soil in a greenhouse.

Days after treatment	Recovery of radioactivity (% OT[a])			
	Methomyl	Oximino compound	Polar fraction	Unextracted residue
0	91	0.3	0.8	3
3	80	0.4	0.6	8
7	72	0.3	1.7	7
15	55	0.3	1.5	14
30	33	0.4	1.5	18
45	21	0.3	1.5	20

[a]OT, original treatment.

CASE GS0028 METHOMYL STUDY 4 PM 22C 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 30 TOPIC 05052010 GUIDELINE 40 CFR 163.62-8b/c

FORMULATION CC - ACTIVE INGREDIENT

FICHE/MASTER ID 00008568 CONTENT CAT C1

Harvey, J., Jr. (1977) Degradation of 14C-Methomyl in Flanagan Silt Loam in Biometer Flasks. (Unpublished study received Feb 28, 1977 under 352-342; prepared in cooperation with Univ. of Delaware, Soil Testing Laboratory, submitted by E.I. du Pont de Nemours & Co., Wilmington, Del.; CDL:096026-B)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -30-05052005

DIRECT RVW TIME = 11 (MH) START-DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
CRG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich DATE: May 1, 1980

APPROVED BY:
TITLE:
CRG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Microorganisms will decompose methomyl in an aerobic silt loam soil with a half-life of about 6 weeks under common environmental temperatures and moisture conditions (~25 C and 70% moisture content). CO_2 will be produced from the C-1 position; small quantities of the oximino degradation product and some unidentified polar compounds will be found in the soil; and increasing amounts of an unidentified, organically bound form will accumulate in the soil with time.

3. Data from this study help satisfy the requirements in Section 163.62-8(b) of EPA's Proposed Guidelines for Registering Pesticides (July 1978) by providing information on aerobic soil metabolism in a silt loam soil.

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Metabolism - Effects of Microbes on Pesticides

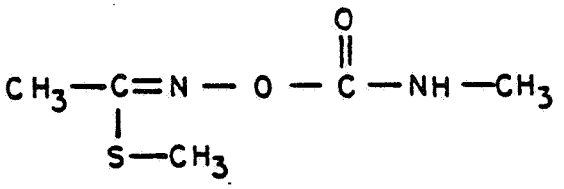
1. This study is scientifically valid.

2. Methomyl will be degraded by microorganisms. After treated silt loam soil was incubated for 45 days, 23% of the applied radioactivity was metabolized to $^{14}CO_2$.

3. Data from this study help satisfy the requirements in Section 163.62-8(f)(2) of EPA's Proposed Guidelines by providing information on the rate of methomyl metabolism by soil microorganisms.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

A Flanagan silt loam (19% sand; 70% silt; 11% clay; 8.3% organic matter; pH 6.5; cation exchange capacity 31.6 meq/100 g) (50 g), inoculated with local soil, was placed in a biometer flask and 0.22 mg S-methyl [1-^{14}C]N-[(methylcarbamoyl)oxy]thioacetimidate (methomyl; E.I. du Pont de Nemours & Co., Inc.; purity not reported) was added to produce a treatment level of 4 ppm. Six of these were prepared, moistened to 70% water holding capacity of the soil, and closed with stopcocks fitted with ascarite filters. Aqueous NaOH was placed in the side tubes; flasks were sealed and placed in a dark incubater at 25 C. The NaOH was periodically removed and analyzed for ^{14}C by a standard scintillation counting technique. Confirmation of $^{14}CO_2$ was made by quantitative precipitation with $BaCl_2$. The system was flushed with oxygen to retain aerobicity whenever the NaOH was removed.

At days 0, 3, 7, 15, 30, and 45 posttreatment, flasks were selected from the incubator. Methomyl extraction by methanol and water and determination by thin-layer chromatography were performed as described in Study 3 (MRID 00008567). Soil from day 45 was further analyzed for residual methomyl after methanol/water extraction. A typical soil organic matter fractionation procedure beginning with a hot alkali extraction as described in Study 3 (MRID 00008567) was used (Figure 1).

A sterile control, consisting of a heat sterilized soil treated with [^{14}C]methomyl under aseptic conditions and incubated as described above, was included in this study (45-day incubation).

REPORTED RESULTS:

Table 1 shows the course of [^{14}C]methomyl degradation in this study. Total recovery of the radioactive material averaged 92%. Very little decomposition was noted in sterile soil under identical treatment conditions. Analysis of the unextracted residue is given in Figure 1.

DISCUSSION:

1. Of the 53% of the "unextractable residue" that was insoluble in hot alkali, only 12% is accounted for as humin (Figure 1). The remaining 41% is probably tightly bound to soil particles as either methomyl or a degradation product. This represents only 11% of the original radioactivity, but could conceivably be much greater on heavier textured soils.

2. The 41% of the radioactivity in the "unextracted residue" unaccounted for, plus the 19% reported as methomyl and/or oximino compound in the fulvic fraction, together show that as much as 60% of the "unextracted residue" may still have been methomyl and/or its degradation products.

3. The inoculation of Flanagan soil with a fresh local soil was probably done to quickly increase the microbial population of a previously air-dried soil. This questionable procedure could have been avoided by moistening and preincubating the soil for 1 or 2 weeks to allow for a natural revival of the population.

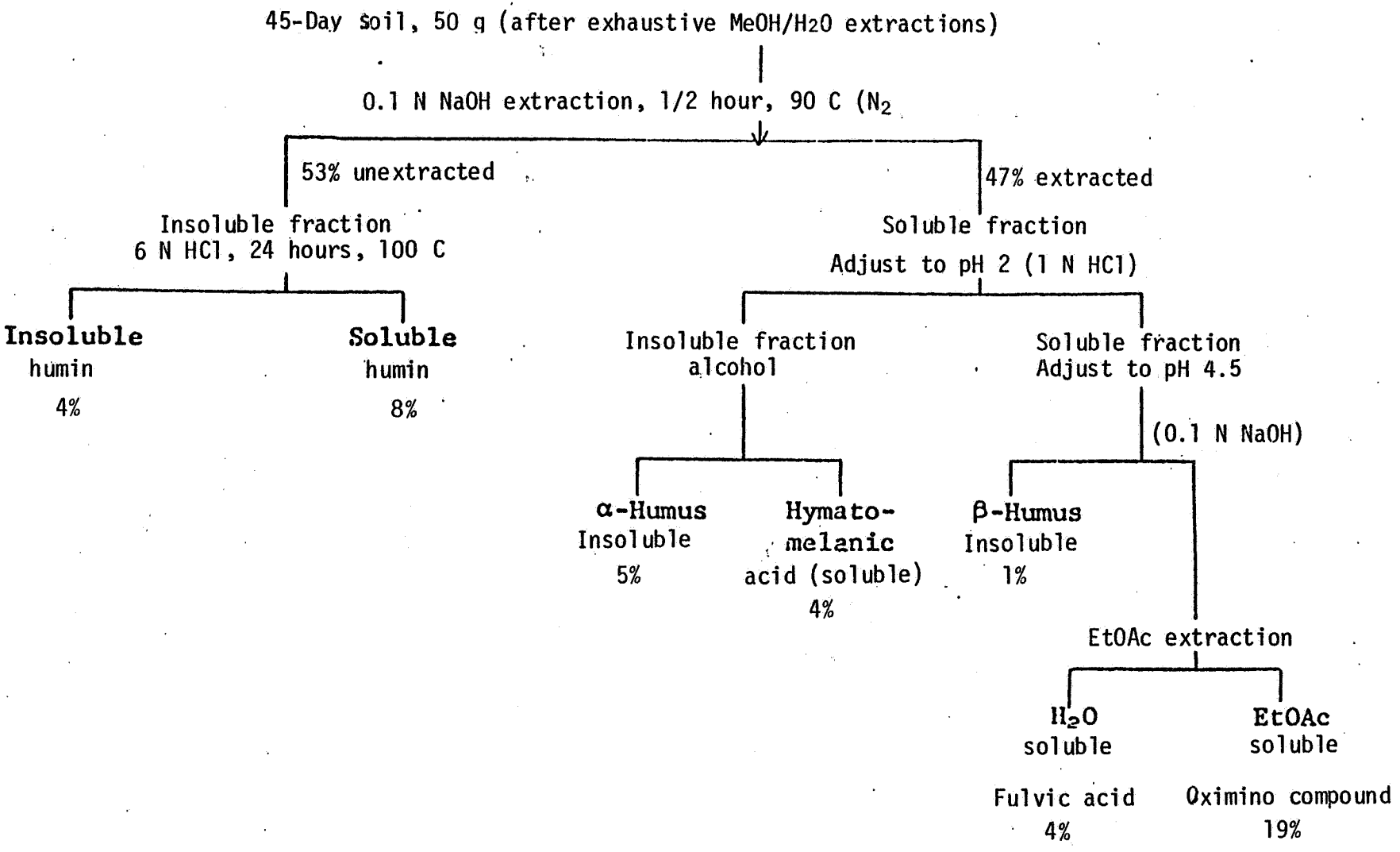


Figure 1. Soil organic matter fractionation procedure.
Results presented as % of the unextracted residue from day 45 soil.

Table 1. Decomposition of [^{14}C]methomyl in Flanagan silt loam in biometer study.

Days after treatment	Distribution of radioactivity (% of original treatment)				
	CO_2	Methomyl	Oximino compound	Polar fraction	Unextracted residue
45 (sterilized)	1.4[a]	89.3	0.5	0.8	8.0
0	0.0	96.7	1.7	1.3	0.9
3	3.5	85.3	1.7	2.0	7.5
7	6.1	78.5	1.0	1.2	13.2
15	11.6	70.0	2.0	2.6	13.8
30	18.1	57.2	0.5	3.1	21.1
45	22.5	47.0	1.4	2.9	26.2

a Only 1/5 of this volatile fraction precipitated as $BaCO_3$.

CASE GS0028 METHOMYL STUDY 5 PM 20C 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 0C - ACTIVE INGREDIENT

FICHE/MASTER ID 00009324 CONTENT CAT C1

Harvey, J., Jr.; Pease, H.L. (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, Del.; CDL:229711-D).

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -30-050530

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M Minnich DATE: May 2, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

The data in this portion of the study (decomposition in soil laboratory study) are contained in part of Study 1 (MRID 00008844) and are evaluated there.

Field Dissipation - Terrestrial

1. This portion of the study is scientifically valid. (Data for three of the soils [Delaware soils] in this section were already included in Study 1 [MRID 00008844] and therefore not evaluated here).

2. Extensive dissipation of methomyl (85-90% in 3-5 months) can be expected to occur in the field in light textured soils. In the same light textured soils, methomyl will not leach more than 11 and 15 inches over 3 and 5 months, respectively.

3. Very little surface runoff of methomyl will be expected to occur from sandy soils under normal field use conditions. Methomyl would likely remain in the upper 6 inches of treated soil.

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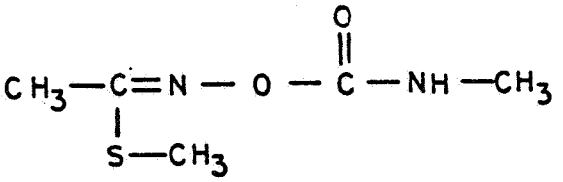
MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Field Decomposition Study

Stainless steel cylinders (4 by 15 inches) were driven into the ground so that 0.5 inch of the cylinder remained above the ground. Three of these were installed in a silt loam soil in Delaware, a fourth in a fine sand soil in Florida, and a fifth in a loamy sand in North Carolina. (The three cylinders in Delaware are reviewed in Study 1 [MRID 00008844]). The top 1.5 inches of soil was removed from the cylinders and the equivalent of 4.5 lb ai/A of S-methyl-[1-^{14}C]N-[(methylcarbamoyl)oxy]thioacetimidate (methomyl; E.I. du Pont de Nemours and Co.; purity not reported) was pipetted onto the exposed surface. The soil that had been removed was placed back into the cylinder and 60 ml of water was added. Weed seedlings that grew in the cylinders were cut and left to decompose on the soil surface during the experiment. To the bottom of the Florida and North Carolina columns, a filter trap and a 2-liter capacity glass vessel were attached. The assembly was reburied in the soil to its original depth. Water leaching through the soil cylinder was collected in the vessel and withdrawn without disturbing the soil. Samples were taken after heavy rains and water was analyzed for radioactivity by liquid scintillation counting (LSC). Harvest was at 3 months in Florida and at 5 months in North Carolina. The soil cores were removed from the cylinders, sectioned, and analyzed for total radioactivity. The soils were extracted with methanol twice and with water four times, centrifuged, and filtered through Celite Filter Aid on a sintered glass funnel. Radioactivity in the extracts was determined by LSC. After extractions, the soil was dried, passed through a 20-mesh sieve, and analyzed by wet combustion. Additionally, the extracted soil from the North Carolina site was analyzed for distribution of the radioactivity in soil organic matter. A cited fractionation procedure involving a hot alkali extraction was followed and radioactivity was determined in each fraction by LSC.

Runoff Study

A hillside farm (10% slope) with a loamy sand soil was cleared of vegetation by rototilling. A 5- by 5-foot area was treated with nonradioactive methomyl (formulation and purity unspecified) at 2 lb ai/A. An adjacent downhill site, also 5 by 5 feet, was left untreated. A ditch was dug on the extreme uphill site to prevent large amounts of water from washing over the test site. A gutter was installed at the base of the untreated area to collect runoff water. The gutter was covered to prevent direct collection of rainwater.

Natural rainwater supplemented with artificial rain totaled 4.1 inches, falling on the 1st, 7th, and 15th days after treatment. On those days, water was sampled from the gutter. Soil samples were taken after 15 days. From the treated area, cores were taken at 0-4 inches, 4-8 inches, and 8-12 inches. Similar cores were taken from the untreated area 1-2 feet and 3-4 feet downhill from the treated area. Soil and water samples were frozen until analyzed by a cited method.

REPORTED RESULTS:

Field Decomposition Study

The residual radioactivity found in the soil cores after harvest is given in Table 1.

No radioactivity was detected in the water that leached into the buried glass collection vessels.

Runoff Study

Methomyl was not detectable (<0.01 ppm) in any of the water samples taken from the drainage gutter at the bottom of the whole plot. Nor was any methomyl detectable (<0.04 ppm) in any of the soil samples.

DISCUSSION:

Field Decomposition Study

No data were submitted to show the dates of the rainfall and subsequent sampling of leachate from the underground vessels; neither the volume of water collected nor the sensitivity of the analytical procedure was given. Thus, estimates of the actual quantities of methomyl that might have been detected in the leachate are not possible.

Runoff Study

Four-inch soil increments on the treated plot would be adequate below the surface, but a 2-inch surface sample would be a more sensitive test for methomyl. The number of soil cores taken was not indicated.

Table 1. Residual radioactivity in soil treated with [^{14}C]methomyl under field conditions.

Depth (inches)	Residual radioactivity (% OT)[a]	
	Florida fine sand (3 months)	North Carolina loamy sand (5 months)
0-3	8.9	11.1
3-7	0.7	3.8
7-11	0.1	0.1
11-15	0.0	0.2

[a]% OT, original treatment = 8.9 µCi.

Rainfall during exposure: 23.6 inches in Florida and 17.3 inches in North Carolina.

CASE GS0028 METHOMYL STUDY 6 PM 200 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 50 TOPIC 25

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05015249 CONTENT CAT 11

Lande, S.S. (1978) Identification and Description of Chemical Deactivation/Detoxification Methods for the Safe Disposal of Selected Pesticides. Washington, D.C.: U.S. Environmental Protection Agency, Office of Solid Waste. (EPA/530/SW-165-C; available from: NTIS, Springfield, VA; PB-285 208)

SUBST. CLASS = S.

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

REVIEWED BY: R. Strieter
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Robert P. Strieter DATE: Apr. 23, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

This study was not given a full review because it contains summary data on methomyl, methomyl metabolites, and methomyl degradation rates without giving procedures.

TDMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 7 PM 200 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 30 TOPIC 0505

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05010536 CONTENT CAT 01

Heywood, D.L. (1975) Degradation of carbamate insecticides in soil. Pages 128-133, °In°Global Aspects of Chemistry, Toxicology and Technology as Applied to the Environment. Edited by F. Coulston and F. Korte. New York: Academic Press. (Environmental quality and safety, vol. 4)

SUBST. CLASS = S.

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

REVIEWED BY: M. Edwards
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Martin L. Edwards DATE: Apr. 21, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

This study was not given a full review because it is a literature review presenting no original data.

CASE GS0028 METHOMYL STUDY 8 PM 20C 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 20 TOPIC 1015 GUIDELINE 40 CFR 163.62-8f3

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05CC8165 CONTENT CAT C1

Gowda, T.K.S.; Patil, R.B. (1972) Effect of pesticides applied to the soil on the biological activity of the soil [abstract]. Biochemical Journal 128(1):56-57.

SUBST. CLASS = S.

DIRECT RVW TIME = ½ (MH) START-DATE END DATE

REVIEWED BY: M. Edwards
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Mark L. Edwards DATE: Apr. 21, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it is an abstract, lacking sufficient information on materials, methods, and results for evaluation.

2. This abstract reports that methomyl (source and purity unstated) at two concentrations (unspecified) had no effect on microbial populations, soil respiration, ammonification, or nitrification when applied to a sandy soil.

CHEM C90301 Methomyl

BRANCH EFB DISC 20 TOPIC 1205 GUIDELINE 40 CFR 163.62-8f3

FORMULATION 06 - WETTABLE POWDER (WP OR W)

FICHE/MASTER ID 05008720 CONTENT CAT 01

Rodell, S.; Funke, B.R.; Schulz, J.T. (1977) Effects of insecticides on acetylene reduction by°Azotobacter° ≠°vinelandii°and soybean nodules. Plant and Soil 47(2):375-381.

SUBST. CLASS = S.

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

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: Apr. 24, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Effects of Pesticides on Microbes

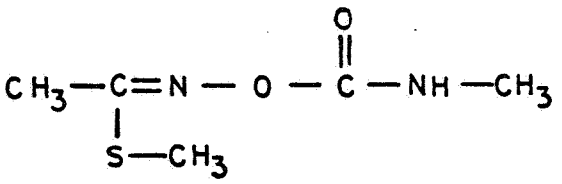
1. This study is scientifically valid.

2. Methomyl at concentrations of 0-250 ppm did not inhibit acetylene reduction by Azotobacter vinelandii in culture. Methomyl at concentrations of 0-50 ppm did not significantly inhibit acetylene reduction by Rhizobium sp. in detached soybean nodules.

3. Data from this study satisfy part of the requirements in Section 163.62-8(f)(3) of EPA's Proposed Guidelines for Registering Pesticides (July 1978) by providing data on the effect of methomyl on nitrogen fixation by bacteria.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Azotobacter vinelandii cultures were grown in 40 ml of nitrogen-free medium (0.64 g K_2HPO_4; 0.16 g KH_2PO_4; 0.2 g $MgSO_4$; 0.2 g NaCl; 0.05 g $CaSO_4$; 20 g mannitol; 0.001 g Na_2MoO_4; 0.003 g $FeSO_4$; 0.01 g EDTA; 3 ml Tween 80; and 1,000 ml distilled H_2O) overnight on a shaker at 30 C. Methomyl solutions were prepared by dissolving 0.1 g of methomyl (90% analytical formulation; source not reported) in acetone.

Triplicate cultures were treated with the methomyl solution at 5, 50, or 250 ppm and incubated for 1 hour at 30 C on a shaking water bath. Control samples were treated with acetone. The bacterial concentrations in the test cultures were adjusted by turbidity. After incubation a 1-ml aliquot of the culture was placed in a vial with a septum type stopper. Acetylene (0.5 ml) was added to the vial by syringe and allowed to react for 30 minutes at 30 C. Gas samples (0.5 ml) were removed from the vial by syringe and analyzed by flame ionization gas chromatography.

Inoculated soybeans (inoculum supplied by Nitragin Co.) were grown in clay pots containing a soil mixture (50% sand; 50% Fargo clay loam), and treated with methomyl (90% wettable powder; source not reported) at 5 or 50 ppm. After treatment the soybeans were incubated in a greenhouse for an undetermined period of time. The soybeans were removed from the pots and the roots were washed with a gentle spray of water. Nodules were detached and blotted dry. One-gram samples of nodules were transferred to vaccine bottles with septum stoppers. Acetylene (3 ml) was injected into the bottle, which was incubated for 30 minutes at 30 C. Gas samples (0.5 ml) were removed and analyzed by flame ionization gas chromatography.

REPORTED RESULTS:

Methomyl did not significantly inhibit the nitrogenase activity of Azotobacter vinelandii in culture (Table 1).

Methomyl did not significantly inhibit acetylene reduction by detached soybean nodules (Table 2).

DISCUSSION:

1. The Rhizobium sp. forming the soybean nodules was not identified.

2. The authors used standard methods that are considered acceptable.

3. It should be noted that, although methomyl did not significantly inhibit acetylene reduction, there was a 15% reduction in ethylene production (compared with controls) after treatment at 5 ppm.

Table 1. Effect of methomyl on the ability of Azotobacter vinelandii to reduce acetylene in culture.

Treatment (ppm)	Ethylene production[a] (10^{-16} moles/cell/hour)
0	3.54
5	4.82
50	5.48
250	5.35

[a] All numbers are not significantly different at the 95% confidence level.

Table 2. Effect of methomyl on the ability of detached soybean nodules to reduce acetylene.

Treatment (ppm)	Ethylene production[a] (10^{-8} moles/gram/hour)			
	Trial 1	Trial 2	Trial 3	Average
0	4.0	4.2	3.5	3.9
5	3.2	3.3	3.4	3.3
50	3.1	7.3	2.9	4.4

[a] All numbers are not significantly different at the 95% confidence level.

CASE GS0028 METHOMYL STUDY 10 PM 20C 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 20 TOPIC 1015 GUIDELINE 40 CFR 163.62-8f3

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID C0C(8581 CONTENT CAT 01

Peeples, J.L. (1977) Effect of Methomyl on Soil Microorganisms. (Unpublished study received Mar 24, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, Del.; CDL: 228749-A)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: EFB -55-1CC5
SEC: EFB -20-1215

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

REVIEWED BY: M. Edwards
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500
SIGNATURE: Martin N. Edwards DATE: Apr. 21, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Effects of Pesticides on Microbes

1. This study is scientifically valid.

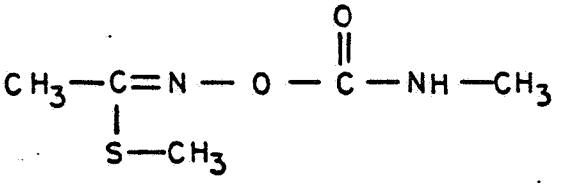
2. Methomyl at 18 ppm (a concentration exceeding that likely to occur after the highest anticipated application) had no effect on fungal or bacterial populations or on total microbial activity in three soils tested (one sand and two silt loams).

3. Data from this study help satisfy the requirements under Section 163.62-8(f)(3) of EPA's Proposed Guidelines for Registering Pesticides (July 1978) by providing information on the effects of methomyl on microbial populations in three soil types, as evidenced by direct counts and by CO_2 evolution.

40

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Microbial population studies were conducted with three soil types, each fortified with methomyl at 18 ppm (20 ppm Lannate 90 WD). Soils were a Leon Immokalee fine sand soil from Florida, a Keyport silt loam from Delaware, and a Flanagan silt loam soil from Illinois (soil characterizations were not provided). Treated and untreated (control) soils (adjusted to 65% field moisture capacity) were incubated at 27 C for 11 days. Dilutions from the incubated soil samples were then taken for soil fungi and soil bacteria counts.

Total microbial activity (as evidenced by CO_2 evolution) in soils treated with methomyl (18 ppm methomyl; 20 ppm Lannate 90 WD) was also determined with the same soils as above. A test tube containing 0.5 N NaOH was placed in each flask containing treated or untreated (control) soils to trap evolved CO_2. Flasks were sealed and incubated at 27 C, and CO_2 was determined titrimetrically after 3, 13, 21, 28, 42, and 56 days of incubation.

REPORTED RESULTS:

Comparisons with untreated controls showed that methomyl (18 ppm) had no effect on fungi or bacteria populations in the three soils tested after 11 days of incubation (Table 1). Similarly, soil microbial activity, as evidenced by CO_2 evolution, was unaffected by methomyl (18 ppm) over the 56-day study period (Table 2).

DISCUSSION:

1. Materials and methods were only briefly described but are valid. Appropriate controls were run. Soil characteristics, however, should have been provided.

2. The concentration of methomyl used in these studies (18 ppm) exceeded the level expected in the 0-4 inch layer under the highest anticipated application rates.

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Table 1. Effect of methomyl on soil microbial populations 11 days after treatment.

Treatment	Microorganisms per gram of soil	
	Fungi x 10^4	Bacteria x 10^6
Florida soil - untreated	3.8	3.0
Florida soil - methomyl[a]	3.4	3.6
Delaware soil - untreated	3.3	9.3
Delaware soil - methomyl[a]	4.0	10.7
Illinois soil - untreated	4.8	27.2
Illinois soil - methomyl[a]	3.9	35.1

[a] Treated with methomyl at 18 ppm.

Table 2. Effect of methomyl on production of CO_2 by soil microorganisms.

Treatment	Milligrams of CO_2 produced per 100 g of soil					
	3 Days	13 Days	21 Days	28 Days	42 Days	56 Days
Florida soil - untreated	15	64	96	120	159	188
Florida soil - methomyl[a]	15	62	91	112	147	175
Delaware soil - untreated	10	39	59	74	102	128
Delaware soil - methomyl[a]	10	37	57	71	97	121
Illinois soil - untreated	16	55	82	102	139	170
Illinois soil - methomyl[a]	15	61	87	108	145	176

[a] Treated with methomyl at 18 ppm.

CASE GS0028 METHOMYL STUDY 11 PM 200 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 1210 GUIDELINE 40 CFR 163.62-8f3

FORMULATION·15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00009328 CONTENT CAT 01

Han, J.C. (19??) Evaluation of Possible Effects of Methomyl on Nitrifying Bacteria in Soil. (Unpublished study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, Del.; CDL:229711-H)

SUBST. CLASS = S.

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: M. Edwards
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Mark J. Edwards DATE: Apr. 21, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Effects of Pesticides on Microbes

1. This study is scientifically valid.

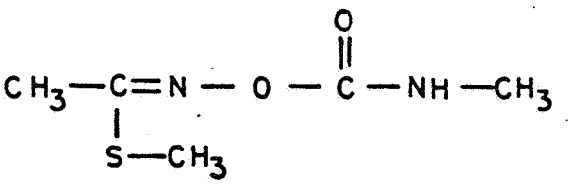
2. A temporary reduction in soil nitrification occurred when methomyl was applied to a silt loam soil at 0.5 ppm, a concentration approximating that occurring at the recommended field application rate. At this concentration, nitrification was reduced by up to 32% but returned to control levels within 19 days. At 5.0 ppm, a concentration exaggerating the recommended field application rate, the reduction in nitrification was more pronounced (up to 82%) and returned to control levels within 4 weeks.

3. Data from this study help satisfy the requirements in Section 163.62-8(f)(3) of EPA's Proposed Guidelines for Registering Pesticides (July 1978) by providing information on the effects of methomyl on nitrification in soils.

44

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

One-hundred-gram samples of air-dried Keyport silt loam soil (soil characteristics not provided) were each inoculated with 1 g of fresh dried garden soil (location, type, and characteristics not provided). Samples were mixed, moistened with tapwater to 50% total water holding capacity, and incubated at 30 C for 2 weeks in the dark. Water losses were adjusted twice weekly by adding distilled water.

After the 2-week incubation period (for the establishment of bacteria), nitrogen (as ammonium sulfate, $(NH_4)_2SO_4$) was added at 200 ppm to the samples, together with technical methomyl (99% purity) at either 0.5 or 5.0 ppm. One control series was run with ammonium sulfate in the absence of methomyl, and another series was run in the absence of ammonium sulfate and methomyl. Samples were incubated at 30 C and were analyzed for nitrate content at 4, 9, and 19 days and 4 and 6 weeks.

REPORTED RESULTS:

Data on the effects of methomyl on soil nitrification are summarized in Table 1. At 0.5 ppm, nitrification was reduced by 32% after 4 days with respect to that in controls but returned to control levels within 19 days. At 5.0 ppm, nitrification was reduced 76 and 82% after 4 and 9 days, respectively, and returned to control levels within 4 weeks.

DISCUSSION:

1. Materials and methods were briefly but adequately described, except that the soils used (both the Keyport silt loam and the "fresh dried garden soil") should have been fully characterized.

2. The data show that methomyl causes a temporary reduction in soil nitrification, which is more pronounced and longer lasting with methomyl at 5.0 ppm as compared with 0.5 ppm (Table 1). The latter concentration approximates that which would result from methomyl application at 0.5 lb ai/acre, the recommended field application rate (assuming a 0-4 inch soil depth).

Table 1. Effect of methomyl on nitrification in soil..

Treatment	Total NO_3^- detected (mg)[a]				
	4 days	9 days	19 days	4 weeks	6 weeks
Control 1 [b]	3.4	4.5	12.8	13.3	15.1
Control 2 [c]	14.0	71.0	110	100	103
0.5 ppm methomyl	9.5	57.5	108	103	104
5.0 ppm methomyl	3.4	12.8	78	100	104

[a]Mean of three samples.

[b]Without ammonium sulfate and methomyl.

[c]Without methomyl.

TDMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 12 EM 20C 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 1010 GUIDELINE 40 CFR 163.62-8g

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00009327 CONTENT CAT 01

Belasco, I.J. (1977) Effect of Methomyl on the Activity of Sewage Microorganisms. (Unpublished study received May 5, 1977 under 352-342; submitted by E.I. du Pont de Nemours & Co., Wilmington, Del.; CDL:229711-G)

SUBST. CLASS = S.

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

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: Apr. 17, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

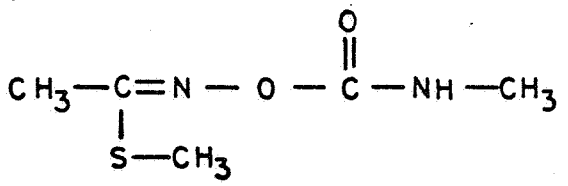
Metabolism - Activated Sludge

This study is scientifically invalid because the investigative methods were not described in adequate detail to permit evaluation.

47

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Activated sludge from the Wilmington sewage treatment plant was washed twice by centrifugation and the solids were resuspended in water. Resuspended activated sludge (200 ml) was added to three flasks, each containing 10 ml of 0.1 M phosphate buffer (pH 7.0-7.2), 100 ml of 0.1% Bacto-peptone, 100 ml of 0.1% meat extract, and 90 ml of water. The mixture was aerated and stirred for 24 hours. Total oxygen demand (TOD) was measured at 0 and 24 hours. The contents of the three flasks were composited.

Activated sludge from the preliminary experiment (amount not reported) was added to flasks containing the medium described above plus methomyl (E.I. du Pont de Nemours and Co.; formulation not reported) at 0, 1, 5, 10, 50, or 90 ppm and enough water to bring the total volume of the system to 500 ml. The system was aerated and stirred for 24 hours. Samples of the suspension were collected at 7 and 24 hours after inoculation with the sludge and analyzed for pH and TOD.

REPORTED RESULTS:

The extent of biodegradation was unaffected after incubation for 7 and 24 hours in the presence of methomyl at concentrations of 1-50 ppm. There was some possible indication of inhibition after incubation for 24 hours in the presence of methomyl at 90 ppm.

DISCUSSION:

1. The methods were not described in adequate detail. The author did not include the amount of sludge used to inoculate the methomyl-treated medium. Also, the method used to determine the total oxygen demand was not described.

2. The author did not determine the concentration of methomyl remaining in the suspended sludge samples. Also, the contribution of methomyl to the total oxygen demand was calculated and not actually measured.

Table 1. Effect of methomyl on the biodegradation of simulated sludge.

Methomyl applied (ppm)	Total oxygen demand (ppm)					
	Initial	Contributed by methomyl (calculated)	After 7 hours	Reduction after 7 hours	After 24 hours	Reduction after 24 hours
Control	1,091	0	434	657	364	727
1	1,040	4	417	623	357	683
5	1,076	18	417	659	357	719
10	1,096	35	432	664	374	722
50	1,218	175	582	636	524	694
90	1,307	316	690	617	682	624

TDMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 13 EM 2CC 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 30 TOPIC 0505

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05010422 CONTENT CAT C1

Fung, K.H.; Briner, G.P. (1977) Leaching of methomyl from some Australian tobacco soils. Tobacco Science XXI:120-121.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: RCBP-05-1015 RCBR-20-150505

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

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: Apr. 17, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

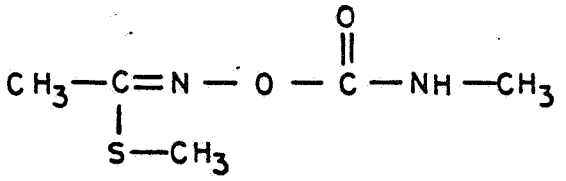
Mobility - Leaching

This study is scientifically invalid because the experimental procedures employed were not described in sufficient detail to permit evaluation.

50

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Soil cores (8.5 cm in diameter) were taken to a depth of 10 cm from two fine sandy loam soils. Alluvial soil group (10.1% clay; cation exchange capacity 10.2 meq/100 g soil; 2.1% organic matter; pH 6.1) and grey-brown podzol group (19.3% clay; cation exchange capacity 12.1 meq/100 g soil; 2.3% organic matter; pH 5.8) were used. The cores were coated with microcrystalline wax and placed on a filter paper in a Buchner funnel. A 250-ml (500 ppm) solution containing 125 mg of methomyl (formulation, purity, and source not reported) was poured into each core. The leachate was collected and the core was allowed to drip dry. The soil core was leached with 573 ml of distilled water. The leachate was added at a rate of 10 ml/minute and collected in 30-ml fractions. Sodium azide (10 M) was added to the leachate to prevent microbial transformation of methomyl. The leachate was analyzed by the gas chromatographic method described in Study 17 (MRID 05008439).

Each soil core was air dried for 3 weeks and divided into four segments. A 50-g subsample of each section was analyzed by the gas chromatographic method described in Study 17 (MRID 05008439).

REPORTED RESULTS:

Both of the fine sandy loam soils showed similar behavior. More than half of the methomyl applied percolated through the soil core prior to elution with distilled water. Of the 47-57 mg of methomyl remaining in the soil 7-8% leached through the soil core. Between 34 and 43% of the methomyl in the soil was lost during the 3-week drying period (Table 1). This loss may have been due to volatilization, transformation by soil microorganisms, or adsorption.

DISCUSSION:

1. Numerous procedures employed were inadequate. The soil cores were only 4 inches long and were coated with wax that could adsorb the methomyl. Between 54 and 62% of the methomyl applied eluted through the cores prior to the addition of water, thus indicating that the soil was saturated with methomyl. The soil was eluted with the equivalent of 4 acre-inches of water, which is insufficient to determine the ability of methomyl to leach.

2. The soil cores were air dried for 3 weeks prior to analysis for methomyl residues. There is a possibility that some of the methomyl remaining in the soil was transformed by microbial or chemical means.

3. The authors did not look for degradation products. The methomyl lost during the course of the experiment may be present in the form of degradation products.

Table 1. Fate of 125 mg of methomyl in two fine sandy loam soils.

Soil number[a]	Eluted with application solution (mg)	Leached with distilled H_2O (mg)	Recovered from soil (mg)	Loss due to other means (mg)
I	77.5	3.77	27.6	16.0
II	67.6	4.12	28.6	24.6

[a] Soil I = Myrtleford fine sandy loam of the alluvial soil group.
Soil II = Ovens fine sandy loam of the grey-brown podzol group.

TLMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 14 PM 20C 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION CC - ACTIVE INGREDIENT

FICHE/MASTER ID 00CC9326 CONTENT CAT 02

E.I. du Pont de Nemours & Company (1971) Methomyl Decomposition in Muck Soil--A Field Study. (Unpublished study received May 5, 1977 under 352-342; CDI:229711-F)

SUBST. CLASS = S.

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

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich DATE: Apr. 29, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Field Dissipation - Terrestrial

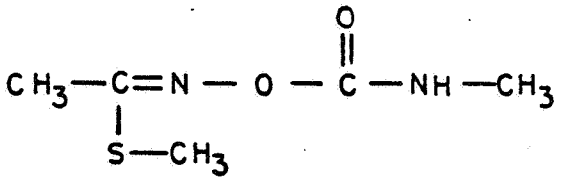
1. This study is scientifically valid.

2. Field dissipation of methomyl on a muck soil resulted in no ethyl acetate extractable methomyl 7-32 days after application.

54

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Methomyl (formulation and purity unspecified; E.I. du Pont de Nemours & Co., Inc.) was applied at 0, 1, and 2 lb/A on field plots of a muck soil (52% organic matter; pH 5.4) in Minnesota in late August. Soil was sampled on days 7, 14, and 32 after treatment at two depth increments, 0-4 and 4-8 inches.

Samples were extracted with ethyl acetate and the extract was purified by a liquid-liquid partitioning procedure involving water, acidified water, n-hexane, and chloroform. Methomyl was then hydrolyzed to the corresponding oxime. The oxime was extracted into an organic solvent and measured by a microcoulometric gas chromatograph.

REPORTED RESULTS:

No methomyl was detected (<0.02 ppm) in any of the soil extracts. Recovery studies showed that 65% recovery was obtained at a spike level of 0.08 ppm and 74% was recovered when 0.2 ppm was added.

DISCUSSION:

1. There was no verification of the initial application. Samples should have been taken immediately after application as a check on both the application rate and entire procedural technique.

2. The high organic matter content of this soil would effect a high adsorptive capacity. Therefore, much of the unextractable methomyl could reasonably be assumed to be bound to soil organic matter.

CASE GS0028 METHOMYL STUDY 15 PM 22C 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 30 TOPIC 100520

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00CC8260 CONTENT CAT 02

Pease, H.L. (1968) Methomyl Residue Analyses--Soils. (Unpublished study received Apr 9, 1971 under 1F1021; submitted by E.I. du Pont de Nemours & Co., Inc., Wilmington, Del.; CDL:095024-I)

SUBST. CLASS = S.

DIRECT RVW TIME = ½ (MH) START-DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich DATE: Apr. 29, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because materials and methods were not presented.

2. The study presents the results of methomyl applications on a sandy loam soil. No residues were detected in the soil after a 17-day sampling period.

CHEM C90301 Methomyl

BRANCH EFB DISC 50 TOPIC 2099

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC OR E)

FICHE/MASTER ID 05008436 CONTENT CAT 01

El-Rafai, A.; Fahmy, F.A.; Abdel-Lateef, M.F.A.; Imam, A.K.E. (1976) Toxicity of three insecticides to two species of fish. International Pest Control 18(6):4-8.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: EEB -35-05251043 EEB -40-05054543

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

REVIEWED BY: R. Strieter
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Robert Paul Strieter DATE: Apr. 24, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it concerns methomyl toxicity to fish and the effectiveness of water treatment techniques in removing pesticides from water and does not pertain to environmental chemistry.

2. Methomyl's TL_m values (50% mortality) were 1.2 and 3.0 mg/liter of water, respectively, for large and small Cyprinus carpio and 0.9 mg/liter of water for large and small Tilapia nilotica exposed to methomyl for 48 hours. Mechanical flocculation with alum, followed by sedimentation and decantation, improved the quality of methomyl-contaminated water by a factor of 1.3.

CASE GS0028 METHOMYL STUDY 17 PM 200 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 100525

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05008439 CONTENT CAT 01

Fung, K.K.H. (1976) Determination and confirmation of methomyl residues in soil and water. Pesticide Science 7(6):571-574.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCBP-05-1015
SEC: RCBP-05-1020 EFB -30-101020

DIRECT RVW TIME = 9½ (MH) START-DATE END DATE

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: Apr. 28, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

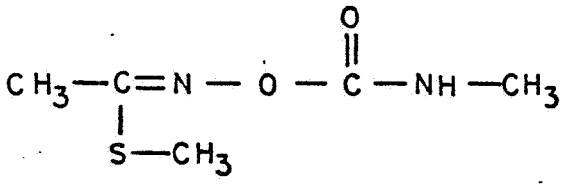
CONCLUSIONS:

1. This method study is scientifically valid.

2. The analytical method presented is acceptable for determining methomyl residue levels as low as 0.01 mg/kg in soil and 0.001 mg/kg in water.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Soil samples were taken from two fine sandy loam (low organic matter) field plots, one of which was treated with methomyl (rate, formulation, source, and purity not reported) and the other an untreated control. The soil samples were air dried, ground, and passed through a 2-mm sieve. Water samples were collected from the Ovens River near an area treated with methomyl and from an untreated tributary of the river. The water samples were passed through filter paper to remove suspended particles.

Methomyl was extracted from the 50-g soil samples, cleaned up, and hydrolyzed to 1-(methylthio)acetaldoxime by using a cited method. The hydrolyzed extracts were analyzed by the flame photometric gas chromatography-mass spectrometer following the same method.

The 1-liter water samples were acidified to pH 2 with 5 ml of 0.5 M H_2SO_4 and extracted with 100 ml of chloroform. The extract was concentrated in a flask on a water bath. The extract was hydrolyzed and analyzed for 1-(methylthio)acetaldoxime.

REPORTED RESULTS:

The detection limits of the method were 0.01 mg/kg for soil and 0.001 mg/kg for water. The recovery rates from spiked samples were 94-96% for soil and 90-93% for water. The method gave consistent results for field-treated samples with a standard deviation of 0.1 mg/kg for soil samples and 0.0006 mg/kg for water samples.

DISCUSSION:

1. The author did not give the rate of application to the field plots. Therefore, it is not possible to determine what percentage of the methomyl applied to the field plots was recovered.

2. The extraction and analytical procedures used were acceptable and the recovery data from spiked samples show that the method is able to adequately determine the concentration of methomyl in soil and water.

TDMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 18 FM 2CC 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 20 TOPIC 0510 GUIDELINE 40 CFR 163.62-8f2

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05008174 CONTENT CAT C3

Fung, K.K.H.; Uren, N.C. (1977) Microbial transformation of S-methyl N-[(methylcarbamoyl)oxy]thioacetimidate (methomyl) in soils. Journal of Agricultural and Food Chemistry 25(4):966-969.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: EFE -30-0505

DIRECT RVW TIME = 12½ (MH) START-DATE END DATE

REVIEWED BY: R. Strieter and D. Harper
TITLE: Staff Scientists
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500
SIGNATURE: Robert P. Strieter & Daniel Harper DATE: May 9, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

This study is scientifically invalid because the rate, type, and degree of methomyl metabolism was not determined. In addition, sterile controls were not run.

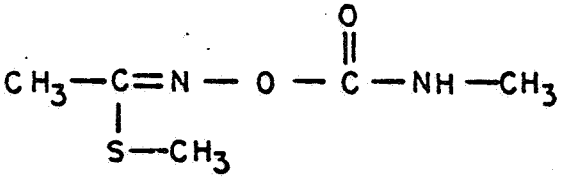
Mobility - Adsorption/Desorption

This study is scientifically invalid because a saturated aqueous solution of $CaSO_4$ and polyvinyl alcohol added to the soil may have altered the soil ionic balance, thus changing the soil's capacity for adsorbing methomyl.

60

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

The upper 15 cm of soil was sampled from areas where methomyl had been applied previously. Samples of a Myrtleford fine sandy loam (Soil I: clay 10.1%; pH 6.1; 2.1% organic matter, cation exchange capacity 10.2 meq/100 g) and an Ovens fine sandy clay loam (Soil II: clay 19.3%; pH 5.8; 2.3% organic matter; cation exchange capacity 12.1 meq/100 g) were passed through a 2-mm sieve and treated with polyvinyl alcohol (to maintain the soils in a flocculated condition). Soil was analyzed for methomyl residues by the gas-liquid chromatography (GLC) method described in Study 17 (MRID 05008439). This method analyzes for 1-(methylthio)-acetaldoxime (methomyl hydrolysis product), methomyl hydrolysis therefore is required.

Metabolism - Aerobic Soil

Duplicate 10-g samples of each soil were placed in perfusion columns, and two additional columns that did not contain soil were used as controls. The soils were equilibrated by perfusion with 230 ml of a saturated aqueous solution of $CaSO_4$ to prevent dispersion of soil colloids.

After 2 days, the $CaSO_4$ solution was removed and replaced with a $CaSO_4$ solution containing 6 ppm methomyl (source, formulation, and purity not reported). The experimental temperature was 25 C.

At 3, 7, 14, 21, 28, 35, and 42 days after treatment, a 10-ml sample of the perfusate was removed and analyzed for methomyl by the GLC method described in Study 17 (MRID 05008439).

After the last sample was collected, the methomyl solution was removed and a fresh 6 ppm solution of methomyl was added to the perfusion apparatus. Sampling and sample analysis of the perfusate were performed as described in the previous paragraph.

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Mobility - Adsorption/Desorption

This experiment followed the procedure described for aerobic soil metabolism, except that 10^{-3} N sodium azide was added to the perfusate at 0 and 42 days after treatment to inhibit microbial activity. Sampling continued at weekly intervals for an additional 2 weeks.

REPORTED RESULTS:

Methomyl residue levels of 0.004 and 0.01 ppm were present in Soils I and II, respectively, prior to perfusion with methomyl. The concentration of methomyl in the controls (perfusate) had declined from 6 to 5.6 ppm 35 days after perfusion with methomyl began. Thereafter the concentration of methomyl remained constant for the duration of the experiment.

Metabolism - Aerobic Soil

The methomyl concentration in the perfusate from Soil I declined 5% over a 3-day period and 58% over a 42-day period. The methomyl concentration in the perfusate from Soil II declined 5% over a 3-day period and 38% over a 42-day period (Figure 1).

When the soils were perfused a second time with a fresh methomyl solution, a rapid decline in the methomyl concentration of the perfusate occurred (Figure 2).

Mobility - Adsorption/Desorption

The concentration of methomyl in the perfusate declined 3-5% over a 21-day period. There was substantial decrease in the methomyl concentration from 21 to 42 days after perfusion began, possibly due to microbial degradation. No further decline in the methomyl concentration was detected after the 42nd day (Figure 1).

DISCUSSION:

1. The soil samples were treated with polyvinyl alcohol, which could serve as a carbon source for microbes or alter the adsorptive capacity of the soil.

2. It was not stated that the experiments were performed in darkness; therefore, some photodegradation of methomyl could have occurred. Also, polyvinyl chloride tubing was used in the perfusion setup. There is a possibility that some of the methomyl was adsorbed to the tubing. However, these losses would have been accounted for in the control columns.

3. Controls for the soil metabolism experiment were not run with sterile soil. Also, a saturated aqueous solution of $CaSO_4$ was added to the soil and some dehydration of the soil may have occurred due to the addition of the $CaSO_4$.

4. The soil samples used in the adsorption experiment were equilibrated with $CaSO_4$ and the methomyl was applied in $CaSO_4$. The addition of $CaSO_4$ to the soil possibly altered the soil ionic balance becuase the Ca^{+2} would bond to the available anionic sites in the clay fraction more readily than methomyl.

5. The perfusate was analyzed for methomyl residues. The soil was not analyzed to determine the concentration of residues present in the soil. In addition, there was no analysis for any methomyl metabolites. Therefore, the amount of methomyl metabolized in the soil could not be determined.

6. Changes in concentration (losses) of solutions indicated that microbial transformations in both soils began after a lag of 7-14 days. Absorption accounted for only 5% of the loss when compared with microbial transformation.

7. The soils used in this experiment were only sampled before studies began, thereafter only the perfusate was analyzed. It was not proven that the amount of pesticide in solution can be correlated with the amount in soil.

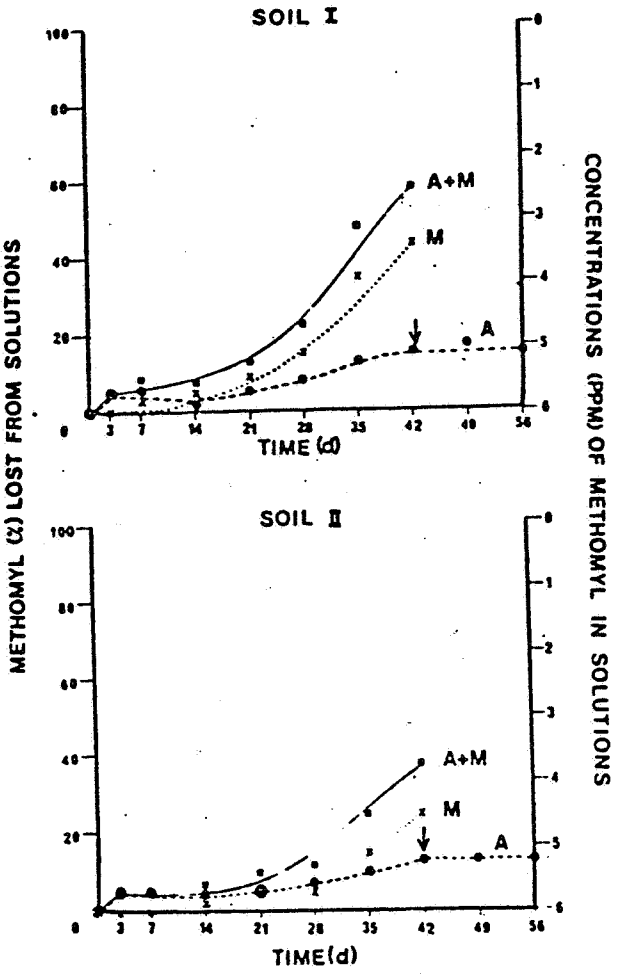


Figure 1. Effects of microbial transformation and adsorption on the rate of methomyl loss.
(A + M) adsorption + microbial transformation
(A) adsorption.
(M) microbial transformation.
(↓) additional NaN_3 added to perfusate.

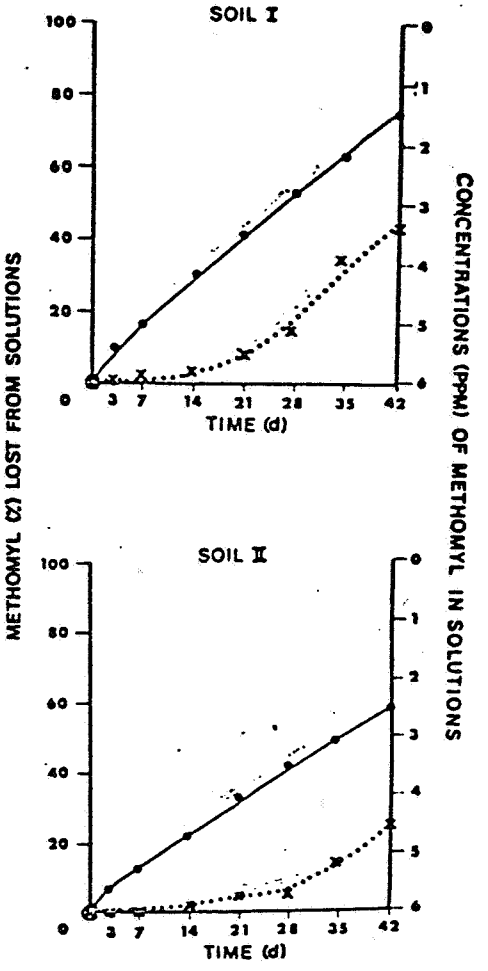


Figure 2. Effects of microbial transformation on the rate of methomyl loss.
A - loss after initial treatment.
B - loss after second treatment.
On both graphs top line is A and bottom line is B.

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 10

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05008448 CONTENT CAT 06

Reeves, R.G.; Woodham, D.W. (1974) Gas chromatographic analysis of methomyl residues in soil, sediment, water, and tobacco utilizing the flame photometric detector. Journal of Agricultural and Food Chemistry 22(1):76-78.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCBP-05-1015

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich DATE: Apr. 23, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

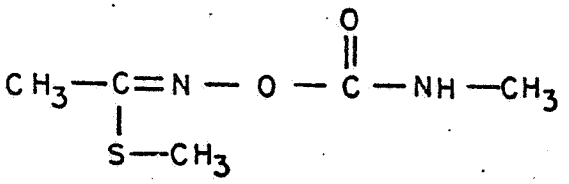
CONCLUSIONS:

1. This is a scientifically valid study.

2. The proposed method for gas chromatographic analysis of methomyl residues had detection limits of 0.05 ppm for soil and sediment and 0.01 ppm for water. Average recoveries of 75, 91, and 80% for water, soil, and sediment, respectively, were obtained.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Representative 150-g soil samples were extracted with 300 ml dichloromethane for 4 hours on a concentric rotator. The extract was filtered through glass wool; 200-ml aliquots were collected and stored in amber bottles under refrigeration pending cleanup.

Sediment samples were extracted and stored by the same procedure except that 150 g Na_2SO_4 was added to each sample to absorb water during the extraction. The moisture content of soil and sediment samples was determined by the classical oven method and all residues were expressed on an oven-dry basis.

Water samples were weighed (300 g) into separatory funnels and extracted with 100 ml dichloromethane. The dichloromethane layer was drained through Na_2SO_4 into amber bottles for storage. Two additional extractions with fresh 100-ml portions of dichloromethane were added to the same bottle and stored as in the previous extractions.

Aliquots from the extractions were transferred to 500-ml Erlenmeyer flasks; 1.0 ml of a 0.1% Nujol-in-hexane solution was added and the solutions were concentrated to approximately 10 ml. Concentrated extracts were transferred to chromatographic columns containing Florisil and washed first with dichloromethane and then with 5 ml of a diethyl ether:dichloromethane (20:80, v:v) solution. Finally, methomyl was eluted with 100 ml of a dichloromethane:acetone (90:10, v:v) solution, 1 ml of 0.1% Nujol-in-hexane was added, and the solvent was evaporated to dryness at 40-50 C. Residues were redissolved in benzene.

The solution was analyzed for methomyl with a gas chromatograph equipped with a flame photometric detector utilizing a 394-nm sulfur interference filter. Linearity ranged between 5.0 and 30.0 nm of methomyl, and precautions were taken to maintain linear conditions at all times due to the narrow range of linearity for the flame photometric detector in the sulfur mode.

REPORTED RESULTS:

Reliable results were reported with the exception of some double peak interference in the untreated sediment sample.

Average recoveries obtained were 75, 91, and 80% for water, soil, and sediment, respectively. Lower detection limits were 0.01 ppm for water and 0.05 ppm for soil and sediment.

DISCUSSION:

The recoveries reported for water and sediments (75 and 80%) were much lower than those for soils (91%), whereas the detection limit for water was supposedly a bit lower than that for soils or sediments. Apparently either a procedural difficulty or an unmarked interference in the analysis occurred. An interesting procedural difference between soils and the other two samples was that Na_2SO_4 was not utilized to remove water from soils. Instead, it was stated, "Traces of water in soil increase the extraction efficiency by deactivating the soil, thereby releasing the pesticide from soil particles." This explanation of the procedural difference should be scrutinized by further testing, especially with regard to the differences between soils and sediments.

(Notes: 1. Tobacco leaf extracts were also extracted and analyzed in this study, with reported methomyl recoveries of 78%.

2. This method was aptly criticized and revised by [Fung, Kenneth K.H. 1975. Determination and identification of S-methyl-N-[(methylcarbamoyl)oxy]thioacetimidate (methomyl) residues in tobacco. J. Agri. Food Chem. 23(4):695-698.] The oxime derivative of methomyl was found to be more sensitive to analysis than the parent compound.)

CASE GS0028 METHOMYL STUDY 20 PM.2CC 01/30/80

CEEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 05

FCRMULATICN 15 - SCIUBLE CONCENTRATE

FICHE/MASTER ID 00CC8259 CONTENT CAT 02

E.I. du Pont de Nemours and Company (1971) Environmental Safety of Lannate Methcmyl Insecticide. Summary of studies 095024-B through C95024-K. (Unpublished study received Apr 9, 1971 under 1F1021; CDL:C95C24-A)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -30-050515 EFB -30-05052C BCBE-20-15

DIRECT RVW TIME = ½ (MH) START-DATE END DATE

REVIEWED BY: M. Edwards
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LCC/TEL: 468-2500

SIGNATURE: Mark N. Edward DATE: Apr. 21, 1980

APPRCVED BY:
TITLE:
ORG:
LCC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it is a literature review presenting no original data or materials and methods.

2. Results of environmental fate and chemistry studies previously conducted with methomyl, including adsorption, soil metabolism, and plant metabolism studies, were summarized.

TDMS XXXXXXXX 0030 DATA EVALUATION RECORD Page 1 of

CASE GS 0028 METHOMYL PM 200 04/24/80

CHEM 090301 METHOMYL

BRANCH _____ DISC ___

FORMULATION _____

FICHE/MASTER ID 05014287

CITATION: The biodegradation of pesticides in the soil. Communications of the Faculty of Agricultural Sciences, State University of Ghent. Vol. 35, Issue 2, pp. 753-783, 1980. ESSER, H.O.

SUBST. CLASS= S.

OTHER SUBJECT DESCRIPTORS
PRIM:

DIRECT REVIEW TIME= 1 (MH) START DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC./TEL: 468-2500

SIGNATURE: M Minnich DATE: Apr. 30, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it is a literature review containing no direct information concerning methomyl.

2. The major degradative reactions of various pesticides are presented as being typical or characteristic of each particular class of pesticide. Methomyl is included in the appendix as a carbamate insecticide. Examples in the text for alkyl carbamates and thiocarbamates include hydrolysis reactions for EPTC, SMDC, nabam, carbaryl, and temik.

CASE GS0028 METHOMYL STUDY 22 EM 2CC 01/30/80

CHEM C90301 Methomyl

BRANCH EFB DISC 20 TOPIC 150520

FORMULATION CC - ACTIVE INGREDIENT

FICHE/MASTER ID 050C8214 CONTENT CAT C3

Kiigemagi, U.; Wellman, D.; Cooley, E.J.; Terriere, L.C. (1973) Residues of the insecticides phorate and methomyl in mint hay and oil. Pesticide Science 4(1):89-99.

SUBST. CLASS = S.

DIRECT RVW TIME = 11 (MH) START-DATE END DATE

REVIEWED BY: R. Strieter and D. Harper
TITLE: Staff Scientists
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Robert Paul Strieter Daniel Harper DATE: May 14, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

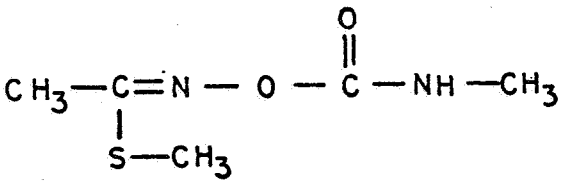
1. The peppermint and spearmint sections of this study conducted in Indiana in 1971 are scientifically valid. However, all other parts of this study are scientifically invalid because either the application, sampling, and harvest dates do not follow in sequence or zero day samples were not analyzed.

2. Methomyl dissipated rapidly in peppermint and spearmint hay samples. Over 80% dissipated by 3 days after treatment and 90-98% dissipated by 7 days after treatment.

3. Methomyl residues were not detected (detection limit 0.04 ppm) in peppermint and spearmint oil distilled from spearmint and peppermint hay containing methomyl residues at levels of <0.02-5.34 ppm.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Fields of peppermint and spearmint were treated with methomyl (foliage applications; 0.36 kg/liter emulsifiable concentrate, 90% ai water dispersible powder, or 10% ai bait; source not specified) at 0.56, 1.1, or 2.2 kg ai/ha. The mint hay was cut at various intervals after treatment (Tables 1 and 2) and allowed to field cure for up to 4 days. Samples of the hay were steam distilled in commercial stills. After distillation, samples of spent hay (mint hay after the oil has been removed) and mint oil were collected.

Mint hay and spent hay samples (50 g) were macerated with 300 ml ethyl acetate and filtered. Water was added to the filtrate and the organic solvent was removed by evaporation. The aqueous phase was filtered, acidified, washed with hexane, and extracted with 150 ml of dichloromethane. Sodium hydroxide was added and the solution was heated until the dichloromethane evaporated and the methomyl was hydrolyzed. The hydrolysis mixture was acidified, extracted with 150 ml of dichloromethane, dried, and concentrated. The extract was analyzed for the oxime of methomyl (S-methyl-N-hydroxythioacetimidate) by flame photometric gas chromatography (GC).

The mint oil samples (10 g) were diluted with 100 ml hexane and extracted four times with 25 ml of water. The combined aqueous phases were acidified with H_2SO_4 and washed with 50 ml hexane. The aqueous solution was extracted with 150 ml dichloromethane. Sodium hydroxide (50 ml) was added and the solution was heated to evaporate the dichloromethane and to hydrolyze the methomyl. The hydrolyzed solution was acidified, extracted with 150 ml of ethyl acetate, dried, and concentrated prior to analysis for the oxime of methomyl by GC.

REPORTED RESULTS:

The limits of detection were 0.02 ppm for mint hay and spent hay and 0.04 ppm for mint oil. The average recovery rates for spearmint and peppermint hay were 84 and 86%, respectively, and that for spent hay was 92%. For spearmint and peppermint oil the rates were 90 and 102%, respectively.

Residue levels from samples taken immediately after treatment (0 days) on spearmint hay were 5-6 times higher than those on peppermint hay, and these higher residue levels remained that way on all sampling dates (Tables 1 and 2). Methomyl residue levels declined to less than half of the posttreatment levels at 4 days after treatment. These results indicate that methomyl losses are associated with the physical (vapor pressure) or chemical (hydrolysis) properties of this pesticide.

No residues were found in the mint oil even with residue levels in the hay as high as 5.34 ppm. This indicates that methomyl is destroyed during distillation or that it does not distill with steam.

DISCUSSION:

1. The mint hay was field cured for up to 4 days after cutting and prior to analysis. It is possible that some of the methomyl residues were lost during field curing.

2. The lack of methomyl in the mint oil might have been because methomyl was not adsorbed in the plants. Alternatively, the hydrolysis product, S-methyl-N-hydroxythioacetimidate, could have formed during the steam distillation, while the samples were only analyzed for methomyl.

3. There are no zero day samples in 1970 for spearmint, therefore the decline pattern for methomyl cannot be determined.

4. Initial methomyl residue levels present in mint hay were proportional to application rates. Also, treatment with an emulsifiable concentrate resulted in lower residue levels than treatment with a wettable powder.

5. The application, sampling, and harvest dates for the peppermint grown in Oregon in 1970 and 1971 do not follow a pattern. It appears that the peppermint was cut and distilled prior to the collection of the 18- and 26-day posttreatment samples.

Table 1. Methomyl residues in peppermint.

Treatment and date	Application rate (kg/ha)	Sampling interval from last application (days)	Methomyl residues (mg/kg)	
			Fresh hay	Spent hay
	1970 - Oregon - Hay cut Aug. 1 and distilled Aug. 2			
1 application, helicopter[a] July 14	0.56	0	2.13	--
		7	<0.02	--
		19	<0.02	<0.02
	1.1	0	4.20	--
		7	0.02	--
		19	<0.02	<0.02
1 application, airplane[a] July 23	0.56	0	7.52	--
		7	0.66	--
		18	<0.02	0.05
	1.1	0	13.8	--
		7	1.19	--
		18	0.02	0.08
	1971 - Oregon - Hay cut Aug. 9 and distilled Aug. 10			
1 application, airplane[b] July 23	1.1	0	13.3	--
		3	1.06	--
		7	0.19	--
		26	<0.02	0.02
	2.2	0	28.0	--
		3	1.64	--
		7	0.55	--
		26	0.02	0.03
	Hay cut and distilled Aug. 18			
1 application, spreader[c] August 8	0.28	13	0.09	<0.02
	1971 - Indiana - Hay cut Aug. 17 and distilled Aug. 30			
1 application, ground sprayer[b] August 13	0.56	0	10.1	--
		3	1.53	--
		7	0.18	--
		14	0.02	0.04
	1.1	0	20.6	--
		3	2.56	--
		7	0.31	--
		14	0.02	0.07
2 applications, ground sprayer[b] July 30 and August 13	0.56	14	0.04	0.07
	1.1	14	0.06	0.13

[a] 0.36 kg/liter (~3 lb/gal) emulsifiable concentrate.

[b] 90% ai water dispersible powder.

[c] 10% ai bait.

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Table 2. Methomyl residues in spearmint.

Treatment and date	Application rate (kg/ha)	Sampling interval from last application (days)	Methomyl residues (mg/kg)	
			Fresh hay	Spent hay
	1970 - Indiana - Hay cut Aug. 12 and distilled Aug. 13			
1 application, ground sprayer[a] July 21	0.56	22	1.51	0.12
2 applications, ground sprayer[a] July 21 August 4	0.56	8	3.59	0.28
	1.1	8	5.34	0.34
	1971 - Indiana - Hay cut Aug. 27 and distilled Aug. 28			
1 application, ground sprayer[b] August 12	0.56	0	56.7	--
		7	3.75	--
		14	0.23	0.11
	1.1	0	133	--
		7	7.50	--
		14	0.16	0.17

[a] 0.36 kg/liter (~3 lb/gal) emulsifiable concentrate.

[b] 90% ai water dispersible powder.

CASE GS0028 METHOMYL STUDY 23 PM 200 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 250026003

FORMULATION CO - ACTIVE INGREDIENT

FICHE/MASTER ID 05013771 CONTENT CAT 01

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

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: TOX -40-05050021 PM-R-50-0520
SEC: EFB -20-250028007 TOX -40-10250521 TOX -55-05150105

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

REVIEWED BY: R. Strieter
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500
SIGNATURE: Robert P. Strieter DATE: May 14, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:
SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it concerns levels of methomyl in mice exposed to treated crop bedding and does not pertain to environmental chemistry.

2. Mice exposed to apple, cotton, and tobacco foliage treated with methomyl (0.5 lb/A) had less than 40% inhibition of cholinesterase, which declined to about 1% inhibition after 24 hours.

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CASE GS0028 METHOMYL STUDY 24 PM 20C 01/30/80

CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 259926003

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00CC7131 CONTENT CAT 02

Shell Chemical Company (1976) Residue Summary: ≠Nudrin]. Summary of studies 232400-B through 232400-E, 232400-G, 232400-I, 232400-M, 232400-O, 232400-P, 232400-R, 232400-T through 232400-V, 232400-Z and 232400-AA. (Unpublished study received Jun 29, 1976 under 201-347; CDL:232400-A)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS

PRIM: RCBR-25-10001010

SEC: RCBR-25-10032010 RCBR-25-1CC9CC10 RCBR-25-1C1C501C
RCBR-25-10069C10 RCBR-25-1CC7CC10 RCBR-25-1CC73010
RCBR-25-10089010 RCBR-25-10125C10 RCBR-25-1C14201C
RCBR-25-1C149C10 RCBR-25-1C193010 RCBR-25-1C240010
RCBR-25-10267010 RCBR-25-1C325C10 RCBR-25-10333010
RCBR-25-10349010 RCBR-25-1C366C10 RCBR-25-1C430010
RCBR-25-10442010 RCBR-25-10455010 RCBR-25-1C463010
RCBR-25-10494010

DIRECT RVW TIME = ½ (MH) START-DATE END DATE

REVIEWED BY: R. Strieter
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Robert P. Strieter DATE: May 13, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This summary study contains data for methomyl applied to various treated crops but gives no data on procedures employed and is therefore not given a full review.

2. Methomyl residue levels were generally found to be below EPA tolerance standards, especially with application levels below 2 lb ai/A.

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CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 150520

FORMULATION 03 - DUST (D)

FICHE/MASTER ID 05CC9351 CONTENT CAT 01

Bull, D.L. (1974) Fate of methomyl on cotton. Environmental Entomology 3(4):723-724.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -20-250028007

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: M. Minnich and W. Hazel
TITLE: Staff Scientists
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich W. Hazel DATE: Apr. 21, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

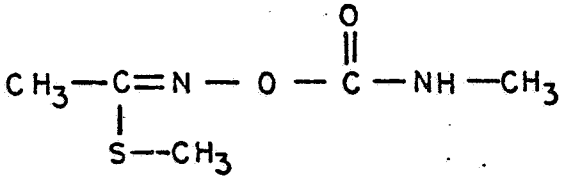
1. This study is scientifically valid.

2. An aqueous solution of methomyl will penetrate cotton leaves within a few hours (40% within 4 hours). At 8 days after treatment, less than 2% of the applied methomyl will remain in the treated cotton leaves.

3. A dust formulation of methomyl will remain on the leaf surface for a longer period of time than an aqueous solution (68% unabsorbed after 4 days).

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Field grown cotton plants were cultivated in the customary manner but without the application of pesticides. Foliar treatments with two formulations of [^{14}C]methomyl were then made in situ on fully expanded leaves in July and August. Absorption and metabolism studies were done using technical [^{14}C]methomyl (E.I. du Pont de Nemours & Co., Inc.) 50 µg in 150 µl of water spread on the surface of each leaf.

Studies of absorption only were done using 25 mg of 5% [^{14}C]methomyl dust distributed over each leaf. Unabsorbed and absorbed radioactivity was extracted at 0, 4, 8, 24, 48, 96, and 192 hours posttreatment from treated leaves, separated into organosoluble and water-soluble components, and analyzed with thin-layer chromatography (TLC) and radiometric techniques. Unextractable radioactivity in leaf tissue was estimated as $^{14}CO_2$ by combustion.

REPORTED RESULTS:

Data on the fate of the aqueous solution of [^{14}C]methomyl are shown in Table 1. Unabsorbed methomyl residues were depleted to less than 2% of the applied dose after 2 days; methomyl was the only radioactive residue detected. The absorbed [^{14}C]methomyl level declined to less than 2% of that applied after 8 days. An unidentified organosoluble compound (Unknown A) was present in trace amounts after 8 hours. Although the concentration of water-soluble radioactivity increased to 14.7% of the applied dose after 48 hours, it apparently included none of the known toxic derivatives of methomyl and was almost depleted after 8 days.

The dust application tests (Table 2) showed that very little of the radioactivity in dust formulations of [^{14}C]methomyl penetrated the leaf surfaces and the unabsorbed residues were relatively persistent.

DISCUSSION:

1. No data were provided comparing the amounts of methomyl experimentally applied with the usual field application rates. This information would be helpful in extrapolating the experimental data to a field situation.

2. Large percentages of applied residues were reported as "lost" or "not accounted for." A more tightly monitored experiment could be done to determine the fate of these residues.

Table 1. Fate of aqueous [^{14}C]methomyl after foliar application to individual cotton leaves.

Hours posttreatment	Distribution of applied dose (%)					
	Unabsorbed	Internal				
	Methomyl	Methomyl	Unknown A	Water soluble	Unextractable	Lost
0	100.0	--	--	--	--	--
4	19.2	39.5	0.0	2.5	1.6	37.2
8	13.2	29.5	0.7	5.4	2.3	38.9
24	6.8	27.6	0.7	9.3	3.8	51.8
48	1.8	9.1	1.1	14.7	5.7	67.6
96	0.0	5.4	0.2	13.4	6.6	74.4
192	0.0	1.5	0.4	1.2	5.1	91.8

Table 2. Absorption of [^{14}C]methomyl after foliar applications of 5% dust formulations to individual cotton leaves.

Hours posttreatment	Percent of applied dose		
	Unabsorbed	Internal	Lost
0	100.0	0.0	0.0
4	91.0	0.0	9.0
8	88.0	0.0	12.0
24	86.0	1.9	12.1
48	81.0	4.3	14.7
96	67.9	6.3	25.8

CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 150515

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00008836 CONTENT CAT 01

Harvey, J., Jr.; Buchanan, J.B. (1967?) Absence of S-Oxide and S, S Dioxide as Potential Metabolites of Methomyl in Soil, Tobacco and Rats. (Unpublished study received Dec 28, 1968 under 8F0671; submitted by E.I. du Pont de Nemours & Co., Inc., Wilmington, Del.; CDL:091179-F)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: TOX -35-05200021 EFB -30-05052C
SEC: EFB -20-259926003

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

REVIEWED BY: M. Edwards
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Martha N. Edwards DATE: Apr. 24, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. A full review of this study is not provided because no original data with respect to the presence of either methomyl S-oxide or methomyl S,S-dioxide as potential soil metabolites of methomyl are presented. The polar fraction extracted from soil 12 months after methomyl treatment (Study 1, MRID 00008844) could not be analyzed for presence of the oxide because the amount of polar fraction collected was too small. Similarly, tests were not conducted to determine the presence of the dioxide. Rather, its absence in a laboratory soil metabolism study (Study 1, MRID 00008844) was deduced based on the findings that (1) the dioxide and S-methyl-N-hydroxythioacetimidate had identical partition ratios in a benzene/water system, and (2) that the material having this ratio in the soil experiment (Study 1, MRID 00008844) was S-methyl-N-hydroxythioacetimidate plus a trace of methomyl.

2. Other portions of this study are not reviewed in detail because they involve characterization of methomyl metabolites in either tobacco or rats.

TDMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 27 EM 2CC 01/30/80

CEEM C90301 Methomyl

BRANCH EFB DISC 20 TOPIC 1005 GUIDELINE 40 CFR 163.62-8f3

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05010223 CONTENT CAT 01

Huang, C.Y. (1978) Effects of nitrogen fixing activity of blue-green algae on the yield of rice plants. Botanical Bulletin of Academia Sinica 19(1):41-52.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -20-1205 EEB -20-201024004

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

REVIEWED BY: R. Strieter
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Robert P. Strieter DATE: May 5, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

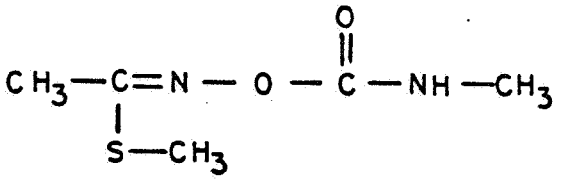
Metabolism - Effects of Pesticides on Microbes

1. This study is scientifically valid.

2. Methomyl reduces the ability of the blue-green alga Anabaena cylindrica to fix nitrogen by about 86% at 40 ppm, as well as reducing the overall algal biomass by over half, by 4 days of exposure. Recovery of the nitrogen-fixing ability of A. cylindrica of up to 40% occurs after methomyl treatment is discontinued.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

One hundred milliliters of blue-green algae (Anabaena cylindrica) stock culture was poured into flasks containing methomyl (Lannate; source, purity, and formulation unspecified), yielding final concentrations of 0, 20, 40, 80, or 160 ppm. Cultures were incubated at 28/24 C (day/night) for 4 days (continuous aeration) with a daily photoperiod (cool white fluorescent light) of 16 hours at 0.13 cal/cm^2/min. The algal suspensions were filtered after incubation, and the filaments were rinsed with distilled water. Aliquots were transferred to serum vials and analyzed for nitrogen-fixing activity by injecting acetylene through the vial stopper into each bottle until an acetylene partial pressure of 0.1 atmosphere was reached. The vials were allowed to sit for 60 minutes, and the reactions of acetylene reduction were then terminated with the addition of 5 ml of 5 N H_2SO_4. Gas samples were withdrawn, and acetylene and ethylene were separated by gas chromatography (GC) using a hydrogen ionization detector. After measuring nitrogen activity for each of the samples, the algal filaments were dried at 75 C overnight and the dry weight was measured and recorded.

REPORTED RESULTS:

Methomyl inhibited both nitrogen fixation and algal biomass most intenseley at 40 ppm (Figure 1, Table 1). At the other concentrations tested (20, 80, and 160 ppm), the compound did not inhibit algae or nitrogen fixation as much as it did at 40 ppm. However, at all concentrations tested, the compound did have some inhibiting effects when compared with the control (0 ppm methomyl). A. cylindrica was found to recover about 40% of its nitrogen-fixing ability after termination of methomyl treatment at all concentrations tested (time unspecified).

DISCUSSION:

1. The source, purity, and formulation of the methomyl tested were not specified.

2. The time elapsed before A. cylindrica recovered its nitrogen-fixing ability after methomyl treatment was terminated was not specified.

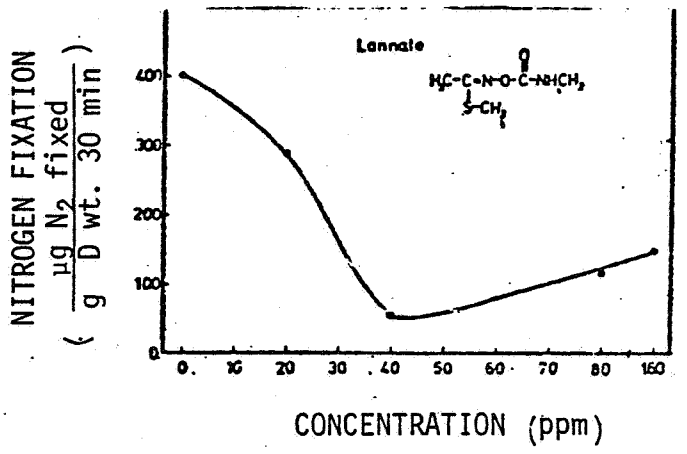


Figure 1. Effect of methomyl on the nitrogen-fixing activity of Anabaena cylindrica.

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Table 1. Effect of methomyl on the nitrogen-fixing activity and total N concent and biomass of A. cylindrica.

Methomyl treatment (ppm)	Algal DW[a]/flask (g/100 ml)	Nitrogen fixation			Total N/DW (µg/g)%	% of N in algal on DW bas
		C_2H_4/DW[b] (µmole/g)	N_2 fixed/DW[b] (µg/g)	N_2fixed released/flask (µg/100 ml)		
0	0.0532	43.02	401.35	1.58	7277	13.68
20	0.0327	31.14	290.50	0.76	3230	9.88
40	0.0244	6.09	56.85	0.33	0478	1.96
80	0.0304	12.53	116.89	1.02	1237	4.07
160	0.0320	15.88	148.11	1.46	1696	5.30

[a]DW - dry weight

[b]During a 30-minute period.

DATA EVALUATION RECORD

METHOMYL STUDY 28

CHEMICAL: Methomyl

FORMULATION: 00 - ACTIVE INGREDIENT

FICHE/MASTER ID: 05012954

CITATION: Harvey, J., Jr., and H.L. Pease. Decomposition of methomyl in soil. Journal of Agricultural and Food Chemistry 21(5):784-786.

DIRECT RVW TIME = ½ (MH) START-DATE END DATE

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: June 17, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

The data from this study are presented in the soil metabolism and field dissipation sections of Study 1 (MRID 00008844) and the field dissipation and mobility sections of Study 5 (MRID 00009324).

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CASE GS0028 METHOMYL STUDY 29 PM 20C 01/30/80

CHEM 090301 Methomyl

BRANCH RCBP DISC C5 TOPIC 1015 GUIDELINE 40 CFR 163.61-7

FORMULATION CC - ACTIVE INGREDIENT

FICHE/MASTER ID C5CC8203 CONTENT CAT C6

Holland, P.T. (1977) Routine methods for analysis of organophosphorus and carbamate insecticides in soil and ryegrass. Pesticide Science 8(4):354-358.

SUBST. CLASS = S.

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Hazel DATE: June 18, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

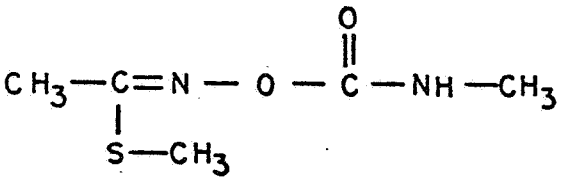
1. This study is scientifically valid.

2. A method was developed to extract methomyl from plant tissue and soil and to identify the residues by gas chromatography. The identification procedures could only detect the presence of carbamates; it was not specific for methomyl.

90

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

A Matangi loam soil developed from volcanic alluvium (9.5% organic matter; allophane is the major clay) and fresh ryegrass (cut foliage allowed to wilt 2 hours) were amended with methomyl (source and purity not given) at 0.1, 1, and 10 µg/g wet weight immediately prior to extraction.

Soil or grass samples were heated (80 C for 10 minutes) in acidified ammonium acetate solution and were shaken (room temperature) for 1 hour. Extracts were then filtered, washed, neutralized with Na_2CO_3, mixed with a small amount of ammonia, and extracted three times with dichloromethane. This extract was dried with Na_2SO_4 and the dichloromethane was evaporated to dryness. The residues were dissolved in methanol (0.5 ml) and 50 µl of 0.05 M NaOH in methanol was added just prior to gas chromatography (GC). The NaOH produced the trans-esterification product methyl methylcarbamate.

REPORTED RESULTS:

The acidified ammonium acetate extraction method, previously in use, was simplified and expanded to include plant samples as well as soil. Three dichloromethane extractions were found to be adequate for up to 97% recovery of methomyl (as well as carbofuran and 2,3-dihydro-3-hydroxy-2,2-dimethylbenzofuran-7-yl methylcarbamate). The NaOH concentration used was found to be optimum for reproducible trans-esterification.

The GC response curve for methomyl (and other carbamates) in methanolic NaOH was linear in the range 2-50 ng. An injection port temperature of 180 C eliminated interfering peaks from grass extracts, as did addition of NaOH just prior to GC rather than earlier. Methomyl was recovered at 79-93% from soil samples and at 83-97% from grass extracts (Table 1). Lowest recoveries occurred at the fortification rate of 0.1 µg/g from both soil and grass. These recoveries are acceptable from the soil used, considering its high organic matter content and highly absorptive nature. This GC technique does not, however, distinguish between carbamates and their methylcarbamate metabolites.

DISCUSSION:

The methods presented, although not directly useful for identification of residues of methomyl or its metabolites, are useful for quantification of total carbamates and methylcarbamate metabolites in either soil or plant tissues.

Table 1. Recoveries of methomyl added to soil and ryegrass.[a]

	Recovery (%)					
	Soil level (µg/g wet wt)			Grass level (µg/g wet wt)		
	0.1	1	10	0.1	1	10
Methomyl	79	87	93	83	94	97

[a] Mean of three determinations.

Adapted from Holland (1977).

CEEM C90301 Methomyl

BRANCH RCBR DISC 25 TOPIC 10032010

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00007684 CONTENT CAT C1

Pease, H.L. (1971?) Rapid Loss of Surface Residues of Methomyl on Treated Plants. (Unpublished study received Sep 2, 1972 under 2F1247; submitted by E.I. du Pont de Nemours & Co., Inc., Wilmington, Del.; CDL:091771-E)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: RCBR-25-10073010 RCBR-25-10125010

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: William J. Hazel DATE: June 18, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

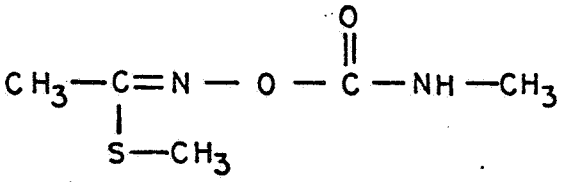
1. This study is scientifically valid.

2. Field reentry hazard due to methomyl diminished rapidly with time, since surface residues on bean, corn, and cabbage plants almost disappeared within 24 hours after application. Residue levels within plants remained fairly constant over this period.

94

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Methomyl (90% WD; E.I. du Pont de Nemours and Co., Inc.) was applied at 0.5 lb ai/A as a spray on beans (38 days old), corn (20 days), and cabbage (53 days at the head-forming stage). Beans and cabbage had received an identical application 2 weeks earlier. Upon drying of the spray (15 minutes), zero time plant samples were collected, as well as prespray and 2, 6, 12, 24, 48, and 72 hour samples. Surface (removed by six water washings) and internal plant residue levels were determined (methods not given) from all samples except prespray, 48, and 72 hour (total residues in/on plant only).

REPORTED RESULTS:

Total methomyl residue levels for bean, corn, and cabbage (Table 1) dropped 70-90% within 24 hours after application and 93-98% by 72 hours. Residue levels in plant tissue remained essentially constant over the 24-hour period, whereas surface residues decreased 88-95% (71-93% by 12 hours). Total residue levels for cabbage at time zero were very low (1.9 ppm) compared with bean and corn, which contained residues at 25 and 49 ppm, respectively. Prespray analyses revealed low total methomyl levels (0.1-0.17 ppm).

DISCUSSION:

Although the data appear to be adequate for determining the relative losses of surface residues with time and are therefore useful in the assessment of reentry hazards, the absolute concentration values are questionable as no methods of residue quantification are presented. No standard curves to determine the efficiency of either the extraction or detection procedures were presented. The method of extraction of residues from the plant tissue was not given. It is also not known whether the reported values are based on dry weight or on wet weight of plant tissue. This could explain the comparatively low methomyl residue levels for cabbage.

Table 1. Methomyl residues in an on plant tissues.

Sample	Methomyl residues			
	In wash H_2O (ppm)[a]	In plant (ppm)	Total on/in plant (ppm)	Percent of residue washed from plant
Bean				
Prespray	--	--	0.1	--
0 hour	22	3.0	25	88
2 hours	17	7.0	24	71
6 hours	4.5	6.5	11	40
12 hours	2.2	5.0	7.2	30
24 hours	1.6	5.6	7.2	23
48 hours	--	--	2.4	--
72 hours	--	--	1.7	--
Corn				
Prespray	--	--	0.17	--
0 hour	44	4.5	49	91
2 hours	16	4.4	21	79
6 hours	4.4	7.3	12	38
12 hours	3.1	4.4	7.5	41
24 hours	2.1	1.7	3.8	55
48 hours	--	--	1.5	--
72 hours	--	--	1.1	--
Cabbage				
Prespray	--	--	0.13	--
0 hour	1.7	0.16	1.9	91
2 hours	1.5	0.33	1.8	82
6 hours	0.44	0.20	0.04	68
12 hours	0.51	0.41	0.92	55
24 hours	0.22	0.32	0.54	41
48 hours	--	--	0.15	--
72 hours	--	--	0.13	--

[a] Based on plant weight.

CASE GS0028 METHOMYL STUDY 31 PM 22C 01/30/80

CHEM 090301 Methomyl

BRANCH RCBR DISC 25 TOPIC 10073010

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00CC9185 CONTENT CAT 02

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

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS

PRIM:	PM-R-50-0520	TOX -55-05150105	TOX -40-05CC0021
SEC:	RCBR-25-10090010	RCBR-25-1C240C10	RCBR-25-10455010
	RCBR-25-1032C10	RCBR-25-10349C10	RCBR-25-1C442010
	RCBR-25-10130010	TOX -55-1C15C105	TOX -35-05CC0021
	TOX -40-05050501	TOX -40-05051C21	TOX -40-05051501

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

REVIEWED BY: R. Rice
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LCC/TEL: 468-2500
SIGNATURE: DATE: June 16, 1980

APPROVED BY:
TITLE:
ORG:
LCC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it is a literature review with no original data.

2. Various investigations covering persistence and degradation of methomyl on leafy crops and dermal, oral, and inhalation toxicity of methomyl in animals are reviewed. Metabolic fate in animals and several documented human exposure events are discussed.

TDMS0030 DATA EVALUATION RECORD PAGE 1 OF

CASE GS0028 METHOMYL STUDY 32 EM 20C 01/30/80

CHEM C90301 Methomyl

BRANCH PM-R DISC 50 TOPIC 0520

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00009189 CONTENT CAT C2

E.I. du Pont de Nemours & Company (19??) Re-Entry Experience in Lannate ~~Treated~~ Fields. (Unpublished study received Jul 29, 1976 under 352-342; CDL:224800-T)

SUBST. CLASS = S.

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

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: William J. Hazel DATE: July 11, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it consisted simply of one table with no supporting or explanatory text.

2. The study presented, in tabular form, case accounts of reentry into fields treated with methomyl (Lannate). Locations, crops, number of people, dosages, and times after treatment, as well as exposure periods, number of exposures, and the observed toxicity effects are all presented. No apparent effects were observed.

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CASE GS0028 METHOMYL STUDY 33 RM 200 05/22/80

CHEM 090301 Methomyl

BRANCH EFB DISC 26 TOPIC 1299 GUIDELINE 40 CFR 163.62-8f3

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 05016149 CONTENT CAT 01

Cassignard, R. (1972) Influence des produits de traitement de la vigne sur la flore microbienne et la fermentation. [Influence of treatments on the microbial flora and fermentation of grapes.] Vignes et Vins 211:15-21.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCBR-25-1020270

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

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: William D. Hazel DATE: July 2, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it concerns the effects of methomyl on wine production and does not pertain to environmental chemistry.

2. Methomyl reportedly did not affect the fermentation rate or the taste of treated grapes or the derived juice, whereas the taste of the resultant wine may have been influenced.

CHEM 090301 Methomyl

BRANCH EFB DISC 22 TOPIC 25-507004

FORMULATION 06 - WETTABLE POWDER (WP OR W)

FICHE/MASTER ID 05018583 CONTENT CAT 01

Kiigemagi, U.; Deinzer, M.L. (1979) Dislodgeable and total residues of methomyl on mint foliage. Bulletin of Environmental Contamination and Toxicology 22(4/5):517-521.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: PM-R-50-0520

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Hazel DATE: July 2, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

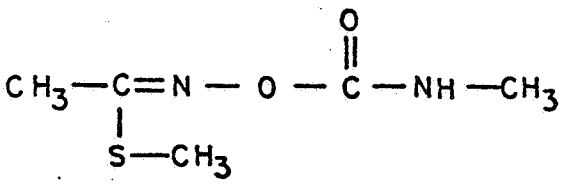
1. This study is scientifically valid.

2. Dislodgeable methomyl residues on peppermint foliage will decline over time but will be present at 2 days after treatment (30-53 ppm when treated with methomyl at 0.9 - 1.8 lb/A).

100

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Peppermint fields (near Jefferson, Oregon) were aerially sprayed with 0.9 or 1.8 lb ai/A methomyl (Lannate, 90% WP) using a final spray volume of 10 gallons of water per acre. Three 2-pound samples were collected from each field at 4, 24, and 48 hours after application.

Dislodgeable methomyl residues were extracted from 100 (1.3 cm) weighed leaf discs (frozen until use) by shaking 20 minutes in 100 ml of water containing a wetting agent. This procedure was repeated twice. The extracts were combined, acidified, and extracted three times with dichloromethane (100 ml each). Fifty milliliters of 0.1 N NaOH was added, the solvent was evaporated, and the sample was subjected to 15 minutes of additional heating. The hydrolysis mixture was acidified and extracted with three 50-ml portions of dichloromethane, and the extract was dried for gas chromatography (GC).

Total methomyl residues were extracted from 50-g leaf samples by maceration in two 250-ml portions of ethyl acetate followed by filtration and an ethyl acetate wash. Water was added and ethyl acetate was evaporated. The aqueous phase was filtered, acidified, washed with hexane, and extracted with three 50-ml portions of dichloromethane. The extract was hydrolyzed as described for dislodgeable residues.

The alkaline hydrolysis product of methomyl, S-methyl N-hydroxythioacetimidate (an oxime), was prepared as above in known amounts to calibrate the GC.

Methomyl residues were quantified by GC using a flame photometric detector with a 394 nm interference filter for sulfur. An average recovery rate of 78% was determined for dislodgeable residues, and the sensitivity was 0.01 $\mu g/cm^2$, or 0.4 ppm, using 100 leaf discs. The recovery rate was 89% for total residues, and the sensitivity was 0.1 ppm with a 50-g sample. The data were not corrected for recoveries. Less than 5% deviation in methomyl residue levels occurred between samples frozen for 14 or 112 days.

REPORTED RESULTS:

Levels of dislodgeable methomyl residues (Table 1) on peppermint foliage decreased from 1.52 to 0.33 $\mu g/cm^2$ between 4 and 48 hours, respectively, after application (0.9 lb ai/A). The half-life was about 24 hours. About 22% of the dislodgeable residues remained at 48 hours, whereas 36% of the total residues remained at that time. At 4 hours 80% of the total residue was dislodgeable, whereas at 48 hours only 50% was dislodgeable.

DISCUSSION:

It would have been a bit more useful to have determined methomyl residues at zero time as well as at 4, 24, and 48 hours.

Table 1. Dislodgeable and total methomyl residues on mint foliage.

Treatment (lb ai/A)	Interval (hours)	Dislodgeable residues		Total residues (ppm)
		µg/cm²	ppm	
Untreated	--	<0.01	<0.4	0.1
0.9	4	1.52	149	187
0.9	24	0.71	60	107
0.9	48	0.33	30	70
1.8	4	2.30	228	296
1.8	24	1.23	114	162
1.8	48	0.63	53	94

CHEM 090301 Methomyl

BRANCH EFB DISC 30 TOPIC 1005

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 05019780 CONTENT CAT 06

Magallona, E.D. (1975) Gas chromatographic determination of residues of insecticidal carbamates. Pages 1-77, In Residue Reviews. Vol. 56. Edited by F.A. Gunther. New York: Springer.

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCRR-25-1005

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

REVIEWED BY: R. Streiter
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: R. Streiter DATE: July 7, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study was not given a full review because it is a literature review with no original data.

2. This study reviews gas chromatographic methods of determining residues of insecticidal carbamates, including methomyl, in soil samples and in plant and animal tissues.

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CASE GS0028 METHOMYL STUDY 36 PM 200 05/22/80

CHEM 090301 Methomyl

BRANCH EFB DISC 3(TOPIC 101045

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 05019317 CONTENT CAT 01

Edwards, R.W.; Nonnemaker, K.A.; Cotter, R.L. (1979) The trace-level determination of organics by high-pressure liquid chromatography. Pages 87-94, "In" Trace Organic Analysis: A New Frontier in Analytical Chemistry, Proceedings of the 9th Materials Research Symposium; Apr 10-13, 1978, Gaithersburg, Maryland. Washington, D.C.: U.S. National Bureau of Standards. (NBS special publication no. 519)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCBP-05-1015

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

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: William J. Hazel DATE: July 2, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This method study was not given a full review because no details on the extraction or identification of methomyl were presented.

2. Agricultural run-off water was spiked with 18 pesticides, including methomyl, at 20 ppb, concentrated 100-fold on a nonpolar column, and analyzed by high-pressure liquid chromatography. A methomyl peak was not indicated on the chromatogram, thus making it impossible to fully evaluate this method.

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CHEM 090301 Methomyl

BRANCH EFB DISC 20 TOPIC 259926003

FORMULATION 99 = FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00009800 CONTENT CAT 01

Leidy, R.B.; Domanski, J.J.; Haire, P.L.; et al. (1975?) Environmental and Flue-Curing Effects on Methomyl Residues on Tobacco. (Unpublished study received Mar 22, 1976 under 352-342; prepared by North Carolina State Univ., Pesticide Residue Research Laboratory, submitted by E.I. du Pont de Nemours & Co., Wilmington, Del.; CDL:224070-A)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -20-259926006 RCB-20-1520

DIRECT RVW TIME = 15½ (MH) START-DATE END DATE

REVIEWED BY: D. Harper
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Daniel Harper DATE: July 7, 1980

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

1. This study is scientifically valid.

2. Greater than 95% of the methomyl applied to tobacco will dissipate within 5 days. Flue-curing will remove 94-98% of the methomyl residues present in harvested tobacco.

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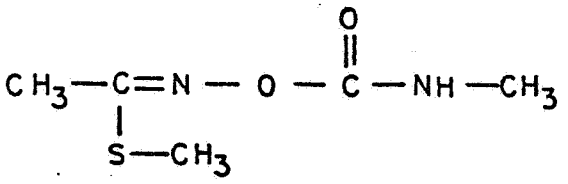
MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

Field plots in North Carolina were treated with diazinon (preplant incorporated) and 'NC-2326' tobacco plants were transplanted to the plots. The tobacco plants were treated with carbaryl or Bacillus thuringiensis and a contact sucker control agent on an unspecified date(s). The tobacco in the plots at Clayton, North Carolina, was treated with methomyl 73 days after transplanting, and the plots at Reidsville, North Carolina, were treated 104 days after transplanting. The tobacco was treated at 0, 0.56, or 1.12 kg/ha (formulation, source, and purity not specified). Rainfall and temperature data were collected.

Leaf samples were collected from each control plot prior to treatment and from treated plots 10 minutes after treatment. At 1, 3, 5, and 9 days after treatment, four discs (5 cm in diameter) were punched from 50 leaves from all plots for analysis. A second sample of leaves was collected from each plot at 1, 3, and 5 days after treatment. These samples were cured by standard flue-curing practices. The cured leaf tissue was ground in a Wiley mill and stored at -18 C until analyzed.

Fresh and cured leaf samples were placed in a plastic bag and weighed. The bag was placed on a block of dry ice until frozen and crushed by hand. Portions of the crushed leaves were extracted with a 9:1 chloroform:methanol mixture in a Soxhlet extractor. The extract was concentrated and transferred to a separatory funnel containing 50 ml of 0.1 N NaOH. The aqueous layer was extracted twice with petroleum ether (100 ml each extraction), and the ether layer was discarded.

The extract was heated in a boiling water bath for 30 minutes to form the oxime of methomyl (methyl-N-hydroxythioacetamidate). After cooling, the extract was neutralized with 1 N H_2SO_4 and extracted three times with 50-ml portions of methylene chloride. The combined extracts were then drained through anhydrous Na_2SO_4. Triethylamine (0.1 ml) was added to the solution (to form the amine salt) and the solution was concentrated. Another 0.1 ml triethylamine was added and further concentration was effected with N_2.

Samples were chromatographed on a column containing Florisil topped with anhydrous Na_2SO_4 and rinsed with 50 ml of petroleum ether. Samples were eluted with 200 ml of 1:1 diethyl ether:petroleum ether. The eluates were concentrated, treated with 0.1 ml of triethylamine, and further concentrated with a stream of N_2.

Aliquots of the concentrated eluates were analyzed on a gas chromatograph with a flame photometric detector. The method sensitivity was 0.05 ppm and the recovery rate was 66.5% for green tobacco and 75.4% for cured samples.

REPORTED RESULTS:

Methomyl residue levels in tobacco samples collected immediately after application were 299 and 383 ppm at the Clayton plots and 128 and 274 ppm at the Reidsville plots for the 0.56 and 1.12 kg/ha applications, respectively. By 5 days after treatment, these residue levels declined to 2.4 and 9.4 ppm in the Clayton plots and to 3.2 and 12.1 ppm in the Reidsville plots for the 0.56 and 1.12 kg/ha applications, respectively (Table 1).

Losses of methomyl during curing averaged 96.2%. There were only slight differences between losses during curing and losses due to dissipation in the field (97.5%) at 5 days after treatment.

DISCUSSION:

1. The tobacco was treated with diazinon and either carbaryl or Bacillus thuringiensis prior to treatment with methomyl. It is assumed that the residues from these pesticides dissipated prior to treatment with methomyl.

2. Samples consisting of four leaf discs were placed in plastic bags, frozen, and crushed. It is possible that some of the methomyl in the samples may have adsorbed to the plastic bag.

Table 1. Concentrations of methomyl at 13% moisture before and after flue-curing of tobacco.

Location	Application rate (kg/ha)	Time from application to harvest (days)	Residue before curing (ppm)	Residue after curing (ppm)	Loss during curing (ppm)	Loss due to dissipation in the field (%)
Clayton	0	0	0.05	NS[a]	--	--
		1	0.32	0.25	--	--
		3	0.11	0.07	--	--
		5	0.05	0.05	--	--
		9	0.05	NS	--	--
	0.56	0	298.99	NS	--	--
		1	61.13	2.14	96.5	79.6
		3	21.02	0.47	97.8	93.0
		5	2.44	0.12	95.1	99.2
		9	0.20	NS	--	99.9
	1.12	0	382.80	NS	--	--
		1	185.59	7.80	95.8	51.6
		3	49.67	1.22	97.5	87.0
		5	9.42	0.43	95.4	97.6
		9	0.76	NS	--	99.8
Reidsville	0	0	0.05	NS	--	--
		1	0.18	0.07	--	--
		3	0.05	0.05	--	--
		5	0.05	0.05	--	--
		9	0.05	NS	--	--
	0.56	0	128.15	NS	--	--
		1	57.89	1.84	96.8	54.9
		3	19.82	0.52	97.4	84.6
		5	3.22	0.16	95.0	97.5
		9	0.57	NS	--	99.6
	1.12	0	273.86	NS	--	--
		1	135.53	7.87	94.2	50.3
		3	41.88	1.32	96.8	84.7
		5	12.12	0.45	96.3	95.6
		9	5.12	NS	--	98.2

[a] NS - Not sampled.

CHEMICAL: METHOMYL, LANNATE, NUDRIN

FORMULATION: 00-Active Ingredient

FICHE/MASTER ID: None

CITATION: Knaak, J.B., T. Jackson, A.S. Fredrickson, L. Rivera, K.T. Maddy, and N.B. Akesson. 1980. Safety effectiveness of closed-transfer, mixing-loading, and application equipment in preventing exposure to pesticides. Arch. Environ. Contam. Toxicol. 9:231-245.

DIRECT RVW TIME = 13 (MH) START-DATE END DATE

REVIEWED BY: M. Minnich
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: M. Minnich DATE: Feb. 11, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

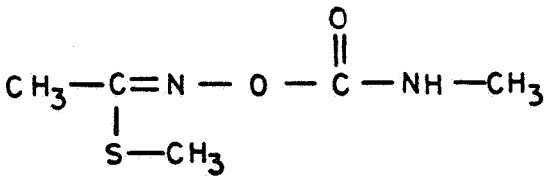
Exposure

1. This study is scientifically valid.

2. A closed transfer system for mixing and loading pesticides can be very effective in maintaining low exposure levels. Airborne methomyl levels were not detectable (detection limit unspecified) except on the day that a water-soluble bag accidently broke. Workers were exposed to an estimated 1,332 $\mu g/m^3$ when the bag broke. Airborn methomyl levels near tractor applicators ranged from 0.0 to 7.5 $\mu g/m^3$.

MATERIALS AND METHODS:

METHOMYL, LANNATE, NUDRIN



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

A closed-transfer system for mixing and loading pesticides, including methomyl (Lannate 8 oz pks; Lannate Liquid; Nudrin), was tested for effectiveness in reducing worker exposure. A schematic of the closed system is shown in Figure 1. Liquid pesticide formulations were transferred from their original containers to a measuring tank via the closed system. Pesticides formulated as powders were introduced into a powder box, the lid was closed and water was used to wash the powder into the mix or vehicle tank. Pesticides were diluted with water in a spray or mix tank. Hoses and centrifugal pumps were used to transfer the spray mixture from the mix tank to aircraft tanks when aerial applications were used. Rear-mounted spray boom rigs were used for ground applications.

Airborne residues were measured July 18-22 around the California work sites of four mixer-loader-applicators and one mixer-loader. Scientists placed sampling apparatus near workers at each job site. Samples were taken with high volume air samplers at 0.566 m^3/min, fitted with a combination filter head of glass fiber and XAD-4 Amberlite resin.

Airborne methomyl during application and between applications was sampled through impingers mounted on tractors. Air was pulled through the impingers at 0.014 m /min by small vacuum pumps. Methomyl was trapped on glass fiber filters and in an ethylene glycol trap. Impingers were turned on at the start of a workday and turned off when the day's work was completed.

The glass fiber filters were extracted with acetone, and aliquots were then analyzed by gas or liquid chromatography.

The amberlite resin was twice extracted with acetone and aliquots were evaporated to dryness. The residue was dissolved in ethylacetate. Aliquots were analyzed by gas chromatography (GC) with a recovery rate of 90%. (Knaak et al., 1980. Arch. Environ. Contam. Toxicol. 9:217-229).

The ethylene glycol solutions were diluted with Na_2SO_4 solution and extracted with dichloromethane. Aliquots of the extract were analyzed by by GC (100% recovery) and by high pressure liquid chromatography.

REPORTED RESULTS:

Results of the air monitors are shown in Table 1. Methomyl was not detected (limit of detection not reported) in the air during mixing and loading operations except on the day when one of the water-soluble bags broke during transfer.

During application, the concentrations of methomyl picked up by the tractor-mounted impingers was 0-7.5 $\mu g/m^3$.

These was no correlation found between the amount collected by the samplers and the amount being applied day-to-day.

DISCUSSION:

Information on weather conditions during applications is lacking. Also the formulations used were only mentioned on the day that the water-soluble bag broke. It is not clear which formulations were mixed or applied on other days.

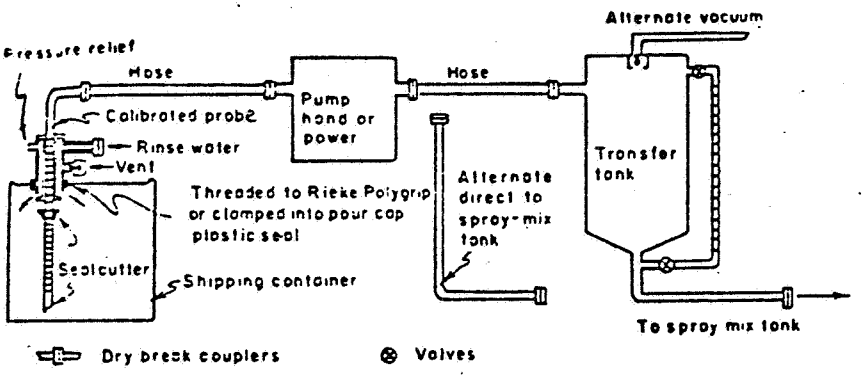


Figure 1. Closed-transfer system for pesticide mixing-loading.

Table 1. Methomyl residues during closed transfer, mixing, loading (T,M,L) and application.

Date	No. of lbs used	Airborne residues	
		During T,M,L ($\mu g/m^3$)	During application ($\mu g/m^3$)
7/18	55.7	ND (5)[a]	3.6
7/19	76.9	ND (5)	7.5
7/20	18.9	8.1[b]	--
	2.3	1,332.0[b]	--
	39.6	ND (3)	--
	60.8	--	3.9
7/21	31.4	ND (3)	0.0

[a]ND, not detected; numbers in parentheses represent the number of batches monitored.

[b]These high values correspond to the accidental opening of one of the water-soluble bags while being placed in the powder box.