US EPA ARCHIVE DOCUMENT

METHAMIDOPHOS

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-5830

Final Report

December 9, 1981

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

Enviro Control, Inc.
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

A Subsidiary of the Dynamac Corporation

This document contains commercial and/or financial information of Enviro Control, Inc. that is privileged or confidential and is therefore subject to the restrictions on disclosure outside the agency to which such document has been submitted, as provided in the Freedom of Information Act (PL 89-554, September 6, 1966, as amended).

METHAMIDOPHOS

Table of Contents

Table of Contents (continued)

15 Baychem Corporation. 1972. Chemagro, Division of Baychem Corporation, residue experiment: Report No. 31933.

Baychem Corporation. 1972. Chemagro, Division of Baychem Corporation, residue experiment: Report No. 31938.

16 Stanley, C.W. 1971. A gas chromatographic method for the determination of Monitor in fish and water.

Chemagro Corporation. 1971. Recovery of Monitor from bass and rainbow trout.

Chemagro Corporation. 1971. Recovery of Monitor from bass and rainbow trout, confirmatory column.

Stanley, C.W. 1971. Analysis of bass and water for Monitor.

17 Tucker, B.V. 1973. Orthene and Ortho 9006 in Daphnia magna living in treated water.

18 Tucker, B.V. 1972. Residues of Orthene and Ortho 9006 in a marine diatom growing in treated water.

19 Tucker, B.V. 1972. Residues in earthworms in Orthene and Ortho 9006 treated soil.

20 Lubkowitz, J.A. 1975. Uptake and degradation of methamidophos by tomato plants and soils.

21 Chevron Chemical Company. 1972. Orthene - and the metabolite - Ortho 9006. Residue analysis by thermionic gas chromatography. Method RM-12A.

Leary, J.B. 1971. Addendum to RM-12A - Extraction procedure for soil.

22 Chevron Chemical Company. 1968. Monitor residue analysis by thermionic gas chromatography. Method RM-10.

CASE GS0043 METHAMIDOPHOS STUDY 1 PM 04/16/81

CHEM 101201 Methamidophos

BRANCH EFB DISC 30 TOPIC 05101505 GUIDELINE 40 CFR 163.62-7b/c

FORMULATION 90 = FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00014039 CONTENT CAT 01

Magee, P.S. (1966) Hydrolysis of Monitor Insecticide. (Unpublished study received Mar 5, 1970 under 0F0956; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:093263-C)

SUBST. CLASS = S.

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

REVIEWED BY: W. Chou and R. Hebert
TITLE: Staff Scientists
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Chou Richard L Hebert DATE: Sept. 28, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

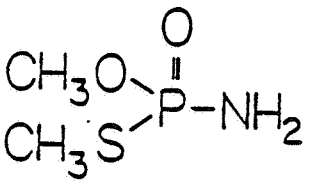
Degradation - Hydrolysis

1. This study is considered to be scientifically invalid because the tested solutions were not maintained in the dark and the starting material was only ~70% pure. However, this study contains valid data on degradation products of methamidophos.

2. The following compounds were identified as degradation products of methamidophos: methanol, methyl mercaptan, O-methyl phosphoric acid, S-methyl phosphorothioate, and ammonia. Due to the deficiencies in the protocols of the study, the mechanisms by which these compounds originated cannot be determined.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Hydrolysis of methamidophos (Chevron Chemical Co.; technical) at 20% (by weight) in 10% NaOH, 5% Na_2CO_3, 10% HCl, water (pH 4-5), and phosphate buffer (pH 7) at 80 C was studied. Hydrolysis was also studied in aqueous methamidophos solutions (20% by weight) refluxed at 80 C. Hydrolyzed solutions were examined by nuclear magnetic resonance (NMR) spectrometry. A freshly prepared water solution of methamidophos was used as a reference. Preliminary experiments showed that water was a suitable solvent. An unidentified impurity was found by NMR in the reference standard, but its presence did not interfere with the study.

REPORTED RESULTS:

After 1 hour, all methamidophos was degraded in 10% NaOH. The NMR spectrum showed two new CH_3OP and CH_3SP doublets, both upfield from those of the reference sample. The intensity of the CH_3OP doublet was over twice that of the CH_3SP doublet. Upfield from each new doublet was a singlet CH_3O and CH_3S with $CH_3S > CH_3O$ by about 4; these corresponded to methanol and methyl mercaptan as the sodium salt. In 5% Na_2CO_3, about 50% of the initial amount of methamidophos remained at 1 hour. Methanol was visible but methyl mercaptan was not detected. Methyl mercaptan probably was lost as gaseous CH_3SH. The new upfield doublets were of comparable intensity at this stage. The hydrolysis pathway in alkaline solutions was postulated (Figure 1). Hydrolysis occurs first at the $P-NH_2$ bond, followed by the cleavage of CH_3SP and CH_3OP bonds, with the rate for CH_3SP greater than that for CH_3OP.

In 10% HCl, hydrolysis was completed within 1 hour. Two new CH_3OP and CH_3SP doublets were observed (same as in alkali) on the spectrum, slightly upfield from those of the reference sample. The intensity of the CH_3OP doublet was five times greater than that of CH_3SP. Neither methanol nor methyl mercaptan was detected. Methyl mercaptan probably was lost as a gas. However, the NH_4^+ ion was visible downfield as a singlet. The hydrolysis pathway in acidic solution was postulated (Figure 1). The hydrolysis rate at the CH_3SP bond was much faster than that at CH_3OP.

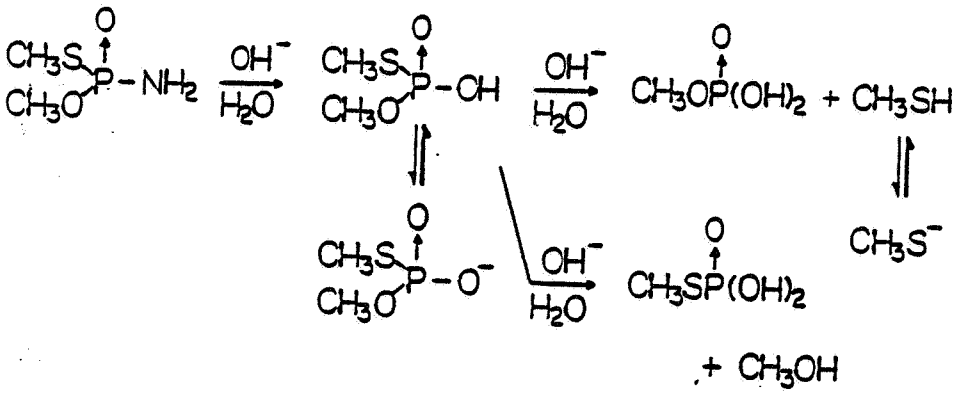
In water (pH 4-5) and phosphate buffer (pH 7), no hydrolysis occurred after 2 hours at 80 C and less than 5% of the initial amount was decomposed by 25 hours. However, this was followed by rapid degradation with about 70% of the methamidophos disappearing within 25-48 hours. This probably was due to acid hydrolysis catalyzed by the reaction products. A methamidophos solution (20%) was refluxed in water for 15.5 hours, and 80-85% of the methamidophos was hydrolyzed. The pH decreased from 4.61 to 4.35, supporting the possibility of autocatalysis. The NH_4^+ ion was not found in neutral, weakly acidic, or alkaline solutions, and it was not certain that hydrolysis under these conditions proceeded by the same mechanism as at lower pH values.

DISCUSSION:

1. The solutions of methamidophos were not kept in the dark and the starting material was technical grade, which is only ~70% pure. Therefore, no conclusions concerning mechanisms of degradation can be made.

2. Most experiments were conducted at 80 C (or higher; refluxing), which is too high to simulate natural environmental conditions.

In alkaline solutions:



In acidic solutions:

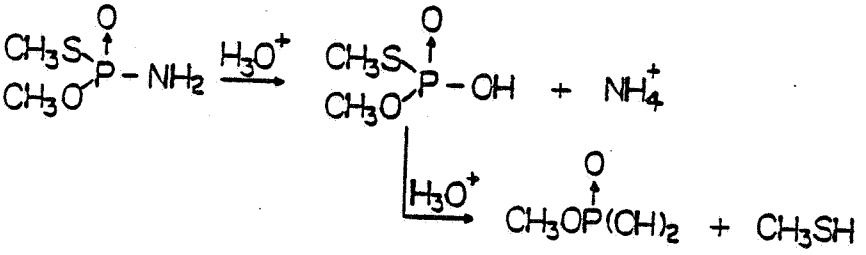


Figure 1. Postulated hydrolytic pathways for methamidophos.

(TDR03R) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 2 PM 04/16/81

CHEM 101201 Methamidophos

BRANCH EFB DISC 30 TOPIC 05101505 GUIDELINE 40 CFR 163.62-7b/c

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00014078 CONTENT CAT 01

Leary, J.B. (1968) Rates of Hydrolysis of Monitor Insecticide in Aqueous Solutions. (Unpublished study received Mar 5, 1970 under 0F0956; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:093264-AQ)

SUBST. CLASS = S.

DIRECT RVW TIME = 5½ (MH) START-DATE END DATE

REVIEWED BY: W. Chou and R. Hebert
TITLE: Staff Scientists
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Chou, Richard L Hebert DATE: Sept. 29, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

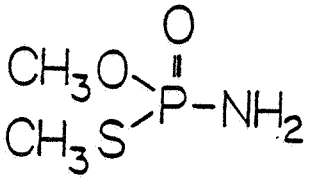
Degradation - Hydrolysis

This study is scientifically invalid because test solutions were not maintained in the dark.

8

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Ammonium acetate buffered solutions at pH 2-10 and an ammonium formate buffered solution (pH 1.5) containing methamidophos (Monitor, Chevron Chemical Co; purity unspecified) at 5 ppm were prepared and incubated at 25 or 37 C. Aliquots were taken at various time intervals and evaporated to dryness on a rotary vacuum evaporator using a cold water bath. The residue was then dissolved in methoxy ethanol and analyzed by gas-liquid chromatography, using Method RM-10 (Study 22, 00014085).

REPORTED RESULTS:

Methamidophos was completely stable at 37 C and pH 3-8 as well as at 25 C and pH 7.

At 37 C and pH 1.5, 2, and 9, methamidophos half-lives were 0.7, 5.6, and 1.5 days, respectively. At 25 C and pH 9, the half-life was 2.5 days.

DISCUSSION:

1. It was not stated if the samples were sterile and maintained in the dark. It is uncertain whether light and/or microbes had any effect on the degradation observed.

2. Degradation products were not identified.

(TDR03B) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 3 PM 02/04/81

CHEM 101201

BRANCH EFB DISC 30 TOPIC 05101505 GUIDELINE 40 CFR 163.62-7b/c

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 00014986 CONTENT CAT 01

Crossley, J. (1972) Hydrolysis of Orthene, (Unpublished study received Feb 23, 1972 under 2G1248; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:091774-T)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCBP-05-05

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

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

SIGNATURE: W. Chou DATE: Sept. 29, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

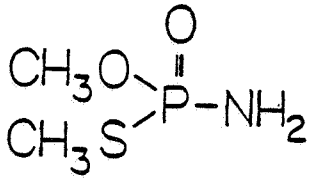
CONCLUSION:

Degradation - Hydrolysis

This study is scientifically invalid because test solutions were not maintained in the dark.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Buffered aqueous solutions (pH 3, 5, 7, and 9) containing methamidophos (Ortho 9006, Chevron Chemical Co.; analytical grade with a purity of 97.6%) at 3,000-4,000 ppm were incubated at 21 and 40 C. Aliquots were taken at 0, 4, 7, 19, and 27 days, diluted in acetone, and analyzed by gas-liquid chromatography (GLC) according to Method RM-12A (reviewed in Study 21, 00014980).

REPORTED RESULTS:

The hydrolysis data and hydrolytic half-lives are presented in Table 1. The kinetics of hydrolysis were pseudo-first-order, showing a straight line for the log percent of undegraded methamidophos versus time. Data indicate that the hydrolysis rate increased with increasing temperature. Methamidophos was relatively stable at 21 C from pH 5 to 7.

DISCUSSION:

1. It was not stated that all solutions were sterile and maintained in the dark; therefore, the degradation mechanisms cannot be determined.

2. Degradation products were not sought.

11

Table 1. Hydrolysis of methamidophos.

Temperature (C)	pH	Percent of applied methamidophos					Half-life (days)
		0 days	4 days	7 days	19 days	27 days	
21	3	100	87	88	51	45	22
	5	100	104	97	90	86	108
	7	100	91	90	75	64	44
	9	100	67	44	21	12	9
40	3	100	59	45	20	9	8
	5	100	112	85	78	49	45
	7	100	104	50	28	16	10
	9	100	16	7	3	0	5

(TDR03R) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 4 PM 04/16/81

CHEM 101201 Methamidophos

BRANCH EFB DISC 30 TOPIC 05101505 GUIDELINE 40 CFR 163.62-7b/c

FORMULATION 90 = FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00014111 CONTENT CAT 01

Leary, J.B. (1968) Photodecomposition of Monitor Insecticide in Solution. (Unpublished study received Jan 9, 1979 under 239-2404; submitted by Chevron Chemical Co., Richmond, Calif.; CDL: 236718-A)

SUBST. CLASS = S.

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

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

SIGNATURE: W. Chou DATE: Sept. 30, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

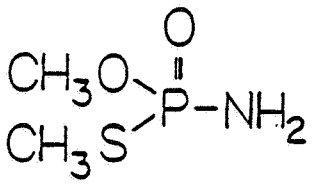
CONCLUSION:

Degradation - Photodegradation in Water

This study is scientifically invalid because a dark control was not used and the samples were not sterilized.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Buffered aqueous solutions at pH 7 containing methamidophos (Monitor, Chevron Chemical Co.; formulation and purity unspecified) at 5 ppm were prepared in duplicate quartz test tubes and exposed to a Honovia germicidal lamp emitting light predominately at 254 nm or a General Electric 15-watt germicidal lamp emitting light predominately at 366 nm. The irradiated solutions were incubated at 28 C. Aliquots were removed at various time intervals, evaporated to dryness on a rotary vacuum evaporator, dissolved in methoxyethanol, and analyzed by gas-liquid chromatography using method RM-10 (Study 22, 00014085). A similar study was carried out using ethylene glycol as the solvent instead of water, and a germicidal lamp emitting light mainly at 254 nm.

REPORTED RESULTS:

Half-lives of 3 and 5 days were obtained in aqueous solutions exposed to light at 254 and 366 nm, respectively. In irradiated ethylene glycol, only 10% degradation occurred after 14 days.

DISCUSSION:

1. Although no dark control was included, it was stated that a previous study showed that methamidophos was stable to hydrolysis in neutral aqueous solutions. However, Crossley (Study 2, 00014986) found that methamidophos was degraded in solutions at pH 7. It was not stated that the test solutions were sterilized. Although germicidal lamps were used, the solutions were not assayed for microbial activity. Therefore, microbial degradation of methamidophos may have occurred. For the above reasons, degradation mechanisms cannot be determined.

2. No attempt was made to isolate and identify degradation products.

CASE GS0043 METHAMIDOPHOS STUDY 5 PM 04/16/81

CHEM 101201 Methamidophos

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 00014076 CONTENT CAT 01

Leary, J.B.; Tutass, H.O. (1968) Degradation of Monitor Insecticide in Soil. (Unpublished study received Mar 5, 1970 under 0F0956; submitted by Chevron Chemical Co., Richmond, Calif.; CDL: 093264-AN)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -30-05052010 EFB -30-05052005

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

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

SIGNATURE: Richard L Hebert DATE: Oct. 7, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. Methamidophos is rapidly metabolized in soil. Under aerobic conditions at 21 C, the half-lives of methamidophos were 2-6 days in silt, loam, and sandy soils. [S-methyl-^{14}C]Methamidophos was degraded to O,S-dimethyl phosphorothioate and an unidentified product, and metabolized to radiolabeled amino acids and carbohydrates.

Metabolism - Anaerobic Soil

1. This portion of the study is scientifically valid.

2. When [S-methyl-^{14}C]methamidophos degradation was studied, 8% of the applied ^{14}C had dissipated after 3 days under anaerobic conditions at 37 C.

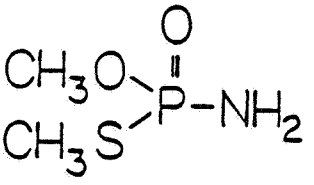
Microbiological - Effects of Microbes on Pesticides

1. This portion of the study is scientifically valid.

2. More than 90% and ~10% of the ^{14}C from [S-methyl-^{14}C]methamidophos dissipated from nonsterile and sterile soils, respectively; indicating that microorganisms metabolize methamidophos.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Methamidophos metabolism was examined in three types of soil: silt (Iowa), loam (New Jersey), and sandy (Florida). The soils were treated with methamidophos (Monitor, Chevron Chemical Co., unspecified purity) at 1 ppm, and samples were incubated in capped vials at 21 C. Duplicate samples removed at various times were Soxhlet extracted with acetone for 2 hours. The extracts were evaporated and the residues were dissolved in methoxyethanol for analysis by gas-liquid chromatography using Method RM-10 (Study 22, 00014085).

Two 10-g samples of Iowa silt soil in flasks were treated with [S-methyl-^{14}C]methamidophos at 0.115 ppm. One sample was incubated for 64 hours at 21 C, and the other at 37 C. The samples were then extracted as described above and analyzed according to Tutass (Metabolism of Monitor insecticide in plants, File 721.2, Oct. 24, 1968). The analysis consisted of separation of the extracts into petroleum ether, cation exchangeable, anion exchangeable, and neutral fractions. Radioautograms of fraction samples were also obtained. The extracted soil was combusted and analyzed by liquid scintillation counting (LSC) according to Tutass (reference cited above).

In a third experiment, 20-g samples of Iowa silt soil were treated with [S-methyl-^{14}C]methamidophos at 0.221 ppm. The soil was placed in a flask connected to a source of air and a CO_2 scrubber system consisting of three traps connected in series. At 24, 48, and 72 hours after treatment, the scrubbers were changed and assayed immediately by LSC. Some soil samples were sterilized by autoclaving at 15 psi for 1 hour. Anaerobic conditions were established by purging one sample with nitrogen 1 hour prior to and continuously for 3 days after treatment. At the end of the experiment (7 days), aliquots of all soil samples were combusted and analyzed by LSC.

16

REPORTED RESULTS:

The half-lives of methamidophos in the silt, loam, and sandy soils were 1.9, 4.8, and 6.1 days, respectively. ←

In the silt soil at 21 C, 40 and 30% of the applied radioactivity were extractable and nonextractable, respectively. The remainder was not accounted for. The respective values at 37 C were 15 and 23%. The petroleum ether fraction contained methamidophos and O,S-dimethyl phosphorothioate (DMPT). The cation exchangeable fraction contained four substances, none of which were methamidophos or DMPT. Ninhydrin sprays of the thin-layer chromatography plates indicated that the compounds were amino acids. The anion exchangeable fraction contained methamidophos, DMPT, and an unidentified product. The neutral fraction contained a few minor radiolabeled compounds shown to be carbohydrates through the use of detection sprays.

About 10% of the applied ^{14}C dissipated after 1 week in sterile soil, versus >90% after 1 week in nonsterile soil.

The differences between aerobic and anaerobic soil degradation are shown in Table 1. Only 8% of the applied ^{14}C was volatilized after 72 hours under anaerobic conditions, versus 70% under aerobic conditions (42% in 24 hours).

DISCUSSION:

1. The incubation temperature for the third experiment was not stated. In this experiment, 30% of the applied ^{14}C remained in the soil after 72 hours. In the second experiment, 70 and 38% remained after 64 hours at 21 and 37 C, respectively. Therefore, the incubation temperature for the third experiment must have been at, or near, 37 C.

2. The identity of the volatilized ^{14}C was presumed to be $^{14}CO_2$, but this was not proven. However, the differences seen between sterile and nonsterile samples, and aerobic and anaerobic samples, clearly demonstrate that methamidophos is rapidly attacked by microorganisms. Furthermore, the detection of radiolabeled amino acids and carbohydrates shows that microorganisms metabolize methamidophos.

3. Although recovery levels for fortified samples were not presented, the data show that >90% recovery occurred for the experimental samples taken immediately after treatment.

Table 1. Distribution of ^{14}C in soil incubated aerobically and anaerobically following treatment with [S-methyl-^{14}C]methamidophos at 0.221 ppm.

Incubation condition[a]	Percent of applied ^{14}C in fraction				
		Acetone extractable			
	Volatilized[b]	Dialyzable	Nondialyzable	Unextractable	Total
Aerobic	69.6	15.7	13.4	--[c]	98.7
Anaerobic	7.6	12.1	43.8	28.7	92.2

[a]For 3 days at 37 C.

[b]Captured in scrubber system.

[c]Data not reported.

CASE GS0043 METHAMIDOPHOS STUDY 6 PM 02/04/81

CHEM 101201

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

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 00014991 CONTENT CAT 01

Tucker, B.V. (1972) Orthene Soil Metabolism--Laboratory Studies. (Unpublished study including supplement, received Feb 23, 1972 under 2G1248; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:091774-Z)

SUBST. CLASS = S.

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: R. Hebert
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500
SIGNATURE: Richard L Hebert DATE: Oct. 7, 1981

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

CONCLUSIONS:

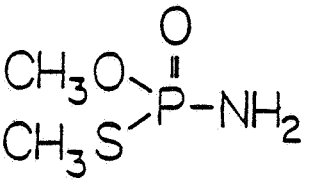
Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Methamidophos had a half-life of about 10-12 days in a sandy loam soil at 24 C.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

The degradation of methamidophos was studied in Hanford loamy sand (sand, 79%; silt, 16%; clay, 5%; organic matter, 0.92%; and pH 5.6) obtained from California. The soil was sieved (unspecified mesh) and the moisture content was determined. Ten-gram samples in glass vials were treated with 200 µg methamidophos (Ortho 9006, unspecified purity; Chevron Chemical Co.) in water; yielding a final concentration of 20 ppm. The moisture content was adjusted to 5 or 15%, and the vials were capped and incubated at 24 C. Samples were removed at various intervals during 35 days and extracted with methanol. The extracts were filtered and evaporated, and the residues were analyzed by gas chromatography using Method RM-12A (Study 21, 00014980). Recovery values ranged from 75 to 90%.

REPORTED RESULTS:

The half-lives for methamidophos were 9.5 and 12 days at soil moisture levels of 15 and 5%, respectively, according to results reported in the text. The table and graph, as well as the summary in the text, showed reverse results.

DISCUSSION:

1. The data for methamidophos appear in a supplement, authored by J. Leary, attached to the main article.

2. The reporting of data was contradictory. In three instances, the half-life values at 5 and 15% moisture contents were reported as 9.5 and 12 days, respectively. In one instance, the values were reversed.

3. It was not stated whether the glass vials were capped loosely or tightly. Therefore, it is uncertain whether conditions remained aerobic throughout the entire 35-day period.

CASE GS0043 METHAMIDOPHOS STUDY 7 PM 04/16/81

CHEM 101201 Methamidophos

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

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 05017741 CONTENT CAT 01

Zidan, Z.H.; Ramadan, E.M. (1976) Degradation of some organophosphorus insecticides by fungi. Egyptian Journal of Microbiology 11(1/2):93-98.

SUBST. CLASS = S.

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

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

SIGNATURE: Richard L Hebert DATE: July 31, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Microbiological - Effects of Microbes on Pesticides

This portion of the study is scientifically invalid because it cannot be determined if proper controls were used.

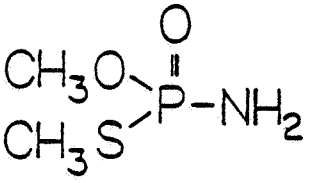
Microbiological - Effects of Pesticides on Microbes

1. The in vitro portion of the study is scientifically valid, but the soil experiments are invalid because application rates were not provided and control data were not obtained.

2. Methamidophos at 200-6,400 ppm and 200-400 ppm did not markedly affect the growth, in culture, of Aspergillus sp. and Penicillium sp., respectively. Growth of Penicillium sp. was noticeably inhibited by methamidophos at ≥800 ppm. Quantitative growth inhibition data were not obtained.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Unspecified soils were treated with different organophosphate insecticides, including methamidophos (Tamaron; unspecified source and purity), at unspecified concentrations. After an unspecified time, the fungi in the soils were isolated on Martin's Rose Bengal medium. The isolates were purified and identified.

The ability of two isolates, Aspergillus sp. and Penicillium sp., to grow in the presence of methamidophos was tested. The growth medium consisted of malt extract, peptone, dextrose, and methamidophos at 200, 400, 800, 1,600, 3,200, and 6,400 ppm. The inoculum preparation was not described. Growth was determined after 4 days' incubation at 25 C. At this time, an aliquot was extracted with chloroform. The extract was concentrated and the residue was analyzed colorimetrically (Getz and Watts. 1964. J.A.O.A.C. 47:1094).

REPORTED RESULTS:

A total of 21 fungal isolates were obtained from methamidophos-treated soils: 8 Aspergillus sp., 6 Penicillium sp., 2 Rhizopus sp., 2 Alternaria sp., 1 Fusarium sp., and 2 unknowns.

Aspergillus sp. grew well in the presence of methamidophos at 200-6,400 ppm. Penicillium sp. grew well in the presence of methamidophos at 200 and 400 ppm, but its growth was inhibited at 800-6,400 ppm.

About 60% of the methamidophos was degraded in Penicillium sp. cultures to which it was applied at 200 ppm. The amount of degradation decreased slightly as the initial concentration increased. Thus, at 6,400 ppm, about 40% was degraded. Similar results were obtained in Aspergillus sp. cultures, with degradation rates ranging from 50 to 25% (at from 200 to 6,400 ppm, respectively).

DISCUSSION:

1. The data from the soil experiments are of no use because application rates were not provided and control soil data were not obtained.

2. The data for the growth experiments were reported as good, slight, or no growth. Therefore, no quantitative conclusions can be derived from these experiments.

3. The protocols of the degradation experiments were not reported clearly. It was stated that the rate of degradation as influenced by the fungus was referenced to the standard sample. Although it was not stated, the standard samples should have been uninoculated sterile broth containing methamidophos and incubated for 4 days. However, the term "standard sample" may have referred to a solution of methamidophos that was assayed immediately. Also, there was no mention of the use of untreated control cultures to determine the extent of possible interference with the colorimetric method by fungal products. These data must be considered invalid due to the uncertainties and ambiguities regarding the protocols used.

CASE GS0043 METHAMIDOPHOS STUDY 8 PM 04/16/81

CHEM 101201 Methamidophos

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

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 05019842 CONTENT CAT 01

Ramadan, E.M.; Zidan, Z.H. (1977) Influence of certain organophosphorus insecticides on soil microflora: 1--Total microbial flora, Actinomycetes, fungi, yeasts and cellulose decomposers (sic). Annals of Agricultural Science 20(2):57-63.

FICHE/MASTER ID 05019841 CONTENT CAT 01

Ramadan, E.M.; Zidan, Z.H. (1977) Influence of certain organophosphorus insecticides on soil microflora: 2--Non symbiotic nitrogen fixers and nitrifying bacteria. Annals of Agricultural Science 20(2):65-71.

SUBST. CLASS = S.

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

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

SIGNATURE: Richard L Hebert DATE: Oct. 21, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

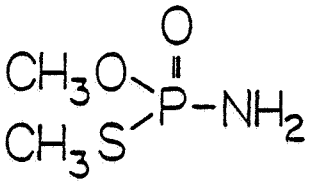
Microbiological - Effects of Pesticides on Microbes

1. This study is scientifically valid.

2. Methamidophos soil treatment under actual use conditions caused a temporary inhibition of growth of most types of microbes in soil. Total microbial flora, fungi, aerobic cellulose decomposers, and aerobic and anaerobic nitrogen fixers were inhibited for ≤2 weeks after treatment with methamidophos. Nitrifying bacteria were inhibited for at least 4 weeks. The populations subsequently recovered and generally reached levels higher than those in untreated soil. Actinomycetes were slightly inhibited for 3 months after treatment. Anaerobic cellulose decomposers were markedly stimulated by methamidophos treatment.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

A plot of soil (unspecified type) in Egypt was planted with clover. Two weeks later, it was sprayed with methamidophos (Tamaron; formulation, source, and purity not specified) at 1.25 liters/200 liters/feddan (1.04 A). The amount of active ingredient per acre was not specified. Untreated soil served as a control. Soil samples were taken 1, 2, 3, 4, 8, and 12 weeks later for microbial analyses. Samples were taken from four treated and four untreated subplots. The following groups of microbes were isolated on media recommended in Allen (1961. Experiments on soil microbiology. Burgess Publishing Co.): actinomycetes, Jensen's medium; aerobic cellulose decomposers, Dubo's medium; anaerobic cellulose decomposers, Omeliansky's medium; aerboic nitrogen fixers, base medium 77; anaerobic nitrogen fixers, modified Winogradsky's medium; and nitrifiers, Stephenson's medium. Total aerobic microbial flora was determined on soil extract agar, and yeasts on malt extract agar. Most probable numbers were determined for dilution methods, and plate counts for the others (total flora, actinomycetes, fungi, and yeasts).

REPORTED RESULTS:

Methamidophos caused deleterious effects in total microbial flora during the first 2 weeks after treatment. Recovery occurred after 3 weeks, when the population was higher than in the control soil and remained so for the next 2 months.

Actinomycete levels were about 10-30% lower in treated soil than in control soil during the 12-week study period.

Methamidophos treatment caused a 50% decrease in fungal populations (mycelial and yeastlike) during the 1st week after treatment. Population levels in treated soil increased to above control levels by the 2nd week, and remained higher throughout the study.

Levels of aerobic cellulose decomposers were reduced about 75% during the 1st week after treatment. The population in treated soil returned to control levels by the 3rd week, and was higher than the control population for the next 2 months.

Methamidophos significantly stimulated anaerobic cellulose decomposers. The population in control soil remained relatively constant throughout the 12-week study period, whereas the population in treated soil increased three- to fourfold.

The population of aerobic nitrogen fixers was reduced about 20% in treated soil as compared with control soil during the first 2 weeks. The population then increased to levels higher than those in control soil after 3 weeks, and the levels remained higher for the next 2 months.

The population of nitrifying bacteria in treated soil was about 50% lower than that in control soil for the first 4 weeks. The population in treated soil recovered to normal levels after 8 weeks.

DISCUSSION:

1. Results were presented for fungi and yeasts. Presumably this means mycelial and yeastlike fungi. Protocols were given for yeast isolation, but not for isolation of mycelial fungi. As all other methods used were standard and adequate, the omission of details for mycelial fungi is not a good reason for invalidating these data.

2. A treatment rate was provided, but the formulation was not specified. Tamaron is a tradename for methamidophos products produced overseas by Bayer Leverkusen. The formulation was diluted and sprayed on clover.

3. Methamidophos exerted an inhibitory effect on all groups of microbes except anaerobic cellulose decomposers. The effect was only temporary and lasted ≤2 weeks, with the exception of nitrifying bacteria, which were inhibited for at least 4 weeks. In most cases, the populations recovered to levels higher than those in untreated soil. Anaerobic cellulose decomposers were also stimulated by methamidophos. Therefore, it would appear that microorganisms are capable of metabolizing methamidophos residues in soil.

CASE GS0043 METHAMIDOPHOS STUDY 9 PM 04/16/81

CHEM 101201 Methamidophos

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

FORMULATION 90 = FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00014082 CONTENT CAT 01

Tutass, H.O. (1968) Leaching of Monitor Insecticide in Soils. (Unpublished study received Mar 5, 1970 under 0F0956; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:093264-AV)

SUBST. CLASS = S.

DIRECT RVW TIME = 12 (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: Aug. 4, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

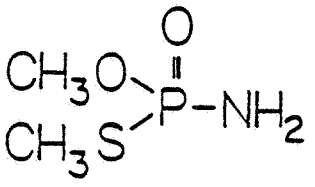
CONCLUSION:

Mobility - Leaching

This study is scientifically invalid because the analytical methods used to measure methamidophos in soil were inadequate..

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Loam, muck, and sandy loam soils were sieved to <6 mesh and placed in aluminum columns (3.5 cm diameter and 30 cm length). The soil in the columns was compacted by dropping the columns on a cement floor five times from a height of 25 cm (final height of soil columns was 21 cm). After the soil columns were moistened to field capacity, the soil was treated with 590 µg of methamidophos (Monitor, Chevron Chemical Corp.; formulation and purity not specified) in 10 ml of distilled water. The columns were then eluted with 160 ml of water (equivalent to 6 acre-inches of water).

The leachate was collected during the course of the experiment. At the conclusion of the experiment the soil was removed from the columns and divided into four equal segments. The water was removed from the samples by using a rotary vacuum evaporator. The dried soil was Soxhlet extracted with acetone for 1.5 hours. The acetone extract was evaporated and the residue was dissolved in ethyl ether. The ethyl ether was then analyzed by gas-liquid chromatography using Chevron method RM-10 (Study 22, 00014085).

REPORTED RESULTS:

More than half of the methamidophos recovered was present in the bottom 5-cm soil segment and in the leachate (Table 1). Between 73 and 91% of the methamidophos applied was unaccounted for.

DISCUSSION:

1. A material balance was not provided. Only 9-27% of the methamidophos applied was recovered. The remaining methamidohpos was either adsorbed to the soil, degraded, or volatilized. However, the experimental design was not adequate to determine the reasons for the poor recovery methamidophos. In addition, the data from the duplicate columns were not similar.

2. Recovery rates for the extraction procedure (Soxhlet extraction with acetone for 1.5 hours) may not have been adequate in view of the poor recoveries of methamidophos from the soil columns.

3. Soil characteristics such as pH, CEC, and percent sand, silt, and clay were not provided.

Table 1. Methamidophos levels in soil columns treated with 590 µg of methamidophos and eluted with the equivalent of 6 acre-inches of water.

Soil	Sample depth (cm)	Methamidophos levels (µg)		Recovery[a] (% of applied)	
		Column A	Column B	Column A	Column B
Moorestown loam	0-5	0	2.41	0	0.4
	5-10	0	3.04	0	0.5
	10-15	0	5.03	0	0.9
	15-20	9.34	18.12	1.6	3.1
	Eluate	64.96	34.26	11.0	5.8
Mount Holly muck	0-5	0	4.29	0	0.7
	5-10	0.09	6.70	<0.1	1.1
	10-15	3.69	8.82	0.6	1.5
	15-20	32.27	30.90	5.5	5.2
	Eluate	24.28	0	4.1	0
Fresno sandy loam	0-5	2.09	9.45	0.4	1.6
	5-10	3.93	21.79	0.7	3.7
	10-15	3.79	35.20	0.6	6.0
	15-20	11.11	91.57	1.9	15.5
	Eluate	119.02	0	20.2	0

[a]Calculated by reviewer.

30

(TDR03R) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 10 PM 04/16/81

CHEM 101201 Methamidophos

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

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00029887 CONTENT CAT 01

Thornton, J.S.; Hurley, J.B.; Obrist, J.J. (1976) Soil Thin-Layer Mobility of Twenty Four Pesticides [sic] Chemicals: Report No. 51016. (Unpublished study received Jan. 28, 1980 under 5F1547; submitted by Mobay Chemical Corp., Pittsburgh, Pa.; CDL: 099216-I)

SUBST. CLASS = S.

DIRECT RVW TIME = 8½ (MH) START-DATE /END DATE

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

SIGNATURE: Daniel Harper DATE: July 31, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Mobility - Leaching

1. This study is scientifically valid.

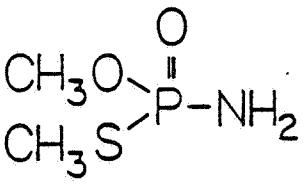
2. Methamidophos was very mobile in sand, sandy loam, sandy clay loam, silt loam, and silty clay soils. The R_f values on soil thin-layer chromatography plates were 0.91-0.98.

3. This study satisfies part of the data requirements in Section 163.163-1 of EPA's Guidelines for Registering Pesticides (1981) by providing information on the rapid leaching of methamidophos in sand, sandy loam, sandy clay loam, silt loam, and silty clay soils.

31

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Six soils (Table 1) were air dried and sieved to <250 or <420 µm. The dried soil was mixed with water to form a slurry and spread evenly in a thin layer on glass thin-layer chromatography (TLC) plates. The soil TLC plates were air dried for 24 hours. [^{14}C]methamidophos (Monitor, Mobay Chemical Corp.; unspecified purity and solvent) was spotted on triplicate soil TLC plates. The plates were developed in distilled water, air dried, and exposed to X-ray film for 5 days.

REPORTED RESULTS:

The average R_f values for methamidophos in sand, sandy loam, sandy clay loam, silt loam, and silty clay soils were 0.97, 0.97, 0.98, 0.95, and 0.91-0.92, respectively. The range of replicate R_f values was never greater than ±0.05.

DISCUSSION:

Acceptable standard procedures were employed.

Table 1. Characteristics of soils used in methamidophos soil TLC mobility studies.

Texture	Sand (%)	Silt (%)	Clay (%)	Organic matter (%)	pH	Kd
Sand	92	1	7	0.8	5.9	.97
Sandy loam	74	14	13	2.8	6.6	.97
Sandy clay loam	56	21	23	0.6	5.5	.98
Silt loam	18	57	25	5.1	7.9	.95
Silty clay	4	53	43.	2.1	6.7	.91
Silty clay	0	41	59	0.5	6.0	.92

CASE GS00431 METHAMIDOPHOS STUDY 11 PM 02/04/81

CHEM 101201

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163,62-9b/c/d

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 00015213 CONTENT CAT 01

Tucker, B.V. (1972) Leachability of Orthene Residues in Soil 150 Days after Orthene Treatment--Greenhouse Test. (Unpublished study received Mar 27, 1973 under 239-EX-60; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:223490-Y)

SUBST. CLASS = S.

DIRECT RVW TIME = 8½ (MH) START-DATE END DATE

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

SIGNATURE: D. Harper DATE: Sept. 2, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

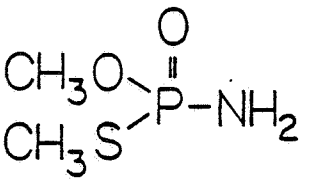
CONCLUSION:

Mobility - Leaching

This study is scientifically invalid because the protocols used were not sufficient to determine the leachability of methamidophos.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Sandy loam soil (78% sand, 12% silt, 10% clay, and pH 6.2) was placed in glass columns (25 x 400 mm) to a depth of 4 inches. The columns were treated with 2.5 µg of methamidophos (Ortho 9006, Chevron Chemical Co., formulation and purity not specified). One column was eluted with the equivalent of 10 acre-inches of water (120 ml) and the other column was eluted with 250 ml of water:methanol:ethyl acetate (1:5:17). Methamidophos levels were determined in the leachate samples by Chevron Method RM-12A-2.

REPORTED RESULTS:

The water and water:methanol:ethyl acetate leachates contained 70 and 64%, respectively, of the applied methamidophos.

DISCUSSION:

1. The soil column was only 4 inches high and was eluted with the equivalent of only 10 acre-inches of water. Therefore, it cannot be determined whether methamidophos will leach to a depth that will cause groundwater contamination.

2. The soil columns were not analyzed for methamidophos or its degradation products, and recovery levels were not given for the analytical method (unavailable for review) used on the leachate samples. Therefore, the measured amounts of methamidophos in the leachates may be less than the actual amounts. Also, it was not stated that the soil was compacted in columns to its apparent dense (natural) state. Water could easily trickle past particles. For these reasons, this study is considered invalid.

CASE GS0043 METHAMIDOPHOS STUDY 12 PM 02/04/81

CHEM 101201

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

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 00014992 CONTENT CAT 01

Tucker, B.V. (1972) Orthene Leaching in Soil. (Unpublished study including supplementary report, received Feb 23, 1972 under 2G1248; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:091774-AA)

SUBST. CLASS = S.

DIRECT RVW TIME = 8½ (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: Aug. 17, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Mobility - Leaching

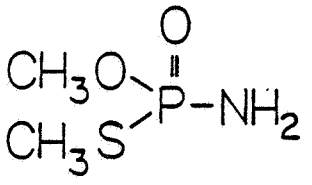
1. This study is scientifically valid.

2. Methamidophos was mobile to very mobile in loamy sand, loam, silty clay loam, and clay soils. Methamidophos was moderately mobile in sandy clay loam soil.

3. This study satisfies part of the data requirements in Section 163.163-1 of EPA's Guidelines for Registering Pesticides (1981) by providing information on the leaching of methamidophos in loamy sand, loam, silty clay loam, sandy clay loam, and clay soils.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Seven soils were sieved to <35 mesh and slurried. The soil slurries were applied to glass plates to make soil thin-layer chromatography (TLC) plates. The soil TLC plates were dried and [^{14}C]methamidophos (RE 9006, Chevron Chemical Co.; purity and solvent not specified) was spotted at the origin. The soil TLC plates were developed in water, air dried, and exposed to X-ray film for 1 week.

REPORTED RESULTS:

The R_f values for the methamidophos were 1.00, 0.88, 0.70, 0.56, 0.61, 0.66, and 0.71 in Ocoee loamy sand, Fresno loam, Norwalk silty clay loam, Mt. Holly sandy clay loam and Greenville, Clarksburg, and Kettleman City clay soils, respectively.

DISCUSSION:

1. Complete soil characteristics such as cation exchange capacity, pH, and percent sand, silt, clay, and organic matter were not provided.

2. The soils used to make the TLC plates were sieved to 35 mesh. This sieving removed all of the coarse sand from the soils, altering their texture. Since mechanical analyses were not given, the extent to which the soils were altered cannot be determined.

(TDR038) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 13 PM 02/04/81

CHEM 101201

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

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00015209 CONTENT CAT 01

Tucker, B.V. (1972) Comparison of Acephate Soil Leaching and Stability in Wet and Dry Soil. (Unpublished study received Mar 27, 1973 under 239-EX-60; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:223490-S)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -30-050520

DIRECT RVW TIME = 8½ (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: Aug. 31, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

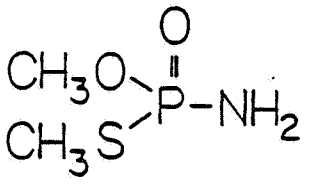
Metabolism - Aerobic Soil

This study is scientifically invalid because the extraction procedure may have caused methamidophos hydrolysis.

78

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Fresno loam and Mt. Holly sandy clay loam soils were sieved to <9 mesh. A portion of each soil was air dried, and a portion was moistened to near field capacity. Ten-gram samples of the soils were treated with 10 µg of [^{14}C]methamidophos (Ortho 9006, Chevron Chemical Co.; purity not specified). The vials containing the soil were sealed, shaken, and maintained at ambient laboratory temperature. At various time intervals duplicate soil samples were removed from the vials. The samples were moistened with 0.05 N HCl and mixed with methanol. The samples were centrifuged and the methanol was decanted. The samples were extracted two more times with methanol. The combined methanol extracts were evaporated to dryness, cleaned up, and analyzed by gas-liquid chromatography.

REPORTED RESULTS:

The rate of methamidophos degradation was faster in wet soil than in dry soil. The half-lives of methamidophos in wet (12.9% moisture) and dry (1.6% moisture) loam soil were 0.5 and 1.5 days, respectively. In the sandy clay loam soil the half-lives of methamidophos were 0.25 and 0.66 days in wet (20.3% moisture) and dry (6.5% moisture) soils, respectively.

DISCUSSION:

Methamidophos may have been hydrolyzed as a result of adding 0.05 N HCl to the soil prior to extraction with methanol. Therefore, this study is considered invalid.

CASE GS0043 METHAMIDOPHOS STUDY 14 PM 02/04/81

CHEM 101201

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

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 05017226 CONTENT CAT 01

Focht, D.D.; Joseph, H. (1974) Microbial activity in soils treated with acephate and Monitor. Journal of Environmental Quality 3(4):327-328.

FICHE/MASTER ID 00015233 CONTENT CAT 01

Focht, D.D.; Joseph, H.A. (1969?) Microbial Activity in Soils Treated with Acephate and Its Major Degradation Product. (Unpublished study received Mar 27, 1973 under 239-EX-60; prepared by Univ. of California--Riverside, Dept. of Soil Science and Agricultural Engineering, submitted by Chevron Chemical Co., Richmond, Calif.; CDL:223489-Q)

SUBST. CLASS = S.

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

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

SIGNATURE: Richard L Hebert DATE: Oct. 22, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

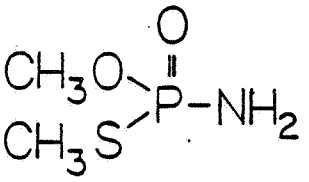
Microbiological - Effects of Pesticides on Microbes

1. This study is scientifically valid.

2. Methamidophos, at 20 ppm, did not exert major effects on populations of bacteria, actinomycetes, and fungi in soil, or on ammonification, nitrification, respiration, and sulfur oxidation in soil.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

These two reports contain identical data for the same study. Samples of the soils shown in Table 1 were sieved to <2 mm. The soils were divided into 2-kg portions, placed in beakers, and moistened to field capacity. Each was treated with methamidophos (70% technical, Chevron Chemical Co.) at 20 ppm. Untreated soil served as a control. The beakers were covered with foil and incubated at 22 ± 3 C. The soil was re-treated 15 and 36 days after the first treatment. Samples (60 g) were taken at several intervals from 0 to 50 days after the first treatment. Samples were frozen until analysis for the following: bacterial, actinomycete, and fungal population counts; ammonium, nitrate, and sulfate contents; and ammonification, nitrification, sulfur oxidation, and oxygen uptake capacities.

Dilution plate counts were performed in duplicate for each sample. Nutrient agar (NA) was used for bacteria. Actinomycetes were selected on NA plus antibiotics (Ab). Fungi were isolated on Ab agar as well as on potato dextrose-Rose Bengal (PD-RB) agar adjusted to pH 3.8 with tartaric acid. NA plates having <150 bacterial colonies from control soil samples (unspecified time) were replica plated onto NA plates with and without methamidophos (10 ppm in 00015233 and 20 ppm in 05017226).

Ammonium and nitrate (forms not specified) were extracted with 2 N KCl, and measured spectrophotometrically by Nessler's and Bray's methods, respectively. Sulfate (form not specified) was extracted with 0.25 N acetic acid and measured turbidimetrically by precipitation with $BaCl_2$.

All biochemical parameters were measured at 28 C. Oxygen uptake was determined within a 24-hour period by standard Warburg manometric techniques. Ammonification was determined by measuring the ammonia liberated after 24 hours of incubation of a 2-g soil subsample with 1 ml of 0.1% nutrient broth. Nitrification rates were determined by incubating 2 g of soil with 1.4 ml of 100 ppm N as $(NH_4)_2SO_4$ and measuring nitrate levels after 5 days. Sulfur oxidation was measured by incubating 2 g of soil with 200 ppm S as $Na_2S_2O_3$ and measuring

sulfate levels after 4 days. Ammonification, nitrification, and sulfur oxidation rates were corrected for ammonium, nitrate, and sulfate levels present at the beginning of the incubation periods.

REPORTED RESULTS:

No significant temporal trend was noted for any parameter measured. Data were then converted to mean values for the entire 50-day incubation period. In 05017226, but not in 00015233, it was stated that the mean numbers of fungi isolated on Ab agar were significantly higher (1% probability level) for control Hanford soil than for treated Hanford soil. As the effect was not seen on PD-RB agar, it was considered inconsequential. In 00015233, but not in 05017226, it was stated that sulfate levels were significantly higher (1% probability level) in treated soils than in control soils. No significant differences were noted for the other parameters.

Replica plating of 216 colonies obtained from the three soils did not reveal any bacteria affected by methamidophos.

DISCUSSION:

1. The manner in which the data were treated is unusual because all values for a parameter were combined to obtain a mean value for the entire incubation period. When the data are closely examined, two other possible treatment effects are apparent: 1) nitrification rates in Domino soil were lower in treated soil than in control soil; however, ammonification, ammonium, and nitrate levels were not affected; 2) ammonium levels were higher in treated Hanford soil than in untreated Hanford soil; however, nitrate levels and ammonification and nitrification rates were not affected.

2. The effect of methamidophos on fungi from Hanford soil isolated on Ab agar appears to have been greatest shortly after soil treatment, with the effect dissipating after a couple of weeks. It is noteworthy that any possible treatment effect seen in one soil was not seen in other soils, and that any differences seen in one parameter did not correlate with differences in a coinciding parameter (e.g., ammonium levels and nitrification, ammonium versus nitrate levels, ammonium levels and ammonification, or nitrate levels and nitrification). Therefore, the results could be artifactual, and it can only be concluded that methamidophos exerts no major effects on the microbial populations and functions studied.

Table 1. Characteristics of soils used to determine the effects of methamidophos on microbes in soil.

Soil	Texture	Field capacity (% saturation)	Organic matter (%)	pH
Hanford	Loamy sand	18	0.92	5.6
Domino	Silt loam	25	1.69	7.6
Altamont	Clay loam[a]	27	2.93	6.3

[a]A sandy clay according to USDA classification scheme.

(TDR038) DATA EVALUATION RECORD PAGE 1 OF

CASE GR0043 METHAMIDOPHOS STUDY 15 PM 04/16/81

CHEM 101201 Methamidophos

BRANCH EFB DISC 30 TOPIC 1010

FORMULATION 01 = TECHNICAL CHEMICAL

FICHE/MASTER ID: 00014015

CITATION: Baychem Corporation. 1972. Chemagro, Division of Baychem Corporation. Residue Experiment: Report No. 31933. (Unpublished study prepared by Baychem Corp.).

FICHE/MASTER ID 00014016 CONTENT CAT 02

Baychem Corporation (1972) Chemagro, Division of Baychem Corporation, Residue Experiment: Report No. 31938. (Unpublished study received on unknown date under 0F0956; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:093266-H)

SUBST. CLASS = S.

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

REVIEWED BY: W. Chou and R. Hebert
TITLE: Staff Scientists
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Chou, Richard L Hebert DATE Oct. 30, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

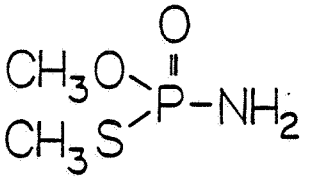
Accumulation - Laboratory Studies - Fish

1. This study is scientifically valid.

2. Bass exposed to methamidophos at 0.8-1.5 ppm did not accumulate the parent compound. The maximum bioaccumulation factor observed was 0.09.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Five 5-gallon glass vessels containing deionized water were kept at 22 C. On day 0, tank No. 1 was treated with methamidophos (Monitor, technical, Chevron Chemical Co.) at 1 ppm, and fish (2- to 3-inch large-mouth bass) were added at ≤2 g/l. On day 7, the fish were transferred to tank No. 2, which was treated with methamidophos at 1 ppm. The procedure was repeated on days 14 and 21 with tank Nos. 3 and 4. On day 28, the fish were transferred to an untreated tank. Duplicate water samples were taken from tanks on the days fish were transferred. The samples were analyzed for methamidophos by gas-liquid chromatography, as described in Chemagro Report No. 30975 (Study 16, 00014018).

REPORTED RESULTS:

The results are shown in Table 1. Very little methamidophos accumulated in the fish; the maximum bioconcentration factor was 0.09 on day 28. Depuration to nonquantifiable levels (<0.014 ppm) occurred on the 1st day of depuration.

DISCUSSION:

In most cases, the protocols used would be inadequate to determine the potential for accumulation of methamidophos in bass, but the very low bioconcentration factors observed demonstrate that methamidophos will not accumulate in bass.

Table 1. Accumulation of methamidophos in bass.

Tank No.	Days after treatment[a]	Depuration time (days)	Methamidophos concentration (ppm)	
			Water[b]	Fish
--	Control	--	--	0.014
1	0	--	0.94	
1	7	--	0.96	0.049
2	0	--	0.91	
2	7	--	1.22	0.050
3	0	--	1.46	
3	7	--	1.21	0.048
4	0	--	1.35	
4	7	--	0.83	0.072
5	--	1	--	<0.014
5	--	2	--	<0.014
5	--	14	--	0.014
5	--	21	--	<0.014

[a]Fish were transferred, every 7 days, to a new tank containing methamidophos at 1 ppm.

[b]Average of two samples; no data are available for the control tank, or during the depuration period.

(TDR038) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 16 PM 04/16/81

CHEM 101201 Methamidophos

BRANCH EFB DISC 30 TOPIC 1010

FORMULATION 90 = FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00014018 CONTENT CAT 06

Stanley, C.W. (1971) A Gas Chromatographic Method for the Determination of ¬(R)¤Monitor in Fish and Water: Report No. 30975. Method dated Sep 30, 1971. (Unpublished study received on unknown date under 0F0956; prepared by Baychem Corp., submitted by Chevron Chemical Co., Richmond, Calif.; CDL:093266-J)

FICHE/MASTER ID: 00014017

CITATION: Chemagro Corporation. 1971. Recovery of Monitor from bass and rainbow trout: Report No. 30,976. Dated Sept. 30, 1971. (Unpublished study prepared by Baychem Corp.).

FICHE/MASTER ID: 00014019

CITATION: Chemagro Corporation. 1971. Recovery of Monitor from bass and rainbow trout: Report No. 30,977. Dated Sept. 30, 1971. (Unpublished study prepared by Baychem Corp.).

FICHE/MASTER ID 00014014 CONTENT CAT 02

Stanley, C.W. (1971) Analysis of Bass and Water for ¬(R)¤Monitor: Report No. 30979. (Unpublished study received on unknown date under 0F0956; prepared by Baychem Corp., submitted by Chevron Chemical Co., Richmond, Calif.; CDL:093266-F)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
PRIM: RCBR-25-10171010

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

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

SIGNATURE: Richard L Hebert DATE: Oct. 29, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

47

CONCLUSIONS:

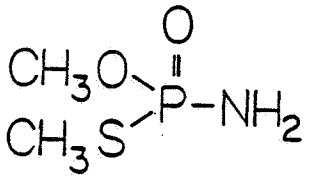
Accumulation - Laboratory Studies - Fish

1. This study is scientifically valid.

2. Methamidophos, at 0.01 ppm, had a bioaccumulation factor of less than 2 in bass on the 8th day of exposure in a static system.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Two bass fingerlings were maintained in each of three jars of water (unspecified source) treated with methamidophos (unspecified purity; Chevron Chemical Co.) at 0.01 ppm. After 8 days, both fish in each jar were removed and combined for analysis. Water samples were taken on days 0 and 8, and each day's samples were composited for analysis.

Water samples were mixed with NaCl and partitioned with acetone: chloroform. The solvent was evaporated and the residue was redissolved in acetone for analysis by gas chromatography (GC). The fish were ground up and then blended with Skellysolve B and acetonitrile separately. The extracts were filtered; the filtrates were combined and shaken. The acetonitrile was removed and evaporated. The residue was dissolved in ethyl ether for cleanup on a silica gel column. Methamidophos was eluted with acetone and analyzed by GC.

Recovery levels of 95% were obtained for bass fortified (at the extraction stage) with methamidophos at 0.1 ppm (00014017 and 00014019). There was 60% recovery from a distilled water sample spiked at 0.01 ppm (00014014).

REPORTED RESULTS:

All fish samples contained methamidophos at <0.02 ppm. The amounts of methamidophos in the water were 0.011 and 0.010 ppm on days 0 and 8, respectively (corrected for low recovery value). The pH's of the water were 8.2 and 7.6 on days 0 and 8, respectively.

DISCUSSION:

1. The data are valid, but too few samples were taken to adequately determine the potential for accumulation of methamidophos in fish.

2. These data indicate that methamidophos was relatively stable in the water used.

STUDY 17

CHEMICAL: METHAMIDOPHOS

FORMULATION: 00 - Active Ingredient

FICHE/MASTER ID: 00015242

CITATION: Tucker, B.V. 1973. Orthene and Ortho 9006 in Daphnia magna living in treated water. Unpublished study prepared by Chevron Chemical Co., Richmond, CA.

DIRECT RVW TIME = 6½ (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: Oct. 2, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

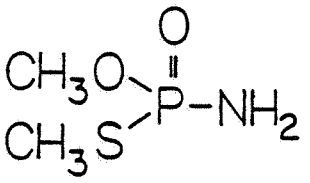
Field Accumulation - Aquatic Non-Target

1. This study is scientifically valid.

2. Methamidophos had a low potential to accumulate in Daphnia magna. When exposed to [^{14}C]methamidophos, D. magna accumulated ^{14}C residues at low levels (bioconcentration factor of 2).

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Six flasks, each containing 500 ml of aquarium water and Daphnia magna (200 adults), were used in the experiment. [S-methyl-^{14}C]-Methamidophos (Ortho 9006, Chevron Chemical Co., purity not specified) was applied at 0.1 ppm. The flasks were gently swirled to mix the solution. Three untreated flasks were used as controls. At 3 days after treatment, the D. magna were transferred to a piece of filter paper, blotted dry, weighed, and frozen. The ^{14}C activity in the D. magna was determined by combustion and liquid scintillation counting (LSC). The ^{14}C activity in the water was determined by LSC.

REPORTED RESULTS:

The water and D. magna contained ^{14}C at average levels of 0.09 and 0.21 ppm, respectively, yielding an average bioconcentration factor of 2.3.

DISCUSSION:

1. The ^{14}C levels in the water and D. magna were not characterized.

2. No attempt was made to determine whether ^{14}C levels in D. magna decrease during a depuration period.

3. Data for the control samples were not reported.

(TDR03B) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 18 PM 02/04/81

CHEM 101201

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

FORMULATION 00 = ACTIVE INGREDIENT

FICHE/MASTER ID 00014496 CONTENT CAT 01

Tucker, B.V. (1972) Residues of Orthene and Ortho 9006 in a Marine Diatom Growing in Treated Water. (Unpublished study received Aug 7, 1972 under 239-2406; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:001571-U)

SUBST. CLASS = S.

OTHER SUBJECT DESCRIPTORS
SEC: EFB -20-0515

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

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

SIGNATURE: Richard L Hebert DATE: Oct. 27, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Field Accumulation - Aquatic Non-Target

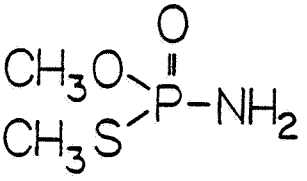
1. This study is scientifically valid.

2. Methamidophos at 1-10 ppm had little effect upon the growth of, and did not accumulate in, the marine diatom Cylindrotheca fusiformis. After 7 days of exposure, growth was inhibited by a maximum of 15% and the bio-accumulation factor was less than 2. ←

52

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

The marine diatom Cylindrotheca fusiformis was cultured in a buffered mineral salts medium (pH 8.1) in flasks on a shaker in a chamber at 50-70 C under a 12-hour light cycle. Cell suspensions for tests were homogenized (to disperse clumps) and counted by using a microscope and counting chamber. A 200-ml aliquot of growth medium was inoculated with 1-3 ml of a cell suspension containing 2 x 10^4 cells/ml, and then treated with methamidophos (Ortho 9006, Chevron Chemical Co.; purity unspecified) at 1 or 10 ppm. - The flasks were incubated in the chamber for 1 week and then analyzed. Untreated controls were also run.

Cell counts were made to determine if methamidophos had any effect on the diatom. The cells were then filtered, dried, and weighed. The average weight of five filter papers was used as a tare weight for the samples. The cells were then extracted with methanol. The extract was dried and redissolved in acetone for gas-liquid chromatography (GLC) analysis using Method RM-12A (Study 21, 00014980). The volumes of the filtrates (spent culture media) were measured and then extracted with ethyl acetate for GLC analysis. Water fortified with methamidophos at 1.25 and 11.5 ppm yielded recoveries of 106-108%. Recovery levels of 98 and 95% were obtained with diatoms fortified at 7.15 and 11.4 ppm, respectively.

REPORTED RESULTS:

Methamidophos had no effect on cell growth, and did not accumulate in the diatoms (Table 1).

DISCUSSION:

1. The cell counts and dry weight data show that there may have been a slight inhibition of growth in the treated cultures relative to the controls ($\leq$15% using average values). Therefore, it would be better to conclude that there was little effect rather than no effect.

2. There was a large variability in the concentrations of methamidophos in diatoms. This may have been due to the manner in which diatom dry weights were determined. Each filter paper used for a sample should have been tared. The five papers used to determine a tare weight varied in weight by 9.2 mg, which represents 20-25% of the diatom weights (Table 1).

Table 1. Methamidophos accumulation by a marine diatom grown in treated water for 7 days.

Nominal methamidophos concentration (ppm)	Cell count (10^6/ml)	Dry weight of diatoms (mg)	Methamidophos concentration at 7 days (ppm)	
			Water	Diatoms
0	4.1	41	<0.01	<0.30
	5.2	41	ND[a]	ND[a]
1	3.4	39	0.81	0.51
	3.7	31	0.79	1.21
10	4.5	43	7.47	14.60
	3.9	28	8.05	5.30

[a]No data; controls used for recovery studies.

STUDY 19

CHEMICAL: METHAMIDOPHOS

FORMULATION: 00 - Active Ingredient

FICHE/MASTER ID: 00014497

CITATION: Tucker, B.V. 1972. Residues in earthworms in Orthene and Ortho 9006 treated soil. Unpublished study prepared by Chevron Chemical Co., Richmond, CA.

DIRECT RVW TIME = 7 (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: Sept. 30, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

This study contains data on the accumulation of methamidophos in earthworms. These data are not presented in this review.

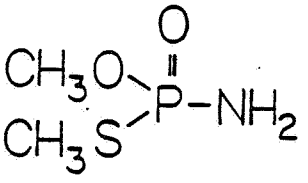
Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Methamidophos levels in soil declined at a moderate to rapid rate. Methamidophos levels declined by about 50% (from 1.3 ppm) within 9 days after the last of three applications.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Autoclaved sandy loam soil (10 kg) was placed in a plastic pan (5 inches deep) and sprayed with methamidophos (Ortho 9006, Chevron Chemical Co.; formulation and purity not specified) at 0.1, 0.3, and 0.8 lb/A on days 0, 27, and 33, respectively. A 1-kg head of cabbage was sprayed with methamidophos (unspecified rate), chopped, and mixed into the treated soil on day zero. Earthworms (150/pan) were added to the soil. The pan was covered with a wet burlap bag and maintained at laboratory temperature. An untreated control was also run under the same conditions.

At various time intervals, 50-g soil samples were removed. The soil was analyzed by gas-liquid chromatography according to Method RM-12A, (Study 21, 00014980). Untreated soil samples and soil samples spiked with methamidophos were also analyzed.

REPORTED RESULTS:

Methamidophos levels in soil were at 0.29, 0.09, 0.46, 1.27, and 0.66 ppm on days 9, 16, 29, 35, and 42, respectively. Methamidophos levels declined about 50% 9 days after the third application (day 42).

DISCUSSION:

1. The amount of methamidophos applied by amending the treated soil with treated cabbage was not reported.

2. A degradation rate cannot be estimated because samples were not collected immediately after treatment with methamidophos, and too few samples were collected after each application.

3. No attempt was made to determine degradation products.

4. Recovery data for the spiked control samples were not presented. However, excellent recovery levels were reported for the analytical method when it was used on other soil types (Studies 6 and 18; 00014991 and 00014496).

STUDY 20

CHEMICAL: METHAMIDOPHOS

FORMULATION: 00 - Active Ingredient

FICHE/MASTER ID: 05017379

CITATION: Lubkowitz, J.A. 1975. Uptake and degradation of methamidophos by tomato plants and soils. Pages 157-163. in Origin and fate of chemical residues in food, agriculture and fisheries. Proceedings and report of two research coordination meetings, Vienna, Austria 1973, 1974.

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

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

SIGNATURE: Richard L Hebert DATE: Nov. 3, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

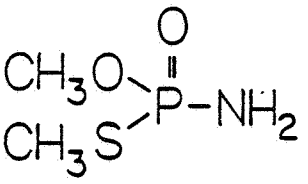
Metabolism - Aerobic Soil

1. The portions of this study dealing with identification of metabolites in soil are valid, but the quantitative data on the decline of methamidophos and accumulation and decline of its metabolites are invalid because the methodology used to obtain the data was not provided.

2. Methamidophos degradation products found in three types of soils incubated at 22 C were: O,S-dimethyl phosphorothioate, S-methyl phosphoroamidothioate, O-methyl phosphoroamidate, O-methyl phosphoric acid, and phosphate ion.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

Methamidophos metabolism was studied in three types of soils: a clay loam with a pH of 7.4 and a high organic matter content (soil A); a loam with a pH of 7.75 (soil B); and an argillaceous clay with a pH of 4.3 (soil C). [^{32}p] or [dimethyl-^{14}C]Methamidophos (synthesized by authors; purity unspecified) was added to soil in beakers at 25 ppm. The soils were incubated at 22 C, and the moisture content was maintained at 20%.

Aliquots were removed at various intervals and extracted with water. Unextractable radioactivity was determined by direct counting of soil suspensions. The extracts were passed through a Sephodex column, and all metabolites were collected in one fraction. The radioactivity in the eluate was counted and an aliquot was chromatographed on silica gel thin-layer chromatography (TLC) plates using two different solvent systems: ethanol:NH_4OH (95:5) and ethanol:water (95:5). Synthetic radiolabeled products (standards) were cochromatographed. The synthetic products were obtained from dilute acid and alkaline hydrolysates, and were identified by nuclear magnetic resonance and mass spectrometry.

REPORTED RESULTS:

For soil treated with [^{32}P]methamidophos, the data were reported as the percent of sample radioactivity that was water extractable or unextractable. The amount of extractable radioactivity decreased rapidly in soils A and P, and more slowly in soil C. About 3-7% of the ^{32}P was water extractable from soils A and B after 4 days, whereas about 25% was extractable from soil C after 9 days. At all times, the total ^{32}P measured represented 90-108% of the applied amount. About 30-40% of the unextractable activity was extracted with Na_2HPO_4 and H_3PO_4. The presence of phosphate ion in these extracts was determined by TLC.

Similar results for the rate of decline of extractable ^{14}C were obtained for soils A and B treated with [^{14}C]methamidophos (soil C was not tested). Methamidophos had an initial half-life of <5 hours in both soils. Less than 5% of the applied amount remained after 2 and 4 days in soils A and B, respectively. Radiolabeled metabolites reached a

maximum level of about 20 and 15% of the applied ^{14}C about 20-30 hours after treatment of soils A and B, respectively. The metabolites in soil B dissipated to negligible levels by the 4th day posttreatment; while in soil A, ~12% of the applied radioactivity remained as metabolites.

The major metabolite found was O,S-dimethyl phosphorothioate (II, Figure 1). Other products found were O-methyl phosphoric acid (VI), O-methyl phosphoroamidate (IV), and S-methyl phosphoroamidothioate (III). The latter two were found in small amounts, and product III was not detected in soil B. The loss of the methoxy group results in CO_2 evolution, because soils treated with [methoxy-^{14}C]methamidophos in closed systems yielded ^{14}C in amine mixture traps. Postulated degradation pathways are shown in Figure 1.

DISCUSSION:

1. Protocols, techniques, and data were not presented for the experiments conducted in closed systems. Also, no proof was presented that the volatile ^{14}C was $^{14}CO_2$. For these reasons, these data are considered invalid.

2. Data were not presented in a manner to show the decline of total radioactivity from soil. Rather, in Figure 4 of the study only the portion of each sample that was extractable or unextractable was given. The text was contradictory in that it stated that the amount of extracted activity was a percentage of original activity. Such data are of little use for developing an environmental fate profile. Also, it was not stated that unextractable activity was determined by combustion methods. Rather, this activity "was determined by counting 50-200 mg suspensions of the dry soil." The methods used to determine methamidophos and its metabolites were not provided. It was stated only that the extracts were counted and then chromatographed for qualitative identification of metabolites. For the above reasons, the quantitative data are considered invalid.

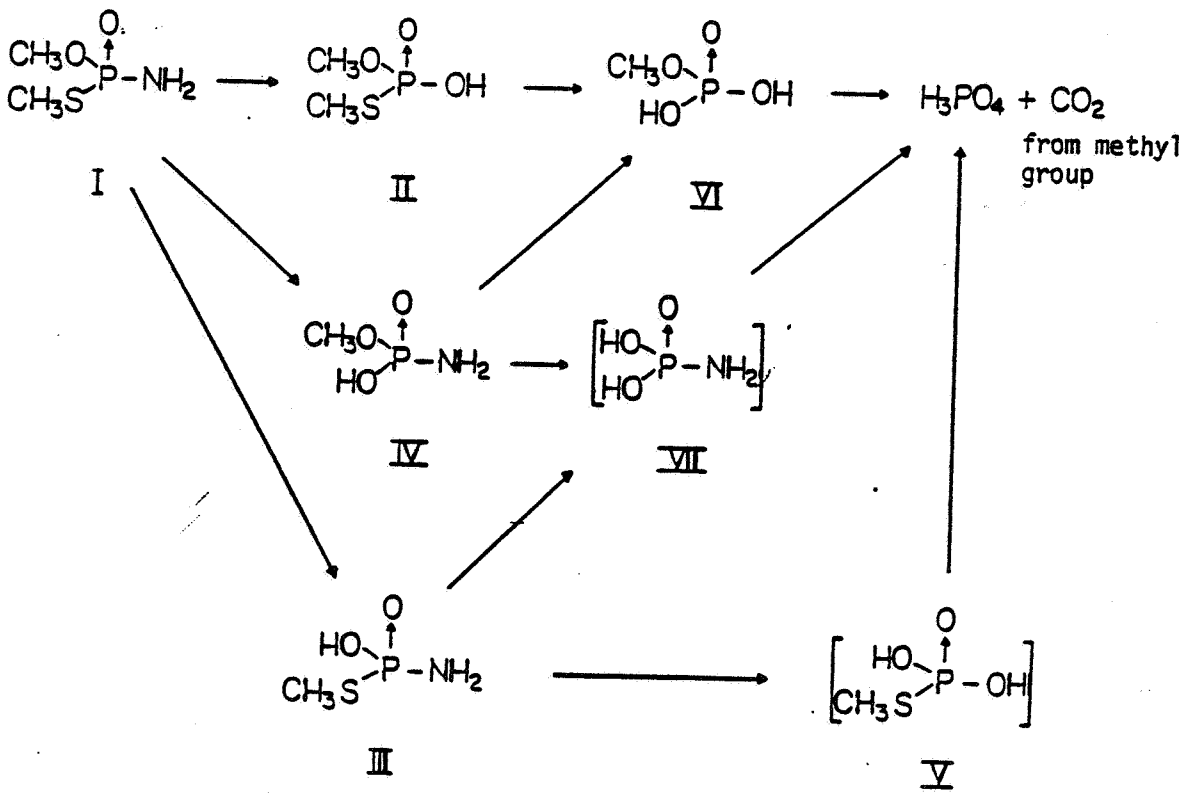


Figure 1. Proposed pathways for the degradation of methamidophos (I) in soil. Compounds in brackets (V and VII) were not detected in this study.

(TDR038) DATA EVALUATION RECORD PAGE 1 OF

CASE GS0043 METHAMIDOPHOS STUDY 21 PM 02/04/81

CHEM 101201

BRANCH EFB DISC 30 TOPIC 1005

FORMULATION 90 = FORMULATION NOT IDENTIFIED

FICHE/MASTER ID: 00014980

CITATION: Chevron Chemical Company. 1972. Orthene- and the metabolite-Ortho 9006. Residue analysis by thermionic gas chromatography. Method RM-12A. (Unpublished study submitted by Chevron Chemical Co., Richmond, CA).

FICHE/MASTER ID 00014997 CONTENT CAT 06

Leary, J.B. (1971) Addendum to RM-12A--Extraction Procedure for Soil, (Unpublished study received Feb 23, 1972 under 2G1248; submitted by Chevron Chemical Co., Richmond, Calif.; CDL: 091774-AF)

SUBST. CLASS = S.

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

REVIEWED BY: R. Hebert
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500
SIGNATURE: Richard P. Hebert DATE: Nov. 11, 1981

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

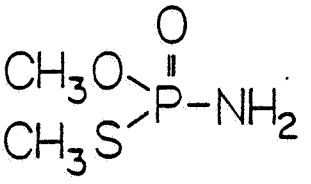
CONCLUSIONS:

1. This method study is scientifically valid.

2. Analytical procedures are described for the determination of methamidophos in soil. The gas chromatographic method appears to be specific, and the extraction procedure yields recovery levels of 90-100%. This method is used in other Chevron Company reports dealing with the environmental fate of methamidophos.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

These reports describe Chevron Method RM-12A for the determination of methamidophos in soil samples. The soil was placed in a glass column, which was then percolated with ethyl acetate saturated with water. The extract was collected and evaporated to dryness. In the initial method (00014980), the residue was transferred to a silicic acid column for cleanup. In a subsequent modification of the method (00014997), the column cleanup procedure was eliminated, and the extraction residue was dissolved in methylisobutylketone for analysis by gas chromatography using a thermionic detector.

REPORTED RESULTS:

Seventeen organophosphorus pesticides were checked for interference and none interfered (00014980). Recoveries obtained were about 80% when the column cleanup procedure was used and about 90-100% without the cleanup procedure (00014997).

DISCUSSION:

Recovery data were not actually presented, but were described in the text.

STUDY 22

CHEMICAL: METHAMIDOPHOS

FORMULATION: 00 - Active Ingredient

FICHE/MASTER ID: 00014085

CITATION: Chevron Chemical Company. 1968. Monitor residue analysis by thermionic gas chromatography. Method RM-10. (Unpublished report prepared by Chevron Chemical Co., Richmond CA).

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

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

SIGNATURE: Richard L Hebert DATE: November 3, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

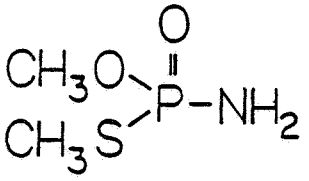
CONCLUSIONS:

1. This method study is valid.

2. A procedure is described for extracting methamidophos from plant tissue, and then identifying the compound by gas chromatography (GC). This method was used in Chevron Company reports dealing with the environmental fate of methamidophos in soil and water. The GC method is considered specific for methamidophos, and the extraction procedure is considered adequate for soil (~80% recovery) and water samples.

MATERIALS AND METHODS:

METHAMIDOPHOS, MONITOR, TAMARON



O,S-Dimethyl phosphoramidothioate

This report describes Chevron method RM-10 for the determination of methamidophos in plants. A sample was macerated in a blender and extracted with ethyl acetate. The extract was filtered and the extraction was repeated two more times. The filtrates were evaporated to dryness and redissolved in ether for cleanup on a silicic acid column. The column was washed with ether and the methamidophos was eluted with acetone. The eluate was evaporated and redissolved in methoxyethanol for analysis by gas chromatography (GC) using a thermionic detector. Standard methamidophos and 14 other organophosphorus compounds were analyzed for their retention times in the GC.

REPORTED RESULTS:

Three of the other pesticides had retention times similar to that for methamidophos, but these were removed by the column cleanup procedure.

DISCUSSION:

No recovery data were presented, nor was any reference made to the applicability of the extraction procedure to soil and water samples. However, the method is virtually identical to method RM-12A, which is described in Study 21 (00014980). The extraction and column cleanup method yielded recovery levels of ~80% for soil samples (Study 21, 00014997). Method RM-10 and RM-12A differ only in some minor details such as the source of the silicic acid and various GC parameters. Therefore, Method RM-10 is considered adequate for soil and water samples.