5-7

Shaughnessy No.: 101201

Date Out of EAB: APR 22 1987

Signature:

To: William Miller
Product Manager PM #16
Registration Division (TS-767)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of...

Reg./File # : 239-2452; 3125-341; 3125-348; 3125-280

Chemical Name: METHAMIDOPHOS

Type Product : INSECTICIDE/ACARICIDE

Product Name : MONITOR

Company Name : CHEVRON CHEMICAL CORPORATION

Purpose : Addendum to a Standard

Action Code: 660

EAB #(s) : 6776, 6777

Date Received: 9/01/86

TAIS Code: 65

Date Completed: 4/16/87

Total Reviewing Time: 4.0

Monitoring study requested: _____

Monitoring study voluntarily: _____

Deferrals to:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch*

_____ Toxicology Branch

DATE: 11/1/85

Confidential Business Information
Does Not Contain National Security Information (E.O. 12065)

12372

(RD PROVIDE) SHAUGNESSY NO.

CHEMICAL NAME: methamidophos 101201-2

Identifying Number	Action Code	Reference Number	Record Number	Study Guideline or Narrative Description	Reg. Std. Review Submission Criteria (SEE BELOW)	Accession Number	(RSERB Provide) MRID Number	(HED/BUD/TSS Complete) Review Results: Acceptable (A)/ Unacceptable(U)
-245	660	4	161563	Soil Volatility	3	259942		
-341	660	2	161564	Confined rotational crop	3	"		

PRODUCT MANAGER (PM) or REVIEW MANAGER (RM) AND NUMBER: W. Miller (16)

PM/RM TEAM MEMBER AND NUMBER: M. MAITZ (3)

RECEIVED (EPA): 10/1/85

RD BRANCH CHIEF INITIALS: 11/1

(APPLICABLE BOX:

- ☐ Adverse 6(a)(2) Data (405,406)
- ☐ Suspect Data (415,416)
- ☐ IBT Data (485,486)
- ☐ Groundwater Data (495,496)
- ☐ Data Waiver Request (Reregistration) (650,651)
- ☐ Formulation Data and Labeling (Reregistration) (655,656)
- ☒ Generic Data (Reregistration) (660,661)
- ☐ Special Review Data (870,871)

AH

NUMBER OF INDIVIDUAL STUDIES SUBMITTED: 2

TO BE COMPLETED BY RSERB

REQUESTED ACTIONS: Refer to attached note

DATE SENT TO HED/BUD/TSS: 11-04-85

INSTRUCTIONS: Review is needed to determine whether soil volatility and field rotational crop studies are to be required under the Temidophos Standard. Copy of data table attached.

PRIORITY NUMBER: 50

PROJECTED RETURN DATE: 01-03-86

DATE RETURNED TO RD (HED/BUD/TSS PROVIDE):

ACTIONS SENT TO:

☐ SIS ☐ TB ☐ RCB ☒ EAB ☐ EEB RD: ☐ TSS BUD: ☐ EAB ☐ SSB

TYPE OF REVIEW	NUMBER OF ACTIONS: Reregistration	Special Review	Other
Toxicology			
Ecological Effects			
Residue Chemistry			
Exposure Assessment	2		
Product Chemistry			
Efficacy			
Precautionary Labeling/Acute Tox.			
Science Support			
Economic Analysis			

FOR DATA SUBMITTED UNDER A REGISTRATION STANDARD: Review Submission Criteria

Policy Note #31

1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria

2 = data of particular concern

3 = data necessary to determine tiered testing requirements

NOTE TO TSS: Return 1 Copy To RSERB

INCLUDE A ORIGINAL AND FIVE (5) COPIES OF THIS COMPLETED FORM BY EACH BRANCH ASSIGNED FOR REVIEW.

REGISTRATION DIVISION DATA REVIEW RECORD

Confidential Business Information — Does Not Contain National Security Information (E.O. 12065)

Screen

1. CHEMICAL NAME: methamidophos

2. IDENTIFYING NUMBER	3. ACTION CODE	4. ACCESSION NUMBER	TO BE COMPLETED BY PM
(a) 239-2452	495	259941	5. RECORD NUMBER (a) 161589 (b) 161590
(b) 3125-341	495	259942	6. REFERENCE NUMBER 1
NOTE: This is data submitted in response to Reg Standard. As per Cunningham's office there was not any ground water data call-in for methamidophos under her DCI program			7. DATE RECEIVED (EPA) 10/1/85
			8. STATUTORY DUE DATE
			9. PRODUCT MANAGER (PM) Heller
			10. PM TEAM NUMBER 16

14. CHECK IF APPLICABLE

☐ Public Health/Quarantine
☐ Substitute Chemical
☐ Seasonal Concern
☐ Minor Use
☐ Part of IPM
☐ Review Requires Less Than 4 Hours
☑ Ground water data Screening

TO BE COMPLETED BY PCB:

11. DATE SENT TO HED/TSS 03/19/86

12. PRIORITY NUMBER 20

13. PROJECTED RETURN DATE 04/18/86

15. INSTRUCTIONS TO REVIEWER

A. HED: ☐ Total Assessment - 3(c)(5)
☐ Incremental Risk Assessment - 3(c)(7) and/or E.L. Johnson memo of May 12, 1977

B. SPRD (Send Copy of Form to SPRD PM)
☐ Chemical Undergoing Active RPAR Review
☐ Chemical Undergoing Active Registration Standards Review

C. ☐ BFSD
D. ☐ TSS/RD
E. ☐ Other

F. INSTRUCTIONS: Screening of ground water data submitted under Registration Std.

NOTE: This fulfills all ground water data required to be submitted under the Std. A copy of the Environmental fate data requirements under the Std. is attached. Also, attached is a copy of the science chapter showing results of data in-house

16. RELATED ACTIONS

17. 3(c)(1)(D)

☐ Use Any or All Available Information
☐ Use Only Attached Data
☐ Use Only the Attached Data for Formulation and Any or All Available Information on the Technical or Manufacturing Chemical

18. REVIEWS SENT TO

☐ TB ☐ EEB ☐ EF ☐ FI
☐ RCB ☐ EFB ☐ CHI ☐ BFSD

19.	To	TYPE OF REVIEW	Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
HED		TOXICOLOGY								
		ECOLOGICAL EFFECTS								
		RESIDUE CHEMISTRY								
	X	ENVIRONMENTAL DATA (Screening)								Screening
RD/TSS		CHEMISTRY								
		EFFICACY								
		PRECAUTIONARY LABELING								
BFSD		ECONOMIC ANALYSIS								

RESUBMISSION

20. ☐ Label Submitted with Application Attached

21. ☐ Confidential Statement of Formula

22. ☐ Representative Labels Showing Accepted Uses Attached

23. Date Returned to RD (to be completed by HED)

24. Include an Original and 4 (four) Copies of This Completed Form for Each Branch Checked for Review

1. CHEMICAL: Common name:

Methamidophos

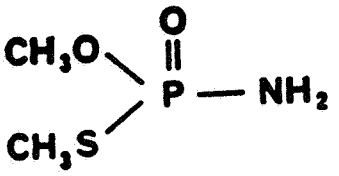
Chemical name:

O,S-Dimethyl phosphoramidothioate

Trade name(s):

Monitor, Tamaron, Bay 71628, Ortho 9006

Structure:



Formulations:

40% SC/L, 60% EC

Physical/Chemical properties:

Molecular formula: $C_2H_8NO_2PS$.
Molecular weight: 141.1
Physical state: Crystalline.
Melting point: 46.1°C.
Vapor pressure: 3×10^{-4} mbar at 30°C.
Solubility: Readily soluble in water or ethanol; <1% in kerosene, <10% in benzene or xylene at room temperature; soluble in alcohols and aliphatic chlorinated hydrocarbons; slightly soluble in ether.

2. TEST MATERIAL

2.1 Hydrolysis: S-methyl [^{14}C] methamidophos, radiochemical purity > 98%, specific activity 25.7 mCi/mmol, Mobay Chemical Corporation.

2.2 Photodegradation in Water: S-methyl [^{14}C] methamidophos, radiochemical purity 98% specific activity 25.7 mCi/mmol, Mobay Chemical Corporation.

2.3 Photodegradation on Soil: S-methyl [^{14}C] methamidophos, radiochemical purity > 98%, specific activity 25.7 mCi/mmol, Mobay Chemical Corporation, on sterile sandy loam soil.

2.4 Anaerobic Aquatic Metabolism: S-methyl [^{14}C] methamidophos, radiochemical purity > 99%, specific activity 78,021 dpm/ug, Mobay Chemical Corporation.

2.5 Leaching/Adsorption/Desorption:

2.5.1 S-methyl [^{14}C] methamidophos, radiochemical purity 98%, specific activity 25.7 mCi/mmol, Mobay Chemical Corporation, on Kansas sandy loam soil, no other description.

2.5.2 [^{14}C] methamidophos (no other description) on sand, sandy loam, sandy clay loam, silt loam, and two silty clay loam soils.

2.6 Laboratory Volatility: Aqueous solution of formulated (40% SC/A) S-methyl [^{14}C] methamidophos radiochemical purity > 99%, specific activity 101,600 dpm/ug, Mobay Chemical Corporation.

2.7 Field Accumulation in Rotational Crops: Methamidophos, no other description, at 3.75, 7.5, 15, and 30 lb ai/A on silty clay loam and sandy, soils in Kansas and Florida, respectively.

2.8 Confined Accumulation in Rotational Crops: Methylthio-labeled [^{14}C] methamidophos, purity 73%, specific activity 2.14 mCi/mmol, at 1 lb ai/A as foliar spray.

3. STUDY/ACTION TYPE:

Addendum to the Methamidophos Registration Standard.

4. STUDY IDENTIFICATION:

Chopade, H.M. 1985a. Hydrolysis of [^{14}C]methamidophos in sterile aqueous buffers. Mobay Report No. 88829. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 1.

Chopade, H.M. 1985b. Photodecomposition of [^{14}C]methamidophos in aqueous solution. Mobay Report No. 88830. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 2.

Chopade, H.M., and P.L. Freeseman. 1985. Photodecomposition of [^{14}C]-methamidophos on soil. Mobay Report No. 88831. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 3.

Murphy, J.J. and R.A. Morris. 1979. Residues of Monitor in rotational crops. Mobay Report No. 68476. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company Richmond, CA. Acc. No. 259942. Reference 8.

Obrist, J.J. 1979. Leaching characteristics of aged monitor soil residues. Mobay Report No. 68005. Prepared by Mobay Chemical Corp., Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 5.

Pack, D.E. 1984. Lack of methamidophos volatility from soil-laboratory study. Prepared and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 7.

Pack, D.E. 1985. The anaerobic aquatic metabolism of [S-methyl-^{14}C]-methamidophos (Monitor). Prepared and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 4.

Thornton, J.S., J.B. Hurley, and J.J. Obrist. 1976. Soil thin-layer mobility of twenty-four pesticide chemicals. Mobay Report No. 51016. Prepared by Mobay Chemical Corp., Kansas City, MO., and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 6.

Strankowski, K.J., G.D. Parker, and J.J. Murphy. 1981. [^{14}C]Monitor rotational crop study. Report No. 69878. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 9.

5. REVIEWED BY:

John H. Jordan, Ph.D.
Microbiologst
EAB/HED/OPP

Signature: John H. Jordan
Date: 4/17/89

6. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #3, EAB/HED/OPP

Signature: E Regelman
Date: APR 22 1987

7. CONCLUSIONS:

7.1 Hydrolysis (161-1): The 1/2 life is >30 days(309 days extrapolated) at pH 5, 27 days at pH 7, and 3 days at pH 9 (25° C). At pH 7 the the major degradate was dimethyldisulfide and at pH 9 it was desmethylmethamidophos; <3% hydrolyzed to deaminated-methamidophos at the three pH's.

The study of Chopade (1985a) fulfilled hydrolysis data requirements for reregistration of methamidophos.

7.2 Photodegradation in Water (161-2): The calculated half-life of methamidophos in sterile water at pH 5 and temperatures ranging from 9 to 42°C is about 90 days; actual measurements over 30 days showed a decline from 12 to 9.4 ppm under these conditions. A somewhat slower decline of 12 to 10.4 ppm was shown in dark controls under similar conditions. Degradates arising from the irradiation of methamidophos in solution include desmethyl-methamidophos, deaminated-methamidophos, and small amounts (< 2% of the applied) of unknown compounds. Desmethyl- and deaminated-methamidophos plus dimethyldisulfide develop in buffered (pH 5) solutions kept in the dark.

The study of Chopade (1985b) fulfilled EPA data requirements, Subdivision N, Section 161-2, for reregistration of methamidophos.

7.3 Photodegradation on Soil (161-3): Data from the Chopade and Freeseman (1985) study indicated that about 33% of the applied ^{14}C was volatilized. The study satisfies the data requirement.

7.4 Anaerobic Aquatic Metabolism (162-3): Although Pack (1985) combined the results of several studies in an attempt to provide the necessary data for anaerobic aquatic metabolism studies, too few sampling intervals and/or incomplete material balances spoiled the results. Because methamidophos has no aquatic or aquatic impact uses, these data are not required.

7.5 Leaching/Adsorption/Desorption (163-1): Two studies were submitted and reviewed, one by Obrist (1979) and the other by Thornton, et al. (1976). Neither study fulfilled EPA Guideline requirements for registering pesticides. The data of Obrist were considered valid but inadequate because after aging for over 30 days, too little of the applied methamidophos remained when leaching was initiated; consequently, a meaningful measurement of the leaching properties of the parent and degradates was not obtained. Thornton, et al. did not characterize the test substance and did not report soil/water relationship (K_d) values. All data must still be provided.

7.6 Laboratory Volatility (163-2): The study of Pack (1984) failed to include data to confirm the application rate or the efficiency of the trapping solution. No material balance was reported and a residue decline curve was not established. Consequently, it does not fulfill EPA data requirements, Section 163-2, for registering pesticides. Laboratory volatility data are still required.

7.7 Confined Accumulation-Rotational Crops (165-1): The study of Strankowski et al. (1981) was made with radiolabeled methamidophos of less than analytical grade (only 73% purity) and degradates in the rotated crops were not characterized. For these and other reasons the study did not fulfill the requirements of Subdivision N, Section 165-1, and all data are still required.

7.8 Field Accumulation-Rotational Crops (165-2): The study of Murphy and Morris (1979) could not be validated for several reasons: Analytical methods followed were only referenced but not described, the source of methamidophos residues (up to 0.03 ppm) in control samples of both crops and soils was not verified, recoveries from fortified samples ranged from 56 to 118% without adequate explanation, residues in soil samples were not given for the 60- and 90-day planting intervals or for any harvest interval, and planting to harvest intervals were not described. The study did not fulfill EPA Guidelines for registration and field accumulation in rotational crop studies may yet be required depending upon the data developed from confined accumulation studies.

7.9 Summary: The following are data gaps:

- o Field crop accumulation - rotation crops (tiered-conditional 165-2)
- o Anaerobic soil metabolism (162-2);
- o Leaching/adsorption/desorption (163-1);
- o Laboratory volatility (163-2); and Field volatility tiered/conditional (163-3)
- o Terrestrial field dissipation (164-1);
- o Confined accumulation in rotational crops (165-1);
- o Reentry studies per Subpart K.

The following data requirements have been satisfied and no additional data are required:

o Aerobic soil metabolism (162-1);

o Long-term terrestrial field dissipation (164-5);

o Fish accumulation (165-4);

o Accumulation in aquatic nontarget organisms (165-5).

o Hydrolysis

o Photodegradation on soil and in water

8. RECOMMENDATIONS

8.1 Accept the following submissions for this addendum for EPA data requirements of Subpart N, Pesticide Assessment Guidelines:

- Chopade, 1985a, hydrolysis;
- Chopade, 1985b, photodegradation in water; and

Require the registrant to submit data for the following studies on the previously set schedule:

- Anaerobic soil metabolism (162-2);
- Leaching/adsorption/desorption (163-1);
- Laboratory volatility (163-2);
- Field volatility - tiered/conditional (163-3)
- Terrestrial field dissipation (164-1);
- Confined accumulation in rotational crops (165-1);
- Field crop accumulation - rotation crops tiered/conditional (165-2)

9. BACKGROUND

A. Introduction:

The Guidance Document for the Registration Standard for methamidophos issued in September 1982 identified data gaps and set forth a schedule for the registrant to submit data to fill those gaps. The data submitted and reviewed herein are in response to the Registration Standard.

B. Directions for Use

Methamidophos is an organophosphorus insecticide and acaricide registered for use on terrestrial food crops (field crops). Of the methamidophos used annually in the United States, about 37-39% is used on potatoes, 24-30% on cotton, 10-19% on tomatoes, and 12-18% on cole crops (cabbage, broccoli, brussel sprouts, cauliflower, and Chinese cabbage). Minor use sites include

lettuce and seed crops of sugar beets, carrots, alfalfa, and clover. Application rates range from 0.5 to 1.0 lb ai/A, and reapplication may be made at 7-10 day intervals as often as needed. Methamidophos is formulated as a 40% soluble concentrate and a 60% emulsifiable concentrate, and can be applied aerially or by ground equipment.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See item No. 7 (Conclusions) and attached reviews of individual studies.

11. COMPLETION OF ONE-LINER: One-liner not completed to date.

12. CBI APPENDIX:

All data reviewed here are considered CBI by the registrant and must be treated as such.

DYNAMAC
CORPORATION

METHAMIDOPHOS ADDENDUM

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate and Exposure Assessment

Contract No. 68-02-4250

NOVEMBER 21,1986

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

METHAMIDOPHOS

Table of Contents

INTRODUCTION

Methamidophos is an organophosphorus insecticide and acaricide registered for use on terrestrial food crops (field crops). Of the methamidophos used annually in the United States, about 37-39% is used on potatoes, 24-30% on cotton, 10-19% on tomatoes, and 12-18% on cole crops (cabbage, broccoli, brussel sprouts, cauliflower, and Chinese cabbage). Minor use sites include lettuce and seed crops of sugar beets, carrots, alfalfa, and clover. Application rates range from 0.5to 1.0 lb ai/A, and reapplication may be made at 7-10 day intervals as often as needed. Methamidophos is formulated as a 40% soluble concentrate and a 60% emulsifiable concentrate, and can be applied aerially or by ground equipment.

CASE GS -- METHAMIDOPHOS STUDY 1 PM —

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Chopade, H.M. 1985a. Hydrolysis of [^{14}C]methamidophos in sterile aqueous buffers. Mobay Report No. 88829. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 1.

SUBST. CLASS = S.

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

REVIEWED BY: P. Perreault
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500

APPROVED BY: J.Jordan
TITLE: Microbiologist
ORG: EAB/HED/OPP
TEL: 557-5457

SIGNATURE: J. Jordan DATE: 4/17/87

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. [^{14}C]Methamidophos (radiochemical purity >98%) degraded with half-lives of >30 days (calculated 309 days) at pH 5, 27 days at pH 7, and 3 days at pH 9 in sterile buffered aqueous solutions maintained in the dark at 25 1°C. The major degradate at pH 7 was dimethyldisulfide; the major degradate at pH 9 was desmethyl-methamidophos. Deaminated-methamidophos was 3% of the applied at all three pH's.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of methamidophos at pH 5, 7, and 9.

MATERIALS AND METHODS:

Experiment 1

Aliquots of S-methyl-labeled [^{14}C]methamidophos (radiochemical purity >98%, specific activity 25.7 mCi/mmol, Mobay Chemical Co.) in sterile distilled water were added at 12 ppm to sterile aqueous solutions buffered at pH 5, 7, and 9 with sodium phosphate buffers (0.2 M). The treated solutions were placed in vials, which were then capped and maintained at 25 ± 1°C in a water bath in the dark. The solutions at pH 5 and 7 were sampled at days 0, 1, 3, 7, 14, 21, and 30 posttreatment, and the solutions at pH 9 were sampled at days 0, 1, 2, 3, 4, 5, and 7. The pH of the solutions was measured on day 0 and at the last sampling interval.

Each sample was divided into three parts. The first part was analyzed for total radioactivity using LSC. The second part was analyzed for [^{14}C]methamidophos and its degradates using reversed-phase HPLC (this procedure did not effectively differentiate between desmethyl-methamidophos and deaminated-methamidophos). The third part was stored frozen at -10°C in the original capped vials and analyzed several months later by ion-pairing HPLC to separate and quantitate desmethyl- and deaminated-methamidophos. Recovery of applied radioactivity was >96% throughout the study.

Experiment 2

Because the portion of each sample which was stored frozen was found to be unstable in the freezer, an additional hydrolysis study using [^{14}C]-methamidophos at 14.5 ppm was conducted using the methods described previously in Experiment 1 in order to obtain fresh (nonfrozen) samples for reanalysis using ion-pairing HPLC. The results of this study were used to calculate the approximate amounts of desmethyl- and deaminated-methamidophos formed in the original study. Recovery of applied radioactivity was >99% throughout the study.

REPORTED RESULTS:

Experiment 1

[^{14}C]Methamidophos, at 12 ppm in sterile buffered solutions incubated in the dark at 25 ± 1°C, degraded with half-lives of >30 days at pH 5, 21-30 days at pH 7, and ~3 days at pH 9 (Table 1). Three degradates were formed and were identified as dimethyldisulfide, desmethyl-methamidophos, and deaminated-methamidophos. The pH of the solutions remained constant during the study.

Experiment 2

[^{14}C]Methamidophos, at 14.5 ppm in sterile buffered solutions incubated in the dark at 25 ± 1°C, degraded with half-lives of >21 days at pH 5, 14-21 days at pH 7, and 3-5.7 days at pH 9 (Table 2). Three degradates, identical to those identified in Experiment 1, were formed.

DISCUSSION:

General

1. Method detection limits were not reported.

2. The initial results of the ion-pair HPLC analysis in experiment 1 were not accurate because the portion of each sample that was analyzed using ion-pair HPLC was stored frozen prior to analysis and was found to be unstable in the freezer. An additional experiment (Experiment 2) was conducted in order to obtain fresh (nonfrozen) samples for reanalysis by ion-pair HPLC.

Table 1. [^{14}C]Methamidophos and its degradates (% of applied) in buffered solutions treated with [^{14}C]methamidophos at 12 ppm and incubated in the dark at 25 ± 1°C (Experiment 1).

Sampling interval (days)	Methamidophos[a]	Dimethyl-disulfide[a]	Desmethyl-methamidophos[b]	Deaminated-methamidophos[b]	Total recovery
			pH 5		
0	99	1	<1[c]	<1	100
1	97	1	<1	<1	99
3	96	<1	<1	<1	97
7	95	2	<1	2	99
14	93	3	1	2	99
21	93	3	1	2	99
30	91	4	1	3	99
			pH 7		
0	98	1	<1	<1	100
1	95	1	<1	<1	97
3	92	4	3	<1	99
7	84	11	5	<1	100
14	69	22	7	<1	98
21	58	32	8	1	99
30	46	41	8	1	96
			pH 9		
0	98	1	<1	<1	100
1	77	7	14	1	99
2	63	12	23	1	99
3	50	16	32	1	99
4	39	19	40	1	99
5	32	23	44	1	100
7	22	26	51	1	100

[a] Separation and quantitation based on reversed-phase HPLC analysis of samples from Experiment 1.

[b] Separation and quantitation based on reversed-phase HPLC analysis of samples from Experiment 1 and ion-pairing HPLC analysis of samples from Experiment 2.

[c] The method detection limit was not reported.

Table 2. [^{14}C]Methamidophos and its degradates (% of applied) in buffered solutions treated with [^{14}C]methamidophos at 14.5 ppm and incubated in the dark at 25 ± 1°C (Experiment 2).

Sampling interval (days)	Methamidophos[a]	Dimethyl-disulfide[a]	Desmethyl-methamidophos[a]	Deaminated methamidophos[a]	Total recovery
			pH 5		
0	98	<1[b]	<1	<1	100
14	94	2	1	2	99
21	95	1	1	3	100
			pH 7		
0	98	<1	<1	<1	100
6	95	2	2	<1	99
14	58	33	7	<1	99
21	37	57	5	<1	99
			pH 9		
0	98	<1	<1	<1	100
1	84	6	9	<1	99
3	60	15	23	<1	99
5.7	38	24	36	<1	99
10.9	15	37	46	1	99

[a] Separation and quantitation based on ion-pairing HPLC analysis.

[b] The method detection limit was not reported.

CASE GS -- METHAMIDOPHOS STUDY 2 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01
Chopade, H.M. 1985b. Photodecomposition of [^{14}C]methamidophos in aqueous solution. Mobay Report No. 88830. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 2.

SUBST. CLASS = S.

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

REVIEWED BY: P. Perreault
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500

APPROVED BY: J. Jordan
TITLE: Microbiologist
ORG: EAB/HED/OPP
TEL: 557-5457

SIGNATURE: J. Jordan DATE: 4/17/87

CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is scientifically valid.

2. [^{14}C]Methamidophos (purity 98%) declined from 12 to 9.4 ppm (calculated half-life 90 days) during 30 days of natural sunlight-irradiation outdoors (17-33°C) in a sterile aqueous solution buffered at pH 5, and from 12 to 10.4 ppm in the dark control during the same interval. [^{14}C]Methamidophos declined from 10 to 8.9 ppm during 5 days of continuous artificial light-irradiation at 33°C in a sterile aqueous solution buffered at pH 5, and from 10 to 9.3 ppm in the dark control during the same period. Degradates in the irradiated solutions in both experiments included desmethyl-methamidophos, deaminated-methamidophos, and one unknown compound (2% of the applied); degradates in the dark controls in both experiments included desmethyl-methamidophos, deaminated-methamidophos, and dimethyldisulfide.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of methamidophos in a sterile buffered solution (pH 5) irradiated with natural sunlight and an artificial source.

MATERIALS AND METHODS:

Experiment 1

S-Methyl-labeled [^{14}C]methamidophos (radiochemical purity 98%, specific activity 25.7 mCi/mmol, Mobay Chemical Corp.) was mixed into a sterile aqueous solution buffered at pH 5 with phosphate buffers for a final concentration of 10 ppm methamidophos. Aliquots of the treated solution were placed in vials, which were then capped and irradiated at 4360 W/cm^2 under a 450-watt medium pressure mercury lamp (spectral characteristics are presented in Table 1) that was filtered through a borosilicate immersion well. The incubation temperature was 33°C. Additional vials containing aliquots of the treated solution were placed in a capped opaque jar and served as dark control samples; the jar was kept at the same distance from the lamp as the test vials. Samples of the irradiated and dark control solutions were taken for analysis on days 0, 1, 2, 3, 4, and 5 posttreatment.

Each sample was divided into three parts. The first part was analyzed for total radioactivity using LSC. The second part was analyzed for [^{14}C]methamidophos and its degradates using reversed-phase HPLC (this procedure did not effectively differentiate between desmethyl-methamidophos and deaminated-methamidophos). The third part was stored frozen at -10°C in the original capped vials and analyzed several months later by ion-pairing HPLC to separate and quantitate desmethyl- and deaminated-methamidophos. Recovery of applied radioactivity was 98% throughout the study.

Experiment 2

S-Methyl-labeled [^{14}C]methamidophos (radiochemical purity 98%, specific activity 25.7 mCi/mmol, Mobay Chemical Corp.) was mixed into a sterile aqueous solution buffered at pH 5 with phosphate buffers for a final concentration of 12 ppm methamidophos. Aliquots of the treated solution were placed in vials which were then capped and arranged at a 60° angle lengthwise on a platform. Additional vials containing aliquots of the treated solution were placed in an opaque jar and served as dark control samples. The platform and the jar were placed outdoors in the sunlight at 8:00 a.m. on August 14, 1984 (field test data during the study are provided in Table 2). The study was conducted at Stilwell, Kansas (latitude 38°49', longitude 94°40', elevation 1050 feet above sea level). Samples of the irradiated and dark control solutions were taken for analysis on days 0, 3, 7, 14, 21, and 30 posttreatment.

Each sample was divided into three parts. The first part was analyzed for total radioactivity using LSC. The second part was analyzed for [^{14}C]methamidophos and its degradates using reversed-phase HPLC (this procedure did not effectively differentiate between desmethyl-methamidophos and deaminated-methamidophos). The third part was stored frozen at -10°C in the original capped vials and analyzed several months later

by ion-pairing HPLC to separate and quantitate desmethyl- and deaminated-methamidophos. Recovery of applied radioactivity was 99% throughout the study.

REPORTED RESULTS:

Experiment 1

After 5 days of continuous irradiation with artificial light, [^{14}C]methamidophos comprised 89% of the applied radioactivity in the aqueous solution (Table 3). Degradates included desmethyl-methamidophos (3% of the applied), deaminated-methamidophos (6% of the applied), and one unidentified compound (2% of the applied). In the nonirradiated control aqueous solution, [^{14}C]methamidophos comprised 93% of the applied radioactivity. Degradates included desmethyl-methamidophos (<1% of the applied), deaminated-methamidophos (3% of the applied), and dimethyldisulfide (2% of the applied). The pH of the test solutions was stable throughout the study.

Experiment 2

After 30 days of irradiation under natural sunlight outdoors, [^{14}C]methamidophos comprised 78% of the applied radioactivity in the aqueous solution (Table 4). The registrant calculated the half-life of the irradiated samples to be 90 days. Degradates included desmethyl-methamidophos (7% of the applied), deaminated-methamidophos (13% of the applied), and one unidentified compound (2% of the applied). In the nonirradiated control aqueous solution, [^{14}C]methamidophos comprised 87% of the applied radioactivity. Degradates included desmethyl-methamidophos (<1% of the applied), deaminated-methamidophos (6% of the applied), and dimethyldisulfide (6% of the applied). The pH of the test solutions was stable throughout the study.

DISCUSSION:

General

1. The incubation temperatures were not maintained at 25 $\pm$ 1°C. The temperature during Experiment 1 was 33°C, and during Experiment 2, the temperature outdoors ranged from 9-42°C with a mean low of 17°C and a mean high of 33°C.

2. Method detection limits were not reported.

3. Samples were frozen for an unspecified length of time prior to analysis by ion-pairing HPLC to quantitate desmethyl- and deaminated-methamidophos. These samples were slightly unstable during frozen storage and degraded to dimethyldisulfide. However, since the combined concentration of desmethyl- plus deaminated-methamidophos was determined in fresh samples, and the frozen samples were used to determine relative amounts, the reported results are adequate.

Table 1. Spectral characteristics of Conrad-Hanovia 450-watt medium pressure quartz mercury-vapor lamp.

Mercury lines (nm)	Energy (watts)
1367 (Infrared)	2.6
1128	3.3
1014	10.5
578 (Yellow)	20.0
546 (Green)	24.5
435 (Blue)	20.2
404 (Violet)	11.0
366 (UV)	25.6
334	2.4
313	13.2
302	7.2
296	4.3
289	1.6
280	2.4
275	0.7
270	1.0
265	4.0
257	1.5
254[a]	5.8
248	2.3
240	1.9
238	2.3
236	2.3
232	1.5
222	3.7

[a] 254 nm line is reversed in medium pressure lamps.

Table 2. Meteorological data during [^{14}C]methamidophos photolysis study using natural sunlight conducted outdoors in Stilwell, Kansas, in August-September, 1984.

Date	Light intensity ($\mu W/cm^2$)			Air temperature (°C)		Rainfall (inches)
	8:30 a.m.	12:30 p.m.	4:30 p.m.	Max.	Min.	
8/14	1100	3600	1700	33	19	0
8/15	1200	3450	1800	34	19	0
8/16	1150	3450	2100	34	19	0
8/17	1150	3100	2550	--	--	0
8/18	1400	3100	3500	34	19	0.35
8/19	1250	3000	2600	29	16	0
8/20	1250	3100	1900	31	18	0
8/21	1200	1500	1750	28	19	0.28
8/22	2500	4850	3550	32	11	0
8/23	3000	4850	3800	25	19	0
8/24	1700	4050	2900	27	13	0
8/25	2700	4200	1400	31	14	0
8/26	1700	3100	1500	34	17	0.12
8/27	2700	4750	3300	36	19	0
8/28	2300	4400	3800	41	21	0
8/29	2550	4950	3100	42	16	0
8/30	2150	4500	3200	33	16	0
8/31	1300	4600	2900	37	21	0
9/01	2200	4600	2700	37	20	0
9/02	400	800	500	36	10	0.04
9/03	2050	4800	3400	26	9	0
9/04	1850	4750	1100	29	10	0
9/05	2350	5000	4500	28	14	0
9/06	1550	4900	2800	36	22	0
9/07	1850	4400	3800	33	13	0.66
9/08	200	1400	500	24	15	0.04
9/09	250	1900	5000	29	16	0
9/10	2000	4600	3300	36	17	0.03
9/11	270	3300	2900	33	18	0
9/12	700	4300	3600	36	21	0
9/13	1450	3100	300	35	17	2.75

Table 3. [^{14}C]Methamidophos and its degradates (% of the applied) in pH 5 buffered aqueous solutions mixed with [^{14}C]methamidophos at 10 ppm and irradiated under artificial light at ~33°C for 5 days.

Sampling interval (days)	Methamidophos	Desmethyl-methamidophos	Deaminated-methamidophos	Unknown compound	Dimethyl-disulfide	Total recovery
			Irradiated samples			
0	98	1	1	ND[a]	ND	100
1	95	<1	3	<1	ND	99
2	93	<1	5	<1	ND	99
3	92	2	5	1	ND	100
4	90	2	5	1	ND	98
5	89	3	6	2	ND	100
			Nonirradiated controls			
0	98	<1	<1	ND	1	100
1	98	<1	<1	ND	<1	99
2	96	<1	1	ND	1	99
3	96	<1	1	ND	2	100
4	95	<1	1	ND	2	99
5	93	<1	3	ND	2	99

[a] Not detected; detection limit not reported.

Table 4. [^{14}C]Methamidophos and its degradates (% of the applied) in pH 5 buffered aqueous solutions mixed with [^{14}C]methamidophos at 12 ppm and irradiated outdoors under natural sunlight at mean temperatures ranging from 17-33°C for 30 days.

Sampling interval (days)	Methamidophos	Desmethyl-methamidophos	Deaminated-methamidophos	Unknown compound	Dimethyl-disulfide	Total recovery
			Irradiated samples			
0	99	<1	<1	ND[a]	ND	100
3	95	<1	3	<1	ND	99
7	93	4	2	1	ND	100
14	89	4	5	2	ND	100
21	82	8	8	2	ND	100
30	78	7	13	2	ND	100
			Nonirradiated controls			
0	99	<1	<1	ND	ND	100
3	98	<1	<1	ND	<1	99
7	97	<1	1	ND	1	100
14	95	<1	2	ND	2	100
21	90	<1	4	ND	5	100
30	87	<1	6	ND	6	100

[a] Not detected; detection limit not reported.

CASE GS — METHAMIDOPHOS STUDY 3 PM —

CHEM 101201 Methamidophos

BRANCH EAB DISC —

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Chopade, H.M., and P.L. Freeseman. 1985. Photodecomposition of [^{14}C]methamidophos on soil. Mobay Report No. 88831. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 3.

SUBST. CLASS = S.

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

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CONCLUSIONS:

Degradation - Photodegradation on Soil

This study is scientifically valid and satisfies the requirement for soil photolysis. The study provides degradation rates and degradates.

MATERIALS AND METHODS:

Sterile sandy loam soil (59% sand, 36% silt, 5% clay, 2.6% organic matter, pH 5.0, CEC 17.0 meq/100 g) was sieved (600 m) and mixed with sterile distilled water to form a slurry, which was then applied to microscope slides. The thin layers of soil were dried and the slides were scraped so that each plate contained 300 20 mg of dry soil. S-Methyl-labeled [^{14}C]methamidophos (radiochemical purity >98%, specific activity 25.7 mCi/mmol, Mobay Chemical Corp.), at 35 ppm in toluene, was applied uniformly to the surface of each slide. The toluene was

allowed to evaporate and the treated slides were placed in capped vials. The vials were arranged in a circle (16-cm radius) around a 450-watt medium pressure mercury lamp filtered with a borosilicate glass immersion well (spectral characteristics are presented in Table 1), and were irradiated at 4330 W/cm^2 and 33°C. Additional vials containing treated soil slides were placed in an opaque jar that was positioned 16 cm from the lamp; these served as control (nonirradiated) samples. Samples were taken from the irradiated and dark control treatments at 0, 24, 45, 63, and 87 hours; additional samples from irradiated vials only were analyzed at 29 hours as well.

The soil samples were mixed with pH 5 aqueous phosphate buffer (0.2 M), centrifuged, and the supernatant was removed. Aliquots of the solution were analyzed for total radioactivity using LSC. The soils were extracted a second time with the phosphate buffer, centrifuged, and the supernatant was combined with the supernatant from the first centrifugation and analyzed for total radioactivity using LSC. Aliquots of the aqueous phase were analyzed for [^{14}C]methamidophos and its degradates using reverse phase HPLC. The sample vials were then stored frozen and later analyzed using ion-pairing HPLC to separate and quantitate desmethyl-methamidophos and deaminated-methamidophos. The extracted soils were then air-dried and combusted, and the resulting $^{14}CO_2$ was trapped and analyzed for total radioactivity using LSC.

In order to characterize the [^{14}C]residues lost by volatilization during irradiation, an additional study was conducted (refer to Discussion Point 3). Sterile, dry sandy loam soil was placed inside 1-dram vials which were vertically suspended in scintillation vials. The soil was treated with [^{14}C]methamidophos at 35 ppm. Either a scintillation solution or methanol:water (2:3) was added to the scintillation vials (the soil was above the surface of the solutions). The vials were capped and maintained at room temperature in the dark. The vials containing scintillation solution were analyzed for total radioactivity using LSC at 0, 16, 24, 36, 48, 90, and 112 hours posttreatment. Aliquots of the vials containing methanol:water were analyzed for [^{14}C]methamidophos and its degradates using reversed-phase HPLC at 90 hours posttreatment.

REPORTED RESULTS:

[^{14}C]Methamidophos degraded with a half-life of about 40 hours. Degradates included desmethyl-methamidophos and deaminated-methamidophos. In nonirradiated control samples, the half-life of [^{14}C]methamidophos was >87 hours. Trace amounts of the degradates desmethyl- and deaminated-methamidophos, as well as occasional traces of dimethyldisulfide, were detected (Table 2).

The dark control experiment conducted to identify volatiles indicated that after a 90-hour incubation period, 13% of the applied radioactivity had volatilized; volatilized dimethyldisulfide accounted for 7% of the applied radioactivity, and volatilized [^{14}C]methamidophos, desmethyl-methamidophos, deaminated-methamidophos, and two unknown compounds each accounted for 1.3% of the applied radioactivity.

DISCUSSION:

1. After about 87 hours of incubation, 33% of the [^{14}C]residues in the irradiated soil had volatilized.

2. The artificial light was compared to natural sunlight in the aqueous photolysis study.

3. Samples were stored frozen for an unspecified length of time prior to analysis by ion-pairing HPLC. The stability of these samples during frozen storage was not investigated.

4. Method detection limits were not reported.

5. The study was conducted at 33°C.

Table 1. Spectral characteristics of Conrad-Hanovia 450-watt medium pressure quartz mercury-vapor lamp.

Mercury lines (nm)	Energy (watts)
1367 (Infrared)	2.6
1128	3.3
1014	10.5
578 (Yellow)	20.0
546 (Green)	24.5
435 (Blue)	20.2
404 (Violet)	11.0
366 (UV)	25.6
334	2.4
313	13.2
302	7.2
296	4.3
289	1.6
280	2.4
275	0.7
270	1.0
265	4.0
257	1.5
254[a]	5.8
248	2.3
240	1.9
238	2.3
236	2.3
232	1.5
222	3.7

[a] 254 nm line is reversed in medium pressure lamps.

Table 2. [^{14}C]Methamidophos and its degradates (% of applied) on sandy loam soil treated with [^{14}C]methamidophos at ~35 ppm and irradiated under artificial light for 87 hours at ~33°C.

Sampling interval (hours)	Metha-midophos	Desmethyl-methamidophos[a]	Deaminated-methamidophos[a]	Unextract-able	Total [^{14}C]
		Irradiated			
0	99	ND[b]	ND	1	100
24	64	10	4	8	86
29	57	11	4	10	82
45	47	15	6	11	79
63	35	20	6	14	75
87	23	24	3	17	67
		Nonirradiated			
0	99	ND	ND	1	100
24	91	<1	<1	3	94
45	80	<1	1	5	85
63	72	<1	2	7	81
87	63	<1	1	9	73

[a] Separation and quantitation based on ion-pairing HPLC analysis.

[b] Not detected; detection limit not reported.

CASE GS -- METHAMIDOPHOS STUDY 4 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Pack, D.E. 1985. The anaerobic aquatic metabolism of [S-methyl-^{14}C]methamidophos (Monitor). Unpublished study prepared and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 4.

SUBST. CLASS = S.

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

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CONCLUSIONS:

Metabolism - Anaerobic Aquatic

This study is scientifically invalid because several incomplete experiments (each containing too few sampling intervals and/or an incomplete material balance) were combined in an attempt to create a complete anaerobic aquatic metabolism study. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because material balances were incomplete and the test water was not characterized.

MATERIALS AND METHODS:

Volatile Residue Study

To establish anaerobic conditions, sandy loam soil (70% sand, 17% silt, 13% clay, 1.0% organic matter, pH 7.1, CEC 7.5 meq/100 g) which had been oven-dried overnight at 120°C was placed in a flask with rice straw, flooded with deionized water (1-inch layer above soil surface), and incubated under nitrogen at 25°C in darkness for 30 days. Following the 30-day incubation period, S-methyl-labeled [^{14}C]methamidophos (radiochemical purity >99%, specific activity 78021 dpm/µg, Mobay Chemical Co.) was added to the sandy loam soil at 10 ppm. A stream of nitrogen

was passed through the test system, then through a 0.5 N sodium hydroxide trap to collect CO_2, and finally through a tube containing cupric oxide heated to 775°C to oxidize organic compounds to CO_2 which was then also trapped in sodium hydroxide. The CO_2 trapping solutions were sampled periodically up to 232 days posttreatment. The water layer and soil were sampled at 232 days posttreatment only.

Radioactivity in the trapping solutions was quantified by LSC. Barium chloride precipitation was performed to confirm that the radioactivity was $^{14}CO_2$. Radioactivity remaining in the water layer was quantified by LSC, and in the soil by LSC following combustion.

To identify the volatilized organic compounds (trapped after oxidation to CO_2), sandy loam soil was placed in a Bartha biometer flask, anaerobic conditions were then established, and the soil was treated with S-methyl-labeled [^{14}C]methamidophos, as described above. Sodium hydroxide (0.5 N) was placed in the side-wells of the flask to trap evolved CO_2, and the flask was sealed. A second flask containing sandy loam soil was treated with sodium [^{14}C]acetate, which is metabolized to [^{14}C]methane by anaerobic bacteria. At 3 weeks posttreatment, gas samples were taken by syringe from both flasks and analyzed for methane, ethane, ethylene, and CO_2 by GC with flame ionization detection.

Soil Residue Study

Samples of sandy loam soil were placed in flasks, anaerobic conditions were established, and the soil was treated with S-methyl-labeled [^{14}C]-methamidophos, at 10 ppm, and incubated under nitrogen gas as described above.

REPORTED RESULTS:

Volatile Residue Study

At 232 days posttreatment, ~50 and 8% of the applied radioactivity had evolved as organic volatiles and CO_2, respectively (Table 1), while ~14% of the applied radioactivity remained in the soil/water system and 28% of the applied was unaccounted for. The organic volatiles were tentatively identified as methane (see Discussion).

Soil Residue Study

Under anaerobic aquatic conditions, S-methyl-labeled [^{14}C]methamidophos, at 10 ppm, degraded in sandy loam soil with a half-life of 7-14 days (Table 2). One uncharacterized degradate was detected in the combined water layer/soil extracts and reached a maximum of ~5% of the applied radioactivity at 1 day posttreatment. After 182 days of incubation, parent methamidophos and the uncharacterized degradate were not detected (detection limit unspecified). Evolved CO_2 and organic volatiles were not trapped. Duplicate soil samples were taken periodically up to 238 days posttreatment.

The water layer was separated from the soil by centrifugation, filtered, and analyzed for radioactivity by LSC. The soil was extracted four times

with methanol, and the methanol extracts were filtered and combined. The water layer and the methanol extract were combined, evaporated to dryness, and the residue was dissolved in methanol. The residue (in methanol) was stored frozen (-20°C) until analysis. The residue was analyzed for methamidophos and its degradates by HPLC. Radioactivity remaining in the extracted soil was quantified by LSC following combustion. Unextractable residues reached a maximum of ~20% of the applied radioactivity at 121 days posttreatment (Table 3).

DISCUSSION:

General

1. When an attempt was made by the reviewer to combine the volatile and soil residue data (which appeared to be the intent of the registrant), complete material balances could not be achieved.

2. Characteristics of the water, including pH, dissolved oxygen content, hardness, and alkalinity, used to flood the soil were not reported. A hydrolysis study by Chopade (1985a) determined that the hydrolytic degradation of methamidophos is pH-sensitive.

Volatile Residue Study

1. The material balance was incomplete. At study termination, the only sampling interval at which the soil, water, and volatiles were all analyzed, ~28% of the applied radioactivity was unaccounted for.

2. The organic volatiles were identified by the study author as methane. However, the characterization was based on the analysis of a sample taken at one sampling interval (3 weeks posttreatment), and the sample was obtained in a study separate from the one which generated the CO_2 and organic volatiles results presented in the report.

Soil Residue Study

1. Three separate anaerobic aquatic metabolism studies were conducted, and the registrant only provided selected "valid" data from each of the studies rather than complete sets of data. The study author stated that parent methamidophos and the uncharacterized degradate were not stable when frozen and that artifacts developed.

2. An attempt to isolate and identify the Unknown was made using liquid-liquid partition chromatography, liquid-liquid extraction, dialysis, preparative HPLC, and TLC; however, the degradate was too unstable for analysis.

Table 1. Radioactivity (% of applied) evolved as CO_2 and organic volatiles following the application of S-methyl-labeled [^{14}C]methamidophos, at 10 ppm, to sandy loam soil incubated under anaerobic aquatic conditions.[a]

Sampling interval (days)	CO_2	Organic volatiles[b]
0	ND[c]	ND
1	0.10	0.08
3	0.62	2.06
7	1.58	9.11
14	2.58	17.24
29	3.94	33.40
60	5.64	43.54
92	6.51	47.51
120	6.97	48.48
179	7.53	49.36
232	7.91	50.06

[a] Results from additional sampling intervals were provided by the registrant, but were not reported in this table.

[b] Proposed by the study author to be methane.

[c] Not detected; the detection limit was not specified.

Table 2. [^{14}C]Methamidophos and its degradates (% of applied radioactivity) in combined water layer and soil extracts following the application of [^{14}C]methamidophos, at 10 ppm, to sandy loam soil incubated under anaerobic aquatic conditions.[a,b]

Sampling interval (days)	Methamidophos	Unknown
	Study initiated November, 1984	
0	96.63	2.96
1	85.62	4.79
3	77.26	3.03
7	57.52	1.30
14	38.98	1.60
28	29.52	0.66
62	10.61	0.69
139	1.47	0.14
	Study initiated June, 1984	
122	1.49	ND[c]
	Study initiated January, 1984	
64	6.39	0.16
121	1.42	ND
182	ND	ND
283	ND	ND

[a] Three anaerobic aquatic metabolism studies were performed, and the registrant only provided selected "valid" data from each study.

[b] Results are the average of separate analyses of duplicate samples.

[c] Not detected; detection limit was not specified.

Table 3. Distribution of radioactivity (% of applied) following the application of [^{14}C]methamidophos, at 10 ppm, to sandy loam soil incubated under anaerobic conditions.[a,b]

Sampling interval (days)	Water layer	Soil		
		Methanol-extractable	Unextractable	Total [^{14}C]
		Study initiated November, 1984		
0	84.07	15.68	0.36	100.12
1	72.53	18.18	0.94	91.65
3	66.37	14.26	6.01	86.63
7	47.65	11.57	6.98	66.21
14	32.73	8.21	16.08	57.02
28	24.12	6.05	10.28	40.45
62	8.30	2.99	12.86	24.15
130	1.14	0.53	9.94	11.61
		Study initiated June, 1984		
122	0.82	0.66	6.53	8.01
		Study initiated January, 1984		
64	3.74	2.80	19.10	25.64
121	2.23	2.21	19.97	24.41
182	1.14	1.27	16.07	18.48
283	0.88	1.43	15.74	18.05

[a] Three anaerobic aquatic metabolism studies were performed, and the registrant only provided selected "valid" data from each study.

[b] Results are the average of separate analyses of duplicate samples.

CASE GS -- - METHAMIDOPHOS STUDY 5 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Obrist, J.J. 1979. Leaching characteristics of aged monitor soil residues. Mobay Report No. 68005. Prepared by Mobay Chemical Corp., Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 5.

SUBST. CLASS = S.

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

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Residues of aged (30-days) [^{14}C]methamidophos (consisting of 0.16 ppm of extractable and 1.95 ppm of unextractable [^{14}C]residues) were somewhat mobile in columns of sandy loam soil; 5.3-5.6% of the radioactivity applied to the columns was recovered in the leachate. Between 78.5 and 87.7% of the applied [^{14}C]residues remained in the upper 1.25 cm of the soil columns. The majority (80%) of the residues that remained in the soil were unextractable.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because parent, degradates and eluate were not quantified in column soil segments. (<2% remained in the extractable fraction) and extractable [^{14}C]residues were not characterized.

MATERIALS AND METHODS:

S-Methyl-labeled [^{14}C]methamidophos (radiochemical purity 98%, speci-

fic activity 25.7 mCi/mmol, Mobay Chemical Corp.), at 10 ppm, was incubated in moist Kansas sandy loam soil (58% sand, 32% silt, 10% clay, 2.8% organic matter, pH 5.1, CEC 15.3 meq/100 g) at room temperature for 30 days.

Three glass columns (4.8 cm inside diameter) were packed to a depth of 3 cm with untreated sandy loam soil. The columns were saturated from the bottom with water, and then allowed to drip to field capacity. A layer (10 g) of the aged soil was spread across the top of each column and covered sequentially with a layer of untreated soil and filter paper. The columns were wrapped with aluminum foil, and leached with 1.25 cm of water every day for 45 days, for a total of 56.25 cm (22.1 inches) of water. The total volume of leachate was collected. Following the leaching period, the soil columns were divided into segments between 1.25 and 2.5 cm in thickness.

Aliquots of the leachate were analyzed for total radioactivity using LSC. Leachates collected on days 8, 9, and 10 were combined, mixed with sodium chloride, and extracted three times with methylene chloride:acetone (4:1). The extracts were combined, evaporated to near dryness, redissolved in methylene chloride, and an aliquot was analyzed using TLC on silica gel plates developed in acetonitrile:methanol:water (6:3:1). The sample was cochromatographed with unlabeled methamidophos as a reference standard. The standard was visualized by iodine vapors; radioactive bands were located using a radiochromatogram scanner. Samples of the aged-prior-to-leaching soil and the soil column fractions were analyzed for total radioactivity using LSC following combustion. The remaining soil was extracted with methylene chloride:methanol (7:3) by refluxing for two hours. An aliquot of the extract was analyzed for total radioactivity using LSC; the remaining extract was analyzed by TLC as described. The extracted soil was stirred with 0.5 N sodium hydroxide for 24 hours, then centrifuged. The supernatant was acidified to pH 1 with hydrochloric acid, centrifuged, and total radioactivity in the supernatant (fulvic acids) and solids (humic acids) were determined using LSC. Total radioactivity remaining in the sodium hydroxide-extracted soil (humin) was determined using LSC following combustion. The detection limit for LSC was 0.0002 ppm in solution and 0.0004 ppm in soil.

REPORTED RESULTS:

Following 30 days of aging, 7.9 ppm of the 10 ppm applied to the soil had been volatilized, 1.95 ppm was unextractable (0.91 ppm as fulvic acid, 0.43 ppm as humic acid, and 0.61 ppm as humin) and 0.16 ppm was extractable. The extractable material contained at least two degradates (~~uncharacterized~~) but not methamidophos.

Following 45 days of leaching, 78.5-87.7% of the radioactivity applied to the columns was recovered in the upper 1.25 cm of the columns (Table 1). Of this, ~2.8% was extractable and ~80.8% was unextractable (40.3% was associated with the fulvic acid fraction, 12.0% with the humic acid fraction, and 28.5% with the humin fraction). Less than 0.1% of the applied radioactivity was recovered from the soil below the 7.5-cm column depth; 5.3-5.6% of the applied was recovered in the leachate. The leachate did not contain methamidophos; radioactive compounds in

the leachate did not form discrete bands using the acetonitrile: methanol:water (6:3:1) solvent system.

DISCUSSION:

1. The pesticide was aged for longer than one half-life prior to initiating leaching. Only 1.6% (0.16 ppm) of the applied radioactivity was extractable at the end of the 30-day aging period, the remaining radioactivity had either been volatilized or was part of the organic fraction of the soil.

2. Extractable [^{14}C]residues in the soil prior to and after leaching, as well as [^{14}C]residues in the leachate, were not characterized. The registrant's explanation that [^{14}C]residues in the leachate did not form discrete bands on the TLC plates suggests that the solvent system used to develop the plates may have been inadequate to separate the residues.

3. The columns were leached over a 45-day period. It is preferable, especially with pesticides that degrade rapidly, such as methamidophos, that the columns be leached continually.

Table 1. Distribution of [^{14}C]residues (% of radioactivity applied to column) in three columns of sandy loam soil treated with aged (30-day) [^{14}C]methamidophos residues and leached with 0.5 inches of water daily for 45 days.

Column depth (cm)	Column 1	Column 2	Column 3
0-1.25	78.5	81.0	87.7
1.25-2.50	0.6	0.5	0.5
2.50-5.0	0.4	0.3	0.3
5.0-7.5	0.2	0.1	0.2
7.5-12.5	<0.1[a]	<0.1	<0.1
12.5-17.5	<0.1	<0.1	<0.1
17.5-22.5	<0.1	<0.1	<0.1
22.5-27.5	<0.1	<0.1	<0.1
27.5-30.0	<0.1	<0.1	<0.1
Leachate	5.6	5.3	5.6

[a] Detection limit was 0.0004 ppm in the soil.

CASE GS -- METHAMIDOPHOS STUDY 6 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Thornton, J.S., J.B. Hurley, and J.J. Obrist. 1976. Soil thin-layer mobility of twenty-four pesticide chemicals. Mobay Report No. 51016. Prepared by Mobay Chemical Corp., Kansas City, MO., and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 6.

SUBST. CLASS = S.

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

REVIEWED BY: K. Patten
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APPROVED BY: J. Jordan
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TEL: 557-7463

SIGNATURE: J. Jordan DATE: 3/9/87

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Methamidophos was very mobile on sand, sandy loam, sandy clay loam, silt loam, and silty clay soil TLC plates, with R_f values ranging from 0.91 to 0.98.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because degradate mobility was not determined, test substance was not characterized, soil/water relationship values (K_d) were not reported and the soil CEC was not reported.

MATERIALS AND METHODS:

Sand, sandy loam, sandy clay loam, silt loam, and two silty clay soils were air-dried, sieved to either 420 m (sand, sandy loam, sandy clay loam soils) or 250 m (silt loam and both silty clay soils),

and mixed with sufficient water to produce slurries. The slurries were spread on glass TLC plates (20 x 20 cm; three plates per soil type) to a thickness between 750 and 1,500 m, then air-dried for 24 hours.

[^{14}C]Methamidophos (test substance uncharacterized) was applied at a distance 2.5 cm from the bottom edge of each plate. The plates were then developed in water to a distance 10 cm from the origin, allowed to dry, and autoradiographed.

REPORTED RESULTS:

R_f values for [^{14}C]methamidophos in the six soils ranged from 0.91 to 0.98 (Table 1).

DISCUSSION:

1. Sieving the soils through 250 and 420 m mesh screens would remove the coarse sand fraction and tend to make the pesticide less mobile than in an unsieved or "normally" sieved soil (a 2000 m mesh screen is used in the majority of soil texture analyses). However, since methamidophos proved to be very mobile, the conclusions about the mobility of the pesticide would not change if an unsieved soil was used.

2. The test substance was not characterized.

3. Values of soil/water relationship (K_d) were not provided.

4. Soil CEC was not reported.

5. Degradate mobility was not determined.

Table 1. Soil characteristics.

Soil	Sand	Silt	Clay	Organic matter	pH	R_f values
	%					
Sand[a]	92	1	7	0.8	5.9	0.97
Sandy loam[a]	73	14	13	2.8	6.6	0.97
Sandy clay loam[a]	56	21	23	0.6	5.5	0.98
Silt loam[b]	18	57	25	5.1	7.9	0.95
Silty clay,[b] Maryland	4	53	43	2.1	6.7	0.92
Silty clay,[b] Kansas	0	41	59	0.5	6.0	0.91

[a] Sieved through a 0.42 mm screen.

[b] Sieved through a 0.25 mm screen.

CASE GS -- METHAMIDOPHOS STUDY 7 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 15 - SOLUBLE CONCENTRATE (SC/L)

FICHE/MASTER ID No MRID CONTENT CAT 01

Pack, D.E. 1984. Lack of methamidophos volatility from soil-laboratory study. Prepared and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 7.

SUBST. CLASS = S.

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

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SIGNATURE: Herbert Boyd DATE: 12-5-86

CONCLUSIONS:

Mobility - Laboratory Volatility

This study could not be validated because the soil was not sampled immediately after treatment to confirm the application rate and no quantitative data on the trapping efficiency of the methanol trapping solution were provided, thus, the concentration of residues volatilized could not be determined. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because a material balance was not provided, a residue decline curve was not established, and the physical properties of methamidophos were incompletely described.

MATERIALS AND METHODS:

Sand soil (92% sand, 6% silt, 2% clay, 1.8% organic matter, pH 7.2, CEC 3.6 meq/100 g) was placed in flasks and surface-treated with an aqueous solution of formulated (40% SC/L) S-methyl-labeled [^{14}C]methamidophos (radiochemical purity >99%, specific activity 101,600 dpm/µg, Mobay Chemical Corp.) at 8.2 ppm. The final moisture content of the soil was 80% of field capacity. The treated soil was maintained at 25°C in an incubator with a relative humidity of 100% (Figure 1), and water-saturated air was passed over the soil at an airflow rate of 100 ml/minute.

Volatilized compounds were trapped in methanol, and the trapping solution was changed at 4, 8, and 24 hours and then daily until 14 days posttreatment.

Methanol trapping solutions were evaporated to dryness at <30°C. The residue was dissolved in methanol, spiked with unlabeled methamidophos, and analyzed by TLC with development in ethanol:water (19:1). Following development, methamidophos was visualized by spraying with 2,6-dibromoquinonechlorimide (0.5% in cyclohexane) and heating at 120°C for 10 minutes. Radioactive areas were detected by autoradiography. The detection limit was 100 dpm (1 ng of [^{14}C]methamidophos).

REPORTED RESULTS:

Note: Methamidophos has a reported vapor pressure of 8×10^{-4} mm Hg at 24°C (Schinski, W.L., "Monitor - vapor pressure and maximum vapor concentration", Chevron Chemical Report, April 27, 1972).

No radioactive areas were seen on the autoradiograms that coincided with the parent methamidophos spot on the TLC plates, except in one 5-day sample. However, the duplicate 5-day sample did not show the radioactive area. Quantitation of samples was not attempted. Based on the detection limit, the concentration of methamidophos in the air was <0.007 $\mu g/m^3$ and the rate of volatilization of methamidophos from the soil was $<1 \times 10^{-6}$ $\mu g/cm^2$/hour.

DISCUSSION:

1. A preliminary experiment was conducted to demonstrate that no methamidophos is lost during evaporation of the methanol. The study author stated that recovery of [^{14}C]methamidophos was quantitative after a solution of [^{14}C]methamidophos in methanol was evaporated and the residue was redissolved in methanol. No quantitative data were provided; therefore, the validity of the analytical method could not be verified.

2. A preliminary experiment was conducted to demonstrate that methanol quantitatively removes methamidophos from the air. Air was passed through a column of glass beads moistened with [^{14}C]methamidophos and then through two successive traps containing methanol. After several hours, the methanol trapping solutions were evaporated to dryness, and the residue was analyzed by TLC. The study author stated that the first methanol trap contained all the [^{14}C]methamidophos, and the second trap contained none. No quantitative data were provided; therefore, the trapping efficiency of methanol could not be verified.

3. The soil was not sampled immediately posttreatment to confirm the stated methamidophos application rate. The registrant reported the application rate as 8.2 ppm and 1 lb ai/A; however, these rates are not equivalent.

4. A material balance was not provided.

5. A residue decline curve was not established.

6. The water solubility and soil sorption constant (K_{OC}) of methamidophos were not reported.

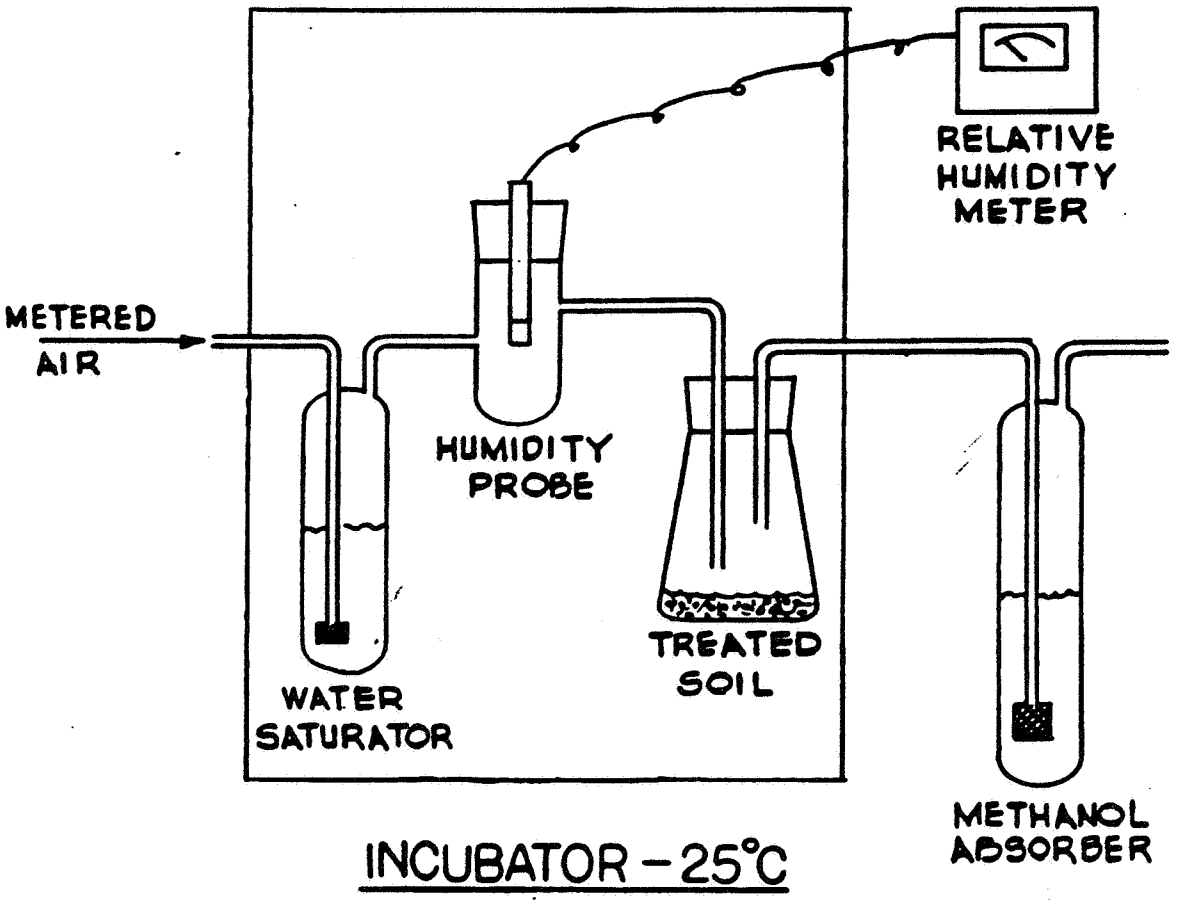

Figure 1. Diagram of soil volatility apparatus.

CASE GS -- METHAMIDOPHOS STUDY 8 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID No MRID CONTENT CAT 01

Murphy, J.J. and R.A. Morris. 1979. Residues of Monitor in rotational crops. Mobay Report No. 68476. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company Richmond, CA. Acc. No. 259942. Reference 8.

SUBST. CLASS = S.

DIRECT RVW TIME = 16 (MH) START-DATE END DATE

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SIGNATURE: Deidre L Boyd DATE: 12-5-86

CONCLUSIONS:

Field Accumulation - Rotaional Crops

This study could not be validated because the analytical methods were referenced rather than described. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was uncharacterized; the residues in soil were not analyzed at the time of treatment, at the 60- and 90-day planting intervals, or at any of the harvest intervals; planting-to-harvest intervals were not provided; a leafy vegetable crop was not planted as a rotational crop; the tops and roots of the root crop (turnips) were not analyzed separately; and the slope of the test site and the depth of the water table were not provided.

MATERIALS AND METHODS:

Cultivated field plots (124-871 feet^2/crop) of silty clay loam soil (8% sand, 62% silt, 30% clay, 3.2% organic matter, pH 6.7, CEC 12 meq/100 g) in Stanley, Kansas, and sand soil (92% sand, 1% silt, 7% clay, 0.8% organic matter, pH 5.9, CEC 1.1 meq/100 g) in Vero Beach, Florida, were

sprayed with methamidophos (test substance uncharacterized) at 3.75, 7.5, 7.5, 15, and 30 lb ai/A.

At ~30, 60, 90, 120, and 365 days posttreatment, carrots or radishes, sorghum or wheat, and snap beans or peas were planted at the Kansas site and corn, turnips, and blackeyed peas were planted at the Florida site. Immediately prior to each planting, the soil was cultivated to a depth of 6 inches. Crops were harvested at maturity. In addition, green forage samples of the grains and green vines from the pod vegetables were taken during the growing season. Soil (0- to 6-inch depth) was sampled at ~30, 120, and 364 days posttreatment. Samples were stored frozen until analysis.

Crop and soil samples were analyzed for methamidophos residues using GC (analytical method referenced; the reference was not provided). The limit of detection for the instrumentation used in residue analysis was 0.01 ppm based on a study using fortified pea samples. However, up to 0.03 ppm of methamidophos was detected in control crop and soil samples; therefore, the limit of detection was set at 0.03 ppm. Recovery from crop samples grown in soil fortified with methamidophos at 0.005-0.5 ppm ranged from 56-118% of the applied. Recovery from soil samples fortified with methamidophos at 0.05-0.5 ppm ranged from 56 to 106% of the applied.

REPORTED RESULTS:

Stanley, Kansas

Methamidophos residues in crop samples were <0.03 ppm, regardless of application rate or planting date (Table 2). At 32 days after the application of methamidophos at 3.75, 7.5, 15, and 30 lb ai/A, methamidophos residues in the silty clay loam soil (0- to 6-inch depth) were 0.04, <0.03, 0.04, and 0.7 ppm, respectively (Table 1). At 120 and 364 days after application, methamidophos residues in soil were <0.03 ppm, regardless of application rate.

From May, 1976 to December, 1977, total rainfall (including irrigation) was 67.8 inches and average monthly soil temperatures (0- to 4-inch depth) ranged from 1 to 28°C.

Vero Beach, Florida

The only crop samples which had residues >0.03 ppm were the green forage samples of corn planted 365 days posttreatment (Table 3). These samples had residues ranging from 0.04-0.15 ppm. Methamidophos residue levels in sand soil (0- to 6-inch depth) were <0.03, regardless of application rate or date or sampling (Table 1).

From July, 1976 to December, 1977, total rainfall was 73.8 inches and average monthly soil temperatures (0- to 4-inch depth) ranged form 12 to 29°C.

DISCUSSION:

1. The test substance was uncharacterized.

2. The analytical methods were referenced but the references not provided for review. The references were:

   Leary, J.B. 1971. Gas chromatographic determination of Monitor (O,S-dimethyl phosphoramidothioate) residue in crops. J. Assoc. Off. Anal. Chem. 54:1396-1398.

   McNamara, F.T. and C.W. Stanley. Mobay Agric. Chem. Report No. 45439.

   Morris, R.A. Mobay Agric. Chem. Report No. 49675.

3. The study authors failed to demonstrate that methamidophos was applied to the soil at the specified rate, since no soil samples were taken immediately after treatment and little or no methamidophos remained in the soil when sampling occurred. In addition, residues in the soil were not analyzed at the 60- and 90-day planting intervals or at any of the harvest intervals.

4. Planting-to-harvest intervals were not provided.

5. A leafy vegetable crop (such as lettuce, mustard, or spinach) was not planted as a rotational crop.

6. It was not indicated which portions of the turnips were analyzed; the tops and roots of the turnips should have been analyzed separately.

7. The recovery of methamidophos from fortified crop and soil samples varied from 56-118% and 56-106%, respectively.

8. Up to 0.03 ppm methamidophos was recovered from both crop and soil control samples. The registrant made the assumption that this was the background level of the pesticide, but did not address the possibility of contamination. Based on control values, the registrant considered the limit of detection to be 0.03 ppm and did not report the specific data <0.03 ppm.

9. Field test data were incomplete; the slope of the test site and depth of the water table were not reported. Also, the reported soil temperatures were not measured at the study sites and may not represent the conditions that existed at the study site. Soil temperatures were measured at Olathe, Kansas (5 miles west of Stanley, Kansas) and at Gainesville, Florida (140 miles northwest of Vero Beach, Florida).

Table 1. Methamidophos residues (ppm) in silty clay loam and sand soil treated with methamidophos at 3.75-30 lb ai/A.[a]

Sampling interval (days)	Treatment rate (lb ai/A)			
	3.75	7.5	15	30
	Silty clay loam (Stanley, KS)			
32	0.04	<0.03	0.04	0.7
120	<0.03[b]	<0.03	<0.03	<0.03
364	0.03	<0.03	<0.03	0.03
	Sand soil (Vero Beach, FL)			
29	<0.03	<0.03	<0.03	<0.03
123	<0.03	<0.03	<0.03	<0.03
364	<0.03	<0.03	<0.03	<0.03
435	<0.03	<0.03	<0.03	<0.03

[a] Methamidophos was applied in Kansas on May 20, 1976, and in Florida on July 8, 1976.

[b] Detection limit 0.03 ppm.

Table 2. Methamidophos residues (ppm) in rotational crops planted in silty clay loam soil treated with methamidophos at 3.75-30 lb ai/A in Stanley, Kansas.[a]

Crop	Plant part	Treatment-to-planting interval (days) 30	60	90	120	365
		3.75 lb ai/A				
Radish[b]	Tops	--[c]	--	--	--	<0.03
	Roots	--	--	--	--	<0.03
Snap beans[d]	Vines	--	--	--	--	<0.03
	Snap beans	--	--	--	--	<0.03
Sorghum[e]	Green forage	--	--	--	--	<0.03
	Grain	--	--	--	--	<0.03
	Dry forage	--	--	--	--	<0.03
		7.5 lb ai/A				
Radish[b]	Tops	--[c]	--	--	--	<0.03
	Roots	--	--	--	--	<0.03
Snap beans[d]	Vines	--	--	--	--	<0.03
	Snap beans	--	--	--	--	<0.03
Sorghum[e]	Green forage	--	--	--	--	--
	Grain	--	--	--	--	<0.03
	Dry forage	--	--	--	--	<0.03
		15 lb ai/A				
Radish[b]	Tops	--	--	--	<0.03	<0.03
	Roots	--	--	--	<0.03	<0.03
Snap beans[d]	Vines	<0.03[f]	<0.03	--	--	<0.03
	Snap beans	<0.03	<0.03	--	--	<0.03
Sorghum[e]	Green forage	<0.03	<0.03	--	<0.03	<0.03
	Grain	<0.03	--	--	--	<0.03
	Dry forage	<0.03	<0.03	--	--	<0.03
		30 lb ai/A				
Radish[b]	Tops	--	--	--	<0.03	<0.03
	Roots	--	--	--	<0.03	<0.03
Snap beans[d]	Vines	<0.03	<0.03	--	--	<0.03
	Snap beans	<0.03	<0.03	--	--	<0.03
Sorghum[e]	Green forage	<0.03	<0.03	--	<0.03	<0.03
	Grain	<0.03	<0.03	--	--	<0.03
	Dry forage	<0.03	<0.03	--	--	<0.03

[a] Methamidophos was applied May 20, 1976.

[b] Carrots were planted at 30, 60, and 90 days posttreatment.

[c] Information not provided or the crop was not sampled, not analyzed, or crop failed.

[d] Peas were planted at 90 days posttreatment.

[e] Wheat was planted at 120 days posttreatment.

[f] Detection limit 0.03 ppm.

Table 3. Methamidophos residues (ppm) in rotational crops planted in sand soil treated with methamidophos at 3.75-30 lb ai/A in Vero Beach, Florida.[a]

Crop	Plant part	Treatment-to-planting interval (days) 30	60	90	120	365
		3.75 lb ai/A				
Turnip	Unspecified	--[b]	--	<0.03	<0.03	--
Blackeyed peas	Vines	<0.03[c]	--	<0.03	--	<0.03
	Peas	<0.03	--	--	--	<0.03
	Pea pods	<0.03	--	--	--	<0.03
Corn	Green forage	<0.03	--	<0.03	<0.03	0.09
	Kernel	<0.03	--	<0.03	--	<0.03
		7.5 lb ai/A				
Turnip	Unspecified	<0.03	--	<0.03	<0.03	--
Blackeyed peas	Vines	<0.03	--	<0.03	--	<0.03
	Peas	<0.03	--	--	--	<0.03
	Pea pods	<0.03	--	--	--	<0.03
Corn	Green forage	<0.03	--	<0.03	<0.03	0.09
	Kernel	<0.03	--	<0.03	--	<0.03
		15 lb ai/A				
Turnip	Unspecified	--	--	<0.03	<0.03	--
Blackeyed peas	Vines	<0.03	--	<0.03	--	<0.03
	Peas	<0.03	--	<0.03	--	<0.03
	Pea pods	<0.03	--	<0.03	--	<0.03
Corn	Green forage	<0.03	--	<0.03	<0.03	0.15
	Kernel	<0.03	--	<0.03	--	<0.03
		30 lb ai/A				
Turnip	Unspecified	--	--	<0.03	<0.03	--
Blackeyed peas	Vines	<0.03	--	<0.03	--	<0.03
	Peas	<0.03	--	<0.03	--	<0.03
	Pea pods	<0.03	--	<0.03	--	<0.03
Corn	Green forage	<0.03	--	<0.03	<0.03	0.04
	Kernel	<0.03	--	<0.03	--	<0.03

[a] Methamidophos applied July 8, 1976.

[b] Information not provided or the crop was not sampled, not analyzed, or crop failed.

[c] Detection limit 0.03 ppm.

CASE GS -- METHAMIDOPHOS STUDY 9 PM --

CHEM 101201 Methamidophos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Strankowski, K.J., G.D. Parker, and J.J. Murphy. 1981. [^{14}C]Monitor rotational crop study. Report No. 69878. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 9.

SUBST. CLASS = S.

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

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TEL: 557-7463

SIGNATURE: DATE: 12-5-86

CONCLUSIONS: Hendrum Boyd

Confined Accumulation - Rotational Crops

1. This study is scientifically valid.

2. Radioactive residues in mature wheat (or oat) heads and stalks, sugar beet tops and roots, and kale planted up to 365 days after the eighth weekly application of methylthio-labeled [^{14}C]methamidophos (purity 73%, specific activity 2.14 mCi/mmol), at 1 lb ai/A, to a loamy sand soil, ranged from 0.343-0.016 ppm for the 30-day treatment-to-planting interval, 0.108-0.006 ppm for the 120-day treatment-to-planting interval, and 0.034-0.007 ppm for the 365-day treatment-to-planting interval. Extractable radioactivity was <0.01 ppm for all crops planted at 30 days posttreatment, except for oat forage, which was 0.035 ppm. [^{14}C]-Residues in soil immediately after the eighth application of methamidophos were 0.463 ppm; radioactivity in soil at planting was 0.379 ppm for crops planted 30 days posttreatment, 0.241 ppm for crops planted 120 days posttreatment, and 0.260 ppm for crops planted 365 days posttreatment. Extractable radioactivity in soil at crop maturity was always <0.004 ppm (detection limit).

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because an analytical grade test substance was not used, degradates were not characterized, meteorological conditions during the study were not provided, planting-to-harvest intervals were not provided, and raw data were not provided.

MATERIALS AND METHODS:

Methylthio-labeled [^{14}C]methamidophos (purity 73%, specific activity 2.14 mCi/mmol), at 1 lb ai/A, was applied as a foliar spray to kale planted outdoors in two bathtubs filled with loamy sand soil (84% sand, 11% silt, 5% clay, 2.7% organic matter, pH 5.0, CEC 10.0 meq/100 g). Applications of methamidophos were made every week thereafter, for a total of 8 weeks. Thirty days after the final methamidophos application, the kale in the first tub was harvested, and the soil was planted with rotational crops of oats, sugar beets, and kale. At 120 days after the final application of methamidophos, the kale in the second tub was harvested, and rotational crops of wheat, sugar beets, and kale were planted. At 365 days after the final methamidophos application, rotational crops of wheat, beets, and kale were planted in the first tub from which the 30-day rotational crops had been harvested. All rotational crops were sampled four times from growth through maturity. Soil samples were taken at each sampling interval.

All crop and soil samples were assayed by LSC following combustion. The mature sample of each crop from the 30-day rotation and the soil samples taken at the harvest of the 30-, 120-, and 365-day crops were also analyzed for extractable residues. Each sample was macerated in chloroform: methanol (7:3) at high speed for 3 minutes, followed by a Soxhlet extraction in the same solvents. An aliquot of the resulting organosoluble fraction was radioassayed using LSC.

REPORTED RESULTS:

As the rotational crops matured, the radioactivity in the plant tissue generally decreased (Table 1). Radioactive residues in the mature samples were 0.343-0.016 ppm in crops planted 30 days posttreatment, 0.108-0.006 ppm in crops planted 120 days posttreatment, and 0.034-0.007 ppm in crops planted 365 days posttreatment. Extractable radioactivity from mature crops planted 30 days posttreatment ranged from <0.004 to 0.035 ppm (Table 2). (Residue data were not expressed in terms of methamidophos.)

Soil sampled after the eighth application of methamidophos contained 0.463 ppm radioactivity. Radioactivity in soil sampled at planting and at crop maturity were 0.379 and 0.183 ppm, respectively, for crops planted 30 days posttreatment; 0.241 and 0.200 ppm for crops planted 120 days posttreatment; and 0.260 and 0.175 ppm for crops planted 365 days posttreatment (Table 1). Extractable radioactivity in soil sampled at crop maturity was always <0.004 ppm (detection limit).

DISCUSSION:

1. An analytical-grade radiolabeled test substance was not used; the purity of the test substance was only 73%.

2. The results were expressed in terms of total extractable radioactivity, and the concentrations of methamidophos and its degradates in samples was not determined. [^{14}C]Residues in samples containing >0.05 ppm total radioactivity should have been characterized.

3. Meteorological conditions during the study were not provided.

4. Planting-to-harvest intervals were not provided.

5. No raw data were provided.

6. The registrant stated that soil samples were taken at each crop sampling time. However, in Table 1, for each set of rotational crops planted on the same day, only one value for soil radioactivity was provided for each sampling interval. Since it is unlikely that all crops matured at the same rate, the registrant has not provided information on soil sampled at maturity of each crop. It was not indicated which crop's sampling intervals correspond to that of the soil data provided.

Table 1. Radioactivity (ppm) in soil and in rotational crops grown in loamy sand soil treated once a week with methamidophos (purity 73%, specific activity 2.14 mCi/mmol), at 1 lb ai/A, for eight consecutive weeks.

Treatment-to planting-interval (days)	Sampling interval	Soil	Wheat[a]			Sugar beets		Kale
			Head	Stalk	Forage	Tops	Roots	
30	Planting	0.379	ND[b]	ND	ND	ND	ND	ND
	1/5 Mature	0.271	ND	0.110	ND	0.075	ND	0.108
	2/5 Mature	0.265	ND	0.099	ND	0.063	ND	0.072
	3/5 Mature	0.375	ND	0.069	ND	0.021	0.174	0.052
	4/5 Mature	0.354	ND	0.058	ND	0.038	0.104	0.047
	Maturity	0.183	0.103	0.041	0.343	0.016	0.041	0.038
120	Planting	0.241	ND	ND	ND	ND	ND	ND
	1/5 Mature	0.343	ND	0.092	ND	0.143	ND	0.050
	2/5 Mature	0.299	ND	0.089	ND	0.079	ND	0.031
	3/5 Mature	0.233	ND	ND	0.993	0.053	ND	0.013
	4/5 Mature	0.187	ND	0.030	ND	0.039	0.126	0.019
	Maturity	0.200	0.016	0.026	0.108	0.013	0.017	0.006
365	Planting	0.260	ND	ND	ND	ND	ND	ND
	1/5 Mature	0.165	ND	0.016	ND	0.015	ND	0.013
	2/5 Mature	0.241	ND	0.006	ND	0.011	ND	0.008
	3/5 Mature	0.226	0.005	0.010	ND	0.007	0.014	0.006
	4/5 Mature	0.189	0.007	0.008	ND	0.007	0.015	0.006
	Maturity	0.175	0.016	0.013	0.034	0.009	0.007	0.008

[a] Oats were planted instead of wheat for the 30-day rotation.

[b] Not detected; the detection limit was 0.004 ppm.

Table 2. Extractable radioactivity (ppm) in mature rotational crops planted in loamy sand soil 30 days after the last of eight weekly applications of methamidophos (purity 73%) at 1 lb ai/A.

Crop	ppm
Oat heads	0.010
Oat stalks	0.005
Oat forage	0.035
Sugar beet tops	ND[a]
Sugar beet roots	ND
Kale	<0.004

[a] Not detected; the detection limit was 0.004 ppm.

EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed in this report but do not fulfill data requirements unless noted in the Recommendations section of this report.

[^{14}C]Methamidophos (radiochemical purity >98%) degraded with half-lives of >30 days (calculated 309 days) at pH 5, 27 days at pH 7, and 3 days at pH 9 in sterile buffered aqueous solutions maintained in the dark at 25 1°C. The major degradate at pH 7 was dimethyldisulfide; the major degradate at pH 9 was desmethyl-methamidophos. Deaminated-methamidophos was 3% of the applied at all three pH's.

[^{14}C]Methamidophos (purity 98%) declined from 12 to 9.4 ppm (calculated half-life 90 days) during 30 days of natural sunlight-irradiation outdoors (17-33°C) in a sterile aqueous solution buffered at pH 5, and from 12 to 10.4 ppm in the dark control during the same interval. [^{14}C]Methamidophos declined from 10 to 8.9 ppm during 5 days of continuous artificial light-irradiation at 33°C in a sterile aqueous solution buffered at pH 5, and from 10 to 9.3 ppm in the dark control during the same period. Degradates in the irradiated solutions in both experiments included desmethyl-methamidophos, deaminated-methamidophos, and one unknown compound (2% of the applied); degradates in the dark controls in both experiments included desmethyl-methamidophos, deaminated-methamidophos, and dimethyldisulfide.

Residues of aged (30-days) [^{14}C]methamidophos (consisting of 0.16 ppm of extractable and 1.95 ppm of unextractable [^{14}C]residues) were somewhat mobile in columns of sandy loam soil; 5.3-5.6% of the radioactivity applied to the columns was recovered in the leachate. Between 78.5 and 87.7% of the applied [^{14}C]residues remained in the upper 1.25 cm of the soil columns. The majority (80%) of the residues that remained in the soil were unextractable.

Methamidophos was very mobile on sand, sandy loam, sandy clay loam, silt loam, and silty clay soil TLC plates, with R_f values ranging from 0.91 to 0.98.

Radioactive residues in mature wheat (or oat) heads and stalks, sugar beet tops and roots, and kale planted up to 365 days after the eighth weekly application of methylthio-labeled [^{14}C]methamidophos (purity 73%, specific activity 2.14 mCi/mmol), at 1 lb ai/A, to a loamy sand soil, ranged from 0.343-0.016 ppm for the 30-day treatment-to-planting interval, 0.108-0.006 ppm for the 120-day treatment-to-planting interval, and 0.034-0.007 ppm for the 365-day treatment-to-planting interval. Extractable radioactivity was 0.01 ppm for all crops planted at 30 days posttreatment, except for oat forage, which was 0.035 ppm. [^{14}C]Residues in soil immediately after the eighth application of methamidophos were 0.463 ppm; radioactivity in soil at planting was 0.379 ppm for crops planted 30 days posttreatment, 0.241 ppm for crops planted 120 days posttreatment, and 0.260 ppm for crops planted 365 days posttreatment. Extractable radioactivity in soil at crop maturity was always <0.004 ppm (detection limit).

RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate of and the exposure of humans and nontarget organisms to methamidophos. The submis-

sion of data relevant to registration requirements (Subdivision N) for terrestrial food crop use sites is summarized below:

Hydrolysis studies: One study (Chopade, 1985a) was reviewed and fulfills data requirements by providing information on the hydrolysis of methamidophos at pH 5, 7, and 9.

Photodegradation studies in water: One study (Chopade, 1985b) was reviewed and fulfills data requirements by providing information on the photodegradation rates and degradates in natural and simulated sunlight.

Photodegradation studies on soil: The Chopade and Freeseman (1985) study is scientifically valid and satisfies the data requirement by giving the rates and degradates of soil photolysis.

Photodegradation studies in air: No data were reviewed for this addendum, but all data may be required depending on the volatility of methamidophos.

Aerobic soil metabolism studies: No data were reviewed for this addendum. Based on data reviewed for the Methamidophos Registration Standard, no additional data are required.

Anaerobic soil metabolism studies: No data were reviewed for this addendum, but all data are required.

Anaerobic aquatic metabolism studies: One study (Pack, 1985) was reviewed and is scientifically invalid because several incomplete experiments (each containing too few sampling intervals and/or incomplete material balance) were combined in an attempt to create a complete anaerobic aquatic metabolism study. In addition, this study would not fulfill data requirements because material balances were incomplete and the test water was not characterized. No data are required because methamidophos has no aquatic or aquatic impact uses.

Aerobic aquatic metabolism studies: No data were reviewed for this addendum; however, no data are required because methamidophos has no aquatic or aquatic impact uses.

Leaching and adsorption/desorption studies: Two studies were reviewed. One study (Obrist, 1979) is scientifically valid but does not fulfill data requirements, because parent and degradates were not quantified (2% remained in the extractable fraction) and extractable [^{14}C]residues were not characterized. The second study (Thornton et al., 1976) is scientifically valid but does not fulfill data requirements because degradate mobility was not determined, the test substance was not characterized, soil/water relationship values (K_d) were not reported, and the soil CEC was not reported. All data are required.

Laboratory volatility studies: One study (Pack, 1984) was reviewed and could not be validated because the soil was not sampled immediately after treatment to confirm the application rate and no quantitative data on the trapping efficiency of the methanol trapping solution were provided, thus, the concentration of residues volatilized could not be determined. In addition, this study would not fulfill data requirements because a material balance was not provid-

ed, a residue decline curve was not established, and the physical properties of methamidophos were incompletely described. All data are required.

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

Terrestrial field dissipation studies: No data were reviewed for this addendum, but all data are required.

Aquatic field dissipation studies: No data were reviewed for this addendum; however, no data are required because methamidophos has no aquatic or aquatic impact uses.

Forestry dissipation studies: No data were reviewed for this addendum; however, no data are required because methamidophos has no forestry uses.

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

Long-term field dissipation studies: No data were reviewed for this addendum. Based on data reviewed for the Methamidophos Registration Standard, no additional data are required.

Confined accumulation studies on rotational crops: One study (Strankowski et al., 1981) was reviewed and is scientifically valid. This study does not fulfill data requirements because an analytical grade test substance was not used, degradates were not characterized, meteorological conditions during the study were not provided, planting-to-harvest intervals were not provided, and raw data were not provided. All data are required.

Field accumulation studies on rotational crops: One study (Murphy and Morris, 1979) was reviewed and could not be validated because the analytical methods were referenced rather than described. In addition, this study would not fulfill data requirements because the test substance was uncharacterized; the residues in soil were not analyzed at the time of treatment, at the 60- and 90-day planting intervals, or at the harvest intervals; planting-to-harvest intervals were not provided; a leafy vegetable crop was not included as a rotational crop; the tops and roots of the root crop (turnips) were not analyzed separately; and the slope of the test site and the depth of the water table were not provided. The data requirement is deferred pending the results of confined rotational crop accumulation studies.

Accumulation studies on irrigated crops: No data were submitted for this addendum; however, no data are required because methamidophos does not have an aquatic food crop or aquatic noncrop use, is not used in and around holding ponds used for irrigation purposes, and has no use involving effluents or discharges to water used for crop irrigation.

Laboratory studies of pesticide accumulation in fish: No data were reviewed for this addendum. Based on data reviewed for the Methamidophos Registration Standard, no additional data are required.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed for this addendum. Based on data reviewed for the Methamidophos Registration Standard, no additional data are required.

Reentry studies: A proposed 24-hour reentry interval was submitted in response to the registration standard. The proposal is under review by EAB.

REFERENCES

The following studies are new submittals reviewed in this report:

Chopade, H.M. 1985a. Hydrolysis of [^{14}C]methamidophos in sterile aqueous buffers. Mobay Report No. 88829. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 1.

Chopade, H.M. 1985b. Photodecomposition of [^{14}C]methamidophos in aqueous solution. Mobay Report No. 88830. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 2.

Chopade, H.M., and P.L. Freeseman. 1985. Photodecomposition of [^{14}C]methamidophos on soil. Mobay Report No. 88831. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 3.

Murphy, J.J. and R.A. Morris. 1979. Residues of Monitor in rotational crops. Mobay Report No. 68476. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company Richmond, CA. Acc. No. 259942. Reference 8.

Obrist, J.J. 1979. Leaching characteristics of aged monitor soil residues. Mobay Report No. 68005. Prepared by Mobay Chemical Corp., Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 5.

Pack, D.E. 1984. Lack of methamidophos volatility from soil-laboratory study. Prepared and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 7.

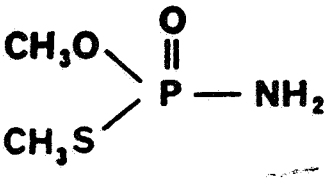
Pack, D.E. 1985. The anaerobic aquatic metabolism of [S-methyl-^{14}C]methamidophos (Monitor). Unpublished study prepared and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 4.

Strankowski, K.J., G.D. Parker, and J.J. Murphy. 1981. [^{14}C]Monitor rotational crop study. Report No. 69878. Prepared by Mobay Chemical Corporation, Kansas City, MO, and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 9.

Thornton, J.S., J.B. Hurley, and J.J. Obrist. 1976. Soil thin-layer mobility of twenty-four pesticide chemicals. Mobay Report No. 51016. Prepared by Mobay Chemical Corp., Kansas City, MO., and submitted by Chevron Chemical Company, Richmond, CA. Acc. No. 259942. Reference 6.

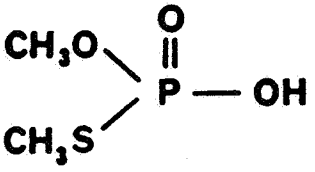
APPENDIX

METHAMIDOPHOS AND ITS DEGRADATES

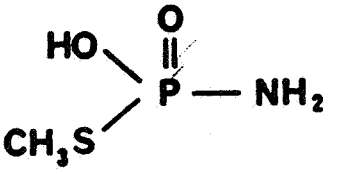


O,S-Dimethyl phosphoramidothioate

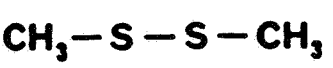
(Methamidophos, Monitor)



Deaminated-methamidophos



Desmethyl-methamidophos



Dimethyldisulfide