

US EPA ARCHIVE DOCUMENT

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Date Out of EFGWB: MAR 29 1989

TO: Jay Ellenberger/R. Whitters
Product Manager 50
Registration Division (TS-767)

FROM:

Paul Mastradone, Acting Section Head *PM*
Environmental Chemistry Review Section #1
Environmental Fate and Groundwater Branch

THRU:

Hank Jacoby, Acting Chief *Hank Jacoby*
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (TS-769C)

Attached please find the EFGWB review of:

Reg./File # : 3125-280 & 3125-341

Chemical Name: Methamidophos

Product Type : Insecticide

Product Name : Monitor 4 Spray

Company Name : Chevron/ Ortho Chemicals

Purpose : Review laboratory volatility study to support registration

standard/review data for new use on safflower/review data on
revised report on confined rotational crop study.

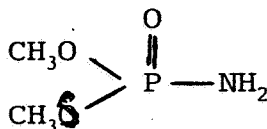
Date Received: 2-28-89/6-14&27-88 Action Code: 660, 335 & 661

Date Completed: 3-7-89 EFGWB No. 903~~9~~3 90171 & 80829

Total Reviewing Time (decimal days): ~~XXXX~~ 10.0
~~XXXX~~

Deferrals to: Ecological Effects Branch, EFED
 Science Integration & Policy Staff, EFED
 Non-Dietary Exposure Branch, HED
 Dietary Exposure Branch
 Toxicology Branch, HED

- 1.0 CHEMICAL: Common Name: Methamidophos
Chemical Name: O , S - D i m e t h y l
phosphoramidate
Trade Name: Monitor
Chemical Structure:



- 2.0 TEST MATERIAL: [S-methyl-¹⁴C]-methamidphos, methamidphos
3.0 STUDY/ACTION TYPE:

Review laboratory volatility study submitted as addendum to registration standard.

- 4.0 STUDY IDENTIFICATION:

Panthani, A. M.. 1988. Laboratory Soil Volatility Study of Methamidophos. Laboratory Project Identification MEF-0087. Chevron Chemical Co. Ortho Agricultural Chemicals Division., Richmond, CA. MRID No. 409852-06.

- 5.0 REVIEWED BY:

Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature
Date:

Clinton Fletcher
3-27-89

- 6.0 APPROVED BY:

Paul J. Mastradone, Ph. D.
Acting Chief, Section 1,
EFGWB/EFED

Signature
Date:

Paul J. Mastradone
3/29/89

- 7.0 CONCLUSION:

The laboratory volatility study is overall scientifically sound. However, before it can be accepted as satisfying the data requirement the following additional information must be submitted by the registrant:

1. Data on the analyses of the storage stability samples stored up to 4 weeks at -20° C.

The author states that no loss and/or degradation of methamidophos was observed during sample storage. However, no quantitative data were provided. Thus, the validity of the storage stability of methamidophos cannot be verified.

2. Data on the soil extraction analyses which confirm the soil extraction efficiency.

The author states that the soil extraction efficiency was 96%. However, no quantitative data were provided. Thus, the validity of the extraction efficiency cannot be verified. The registrant should verify this efficiency by submitting results wherein the soil was sampled immediately post-treatment. This would also verify the soil application rate.

3. Based on this preliminary review of the study, the average rate of volatilization of parent methamidophos was 1.8×10^{-3} ug/cm²/hr and the average air concentration was 58 ug/m³ over the 10 day test period. The maximum amount of volatilized methamidophos was at day 4 when 1.1% (4.8 ug) of the applied ¹⁴C was found in the methanol trap. This calculated to a maximum air concentration 4 days after soil treatment of 171 ug/m³.

8.0 RECOMMENDATION:

1. EFGWB/EFED concludes that the submitted laboratory volatility study is overall scientifically sound. However, before the study can be accepted as satisfying this data requirement, the following additional information must be submitted:

1. Data verifying the storage stability of methamidophos, and
2. Data verifying the soil extraction efficiency of the extraction medium.

2. The registrant should be informed that a field volatility study may be required. This study will provide data to determine an adequate re-entry period for entry into treated fields.

9.0 BACKGROUND:

The registrant, Chevron Chemical Co., has submitted a new laboratory soil volatility study to satisfy this data requirement for methamidophos. The previously submitted study was found to be deficient.

10.0 DISCUSSION OF INDIVIDUAL STUDY:

See separate DATA EVALUATION RECORD.

11.0 COMPLETION OF ONE-LINER: N/A

12.0 CBI APPENDIX:

There is no CBI in this submission.

DATA EVALUATION RECORD

STUDY IDENTIFICATION: Panthani, A. M. 1988., Laboratory Soil Volatility Study of Methamidophos. Laboratory Project Identification MEF-0087. Chevron Chemical Co. Ortho Agricultural Chemicals Division, Richmond, CA. MRID No. 409852-06.

REVIEWED BY:

Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature: *Clinton Fletcher*
Date: 3-27-89

APPROVED BY:

Paul J. Mastradone
Acting Chief, Section 1, EFGWB/EFED

Signature: *Paul J. Mastradone*
Date: MAR 29 1989

TYPE OF STUDY:

Laboratory Volatility Study

CONCLUSIONS:

1.0 This study is overall scientifically sound and will satisfy the data requirement for a laboratory volatility study provided the following additional data is submitted:

1. Data verifying the storage stability of methamidophos, and
2. Data verifying the soil extraction efficiency of the extraction medium.

2.0 Based on preliminary review of the results of the study, EFGWB concludes that the average rate of volatilization for parent methamidophos over the 10 day test period was 1.8×10^{-3} ug/cm²/hr and the average air concentration was 58 ug/m³. The maximum air concentration occurred 4 days after soil treatment with a calculated maximum air concentration of 171 ug/m³. The rate of loss of ¹⁴C from the soil was calculated to be 2.8×10^{-2} ug/cm²/hr.

Methamidophos degraded in the soil with a calculated half-life of 6 days. Degradation products included methyl mercaptan and its volatile derivatives.

MATERIALS AND METHODS:

[S-methyl ¹⁴C]-methamidophos (spec. act. 25.7 mCi/mM. See figure 8 for position of radiolabel) and methamidophos were mixed to formulate the EP MONITOR 4 SPRAY solution (spec. act. 11.37 mCi/mM and 94-96% radiopurity). This solution was applied to a series of cylindrical filter tubes containing sandy soil (see Table 1 for soil characteristics) at an approximate rate of 9 ppm (3X normal field rate) methamidophos. Soil was at 75% field moisture capacity. Humidified air was passed through the soil from the bottom of the fritted tube. The exiting air passed through a methanol (volatile organics) trap and a NaOH (CO₂) trap. The tubes were maintained at 25^o C. Volatile trap solutions were replaced daily with fresh solutions. Duplicate soil samples were taken at 0, 1, 2, 4, and 10 days after treatment.

Methanol traps were evaporated at 30° C and residues were stored in freezer at -20° C until analysis. Soil samples are taken and kept at -20° C for up to 10 days. Part of the 0 day soil sample was stored for 4 weeks for to determine storage stability of residues. Soil samples were extracted with acetonitrile then methanol/water (1:1,v/v). Total radioactivity was determined in soil by combustion and quantitated with liquid scintillation counting. All radioactivity in aliquots was also quantitated by LSC. Qualitative analysis was by thin-layer chromatography (TLC) and High Performance liquid Chromatography (HPLC). Methanol trap solutions from days 6, 7, and 8 were extracted by acid and base hydrolysis and derivatized then analyzed by HPLC. The NaOH traps were acidified then analyzed for radioactivity other than $^{14}\text{CO}_2$.

Extraction efficiencies of the solvents used was determined by extracting a soil sample spiked with a known amount of ^{14}C -methamidophos. Trapping solution efficiency was determined by passing air over ^{14}C -methamidophos applied to glass beads and evaluating various trapping media and air flow rates.

REPORTED RESULTS:

The author reported that the methanol trap solution and an air flow rate of 10 ml/min gave the best recovery in which 112% of the total applied ^{14}C was recovered with 4.4% and 0.1% of the applied radioactivity found in the methanol (organics) trap and NaOH trap, respectively.

The author stated that there was no loss and/or degradation of methamidophos was observed during the storage stability study

Methamidophos degraded in the soil with a half-life of about 6 days and parent methamidophos accounted for less than 10% of the applied ^{14}C remaining in the soil 10 days after treatment. Methamidophos degraded in the soil to volatile methyl mercaptan and its derivatives. A degradation pathway was proposed. (See figure 8.)

After 10 days incubation, 27.5% and 5.1% of the soil applied ^{14}C was present in the methanol and NaOH traps, respectively. (See Tables IV and V.) For the NaOH traps approximately 80% of the trapped radioactivity was $^{14}\text{CO}_2$ at 1 and 2 days after treatment. At 3 and 4 days after treatment, 60% and 40%, respectively, of the ^{14}C in the NaOH traps as $^{14}\text{CO}_2$. The author stated that it was possible that some of the volatile products were not trapped in the methanol solution and were carried over to the NaOH trap. The identity of these volatiles was not pursued.

HPLC analysis of the methanol traps taken daily indicated that dimethyl sulfide as the major volatile trapped on days 1 and 2 after treatment. O,S-dimethyl phosphorothioate (DMPT) was the major volatile trapped on day 3. Parent methamidophos was found in the methanol trap at days 4, 7, and 10 days after treatment (for a total of 1.9% of the applied radioactivity) along with an apparent methyl mercaptan derivative that, because of its volatile nature, its identity could not be confirmed. (See Table VIII.)

Analysis of the soil extracts by TLC and HPLC indicated that methamidophos accounted for 8.86 ppm of the total radioactivity applied at day 0 and declined to 0.74 ppm 10 days after treatment. O-Desmethyl methamidophos and O,S-dimethyl phosphorothioate were the two major degradation products also formed in soil. (See Table IX.) The author stated that methamidophos degraded in soil to volatile methyl mercaptan and its derivatives. A degradation pathway was proposed.

The author reported that 1.9% (8.3 ug) of the soil applied radioactivity was volatilized methamidophos. The average rate of volatilization over the 10 day study period was 1.8×10^{-3} ug/cm²/hr and the average air concentration was 58 ug/m³.

The maximum amount of volatilized methamidophos was at day 4 when 1.14% of the applied radioactivity was found in the methanol (organics) trap. This calculates to a maximum air concentration of 171 ug/m³ at 4 days after soil treatment.

The rate of loss of ¹⁴C from the soil was calculated to be 2.8×10^{-2} ug/cm²/hr.

The author reports that the vapor pressure of methamidophos is 8×10^{-4} mm Hg at 24° C. The maximum air concentration, based on the vapor pressure, is calculated to be 639 ug/m³.

DISCUSSION:

This study is overall scientifically sound. However, there are data deficiencies that do not allow the study to satisfy the data requirement for a laboratory volatility study:

1. The author states that no loss and/or degradation of methamidophos was observed during the period the samples were stored before extraction. However, no quantitative data were provided. Thus, the validity of the storage stability of methamidophos cannot be verified. Data on the storage stability of methamidophos should be provided.
2. The author reports the soil extraction efficiency as being 96%. However, no quantitative data were provided. Thus, the validity of the extraction efficiency cannot be verified. The registrant should verify this extraction efficiency by submitting results wherein the soil was sampled immediately post-treatment. This data would also verify the application rate.

Based on preliminary review of the study, parent methamidophos had an average rate of volatilization of 1.8×10^{-3} ug/cm²/hr and an average air concentration of 58 ug/m³. The maximum air concentration of 171 ug/m³ occurred 4 days after soil treatment. The rate of ¹⁴C loss from the soil during the study was 2.8×10^{-2} ug/cm²/hr.

The reported vapor pressure of methamidophos is 8×10^{-4} mm Hg. The maximum air concentration, based on the vapor pressure, is calculated to be 639 ug/m³.

MEMORANDUM FOR THE RECORD

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BEST ORIGINAL
COPIES AS IN ECB FILE

2. Leaching/adsorption/desorption study

Two studies have been reviewed (Obrist, 1979, and Thorton et al., 1976). Neither study satisfied EPA Guideline requirements. The data of Obrist were considered vaild 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 potential of the parent and degradate was not obtained.

The soil TLC study (Thorton, et al.) did not characterize the test substance and did not report soil/water relationship (K_d) values for methamidophos. However, preliminary review of this study indicated that methamidophos was very mobile in the soils tested with soil TLC R_f values of 0.9 to 0.98.

3. Accumulation--Confined rotational crop study

The study of Strankowski et al. was initially reviewed in 1981 (Enviro Control, 12/9/81) and again in 1987 [(then) EAB review dated 4/22/87] and found deficient. The study conducted using radiolabeled methamidophos with technical methamidophos (only 73% purity) and degradates in the rotated crops were not characterized. Additional deficiencies were noted.

This study was revised by the registrant to correct deficiencies and was resubmitted. However, in the preliminary review of the revised report, the study is still considered unacceptable. No rotational crop intervals can be established from the data provided. Also, the registrant did not resolve all noted deficiencies: The registrant failed to take sufficient soil samples; the identity of residues in crop and soil samples comprising up to 0.11 and 0.43 ppm residues were not determined; the method of soil sampling was not described; storage stability data were not provided; and it was unclear which parts of oat and wheat plants were sampled.

The Murphy and Lewis (1979) rotational crop study was found unacceptable in the EAB review dated 4/22/87. This study had similar deficiencies as those described above.

4. Accumulation--Field rotaional crop study

The study submitted (Murphy and Morris, 1979) could not be validated. deficiencies included: analytical methods referenced but not described, the source of methamidophos residues in control samples was not verified, recoveries from fortified samples ranged from 56% to 118% without adequate explanation, residues in soil samples are not given for the 60 and 90-day intervals or for any harvest interval, and planting to harvest intervals were not described. Field rotational crop studies may still be required depending on the data developed in the confined rotational crop study.

4. Laboratory volatility

The study recently submitted (Panthani, 1988) is deficient in that data on the storage stability of methamidophos was not submitted. The author only stated there was not degradation during storage of samples before analysis. Also, data on the extraction efficiency of the soil extraction medium were not submitted. The author only stated that extraction efficiency was 96% efficient.

5. Terrestrial field dissipation

No data have been submitted for review. However, the (then) EAB review dated 4/22/87 notes that the long term field dissipation study data requirement has been satisfied. However, this reviewer cannot find any record of review for this study.

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

Hydrolysis
 Photolysis on soil and in water
 Aerobic soil metabolism
 Fish accumulation

The review by (then) EAB dated 4/5/88 indicated that a 48 hour reentry interval will be required for products containing methamidophos.

8.0 RECOMMENDATIONS:

Require the registrant to submit data for the deficiencies described in CONCLUSIONS (7.0), above.

9.0 BACKGROUND:

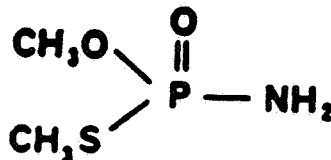
The registrant has submitted a request to register methamidophos (Monitor 4 Liquid Insecticide) for use on safflower to control aphids, armyworm, loopers, and lygus (California and Arizona only). The proposed label calls for applying 1 to 2 pints of Monitor 4 in sufficient water for good spray coverage by air or ground equipment. Use higher rate for control of heavier pest infestations. Apply as needed prior to bloom.

10.0 DISCUSSION OF INDIVIDUAL STUDIES: N/A

11.0 COMPLETION OF ONE-LINER: N/A

12.0 CBI APPENDIX: N/A

1.0 CHEMICAL: Common Name: Methamidophos
Chemical Name: O,S-Dimethyl phosphoroamidithioate
Trade name: Monitor
Chemical structure:



2.0 TEST CHEMICAL: N/A

3.0 STUDY/ACTION TYPE:

Review revised study report submitted in response to EFGWB review dated 4/22/87.


4.0 STUDY IDENTIFICATION:

Strankowski, K.J., G.D. Parker, and J.J. Murphy. 1981, Revised 1988. [¹⁴C]-MONITOR Rotational Crop Study. Report 69878. Mobay Corp., Agricultural Chemical Division, Stilwell, KS. MRID No. 404843-01

[Note: This is a revised report of a previously submitted and reviewed study.]

5.0 REVIEWED BY:

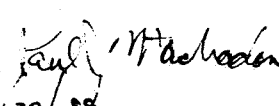
Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature: 

Date: 3-24-85

6.0 APPROVED BY:

Paul J. Mastradone
Acting Chief, Section 1, EFGWB/EFED

Signature: 

Date: 3/29/85

7.0 CONCLUSIONS:

1. EFGWB concludes that this revised study report does not satisfy the requirement for a confined rotational crop study. The study still contains numerous data deficiencies.

2. It does not satisfy the data requirement for the rotational crop-confined study for the following reasons:

The registrant failed to confirm the application rate. No day 0 soil samples were taken. Therefore, the extent of methamidophos uptake by the rotational crop in relation to the concentration of methamidophos in the soil could not be determined;

Total methamidophos residues in crop and soil samples comprising 0.11 and 0.403 ppm residues in crop and soil samples, respectively, were not analyzed for methamidophos and degradates;

The method of soil sampling was not described;

Storage stability data were not provided;

Extraction efficiency data must be provided to verify that all methamidophos residues are in the "organosoluble fraction." Provide data on the other fractions, e.g., aqueous and unextractable fractions.

It is unclear which parts of the oat and wheat plants were sampled. Clarify "forage" in mature crops ("forage" usually refers to immature stages of growth) and "stalks" in immature crops ("stalks" usually refer to mature stages of growth).

3. EFGWB concludes that, while the ¹⁴C residues were not identified and other deficiencies exist in the study, the data suggest that methamidophos will not accumulate in leafy green and root rotational crops planted 30 days after last application and in grain crops planted 120 days after last application.

4. The registrant must verify that all of the methamidophos residues are quantitatively extracted in the organosoluble fraction, supply quantitative data on the aqueous and unextractable fractions and provide the information to satisfy the other deficiencies listed above.

8.0 RECOMMENDATIONS:

Require the registrant to submit information resolving the deficiencies described in CONCLUSIONS (7.0), above.

9.0 BACKGROUND:

The registrant has revised the referenced study to include additional data and requests it be considered as an addendum to the Registration Standard.

10.0 DISCUSSION OF INDIVIDUAL STUDIES:

See attached DATA EVALUATION RECORD.

11.0 COMPLETION OF ONE LINER: N/A

12.0 CBI APPENDIX: N/A

DATA EVALUATION RECORD

STUDY 1

CHEM 101201

Methamidophos

§165-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40484301

Strankowski, K.J., G.D. Parker, and J.J. Murphy. 1981, Revised 1987. [¹⁴C]MONITOR rotational crop study. Report No. 69878. Prepared and submitted by Mobay Corp., Ag. Chem. Division, Stilwell, Kansas.

DIRECT REVIEW TIME = 8

REVIEWED BY: E. Hirsh

TITLE: Staff Scientist

EDITED BY: T. Colvin-Snyder

TITLE: Staff Scientist

APPROVED BY: W. Spangler

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TEL: 557-7495

C. Fletcher
3-24-89

SIGNATURE:

CONCLUSIONS:

Confined Accumulation - Rotational Crops

This revised study is unacceptable because the registrant failed to confirm the application rate; therefore, the extent of pesticide uptake by the rotational crops in relation to the concentration of pesticide in the soil could not be determined. In addition, this study would not fulfil EPA Data Requirements for Registering Pesticides because total methamidophos residues in crop and soil samples comprising up to 0.110 and 0.403 ppm were not analyzed for methamidophos and degradates, the method of soil sampling was not described, storage stability data were not provided, and it was unclear which parts of oat and wheat plants were sampled.

SUMMARY OF THE DATA BY REVIEWER:

[¹⁴C]Methamidophos residues accumulated in mature and immature oats, wheat, beets, and kale planted in loamy sand soil 30, 120, and 365 days following the last of eight weekly foliar applications of methylthio-labeled [¹⁴C]methamidophos (radiochemical purity >99%) to kale at ≈1 lb ai/A/application. In oats planted at 30 days posttreatment (days after the last application), [¹⁴C]methamidophos residues were 0.103 ppm in mature heads, 0.041 ppm in mature stalks, 0.343 ppm in mature forage, and 0.058-0.110 ppm in immature (87-143 days posttreatment, ≈57-113 days postplanting) stalks. In beets planted at 30 days posttreatment, [¹⁴C]methamidophos residues were 0.016 ppm in mature tops, 0.041 ppm in mature bulbs, 0.21-0.075 ppm in immature (87-143 days posttreatment, ≈57-113 days postplanting) tops, 0.104-0.107 ppm in immature (112-143 days posttreatment, ≈92-113 days postplanting) bulbs. In kale planted at 30 days posttreatment, [¹⁴C]methamidophos residues were 0.047 ppm in mature kale and 0.052-0.108 ppm in immature (87-122 days posttreatment, ≈57-92 days postplanting) kale. In mature crops, extractable radioactivity was 0.015 ppm in the oat heads; 0.016 ppm in the oat stalks; 0.031 ppm in oat forage; and not detected (<0.004 ppm) in beet tops, beet bulbs, and kale.

In wheat planted at 120 days posttreatment, [¹⁴C]methamidophos residues were 0.016 ppm in mature heads, 0.026 ppm in mature stalks, 0.108 ppm in mature forage, 0.03-0.092 ppm in immature (143-261 days posttreatment, ≈23-141 days postplanting) stalks, and 0.993 ppm in immature (194 day posttreatment, ≈74 days postplanting) forage. In beets planted at 120 days posttreatment, [¹⁴C]methamidophos residues were 0.013 ppm in mature tops, 0.017 ppm in mature bulbs, 0.039-0.143 in immature (143-226 days posttreatment, ≈23-106 days postplanting) tops, and 0.126 ppm in immature (226 days posttreatment, ≈106 days postplanting) bulbs. In kale planted at 120 days posttreatment, [¹⁴C]methamidophos residues were 0.006 ppm in mature kale and 0.013-0.050 ppm in immature (143-273 days posttreatment, ≈23-153 days postplanting) kale.

In wheat planted at 365 days posttreatment, [¹⁴C]methamidophos residues were 0.016 ppm in mature heads, 0.013 ppm in mature stalks, 0.034 ppm in mature forage, 0.005-0.007 ppm in immature (436-457 days posttreatment, 71-92 days postplanting) heads, 0.006-0.016 ppm in immature (390-418 days posttreatment, 25-53 days postplanting) stalks, and 0.008-0.010 ppm in immature (436-457 days posttreatment, 71-92 days postplanting) forage. In beets planted at 365 days posttreatment, [¹⁴C]methamidophos residues were 0.009 ppm in mature tops, 0.007 ppm in mature bulbs, 0.007-0.015 ppm in immature (390-457 days posttreatment, 25-92 days postplanting) tops, and 0.014-0.015 ppm in immature (436-457 days posttreatment, 71-92 days postplanting) bulbs. In kale planted at 365 days posttreatment, [¹⁴C]methamidophos residues were 0.008 ppm in mature kale and 0.006-0.013 ppm in immature (390-457 days posttreatment, 25-92 days postplanting) kale.

In the soil (depth unspecified) total [¹⁴C]methamidophos residues were 0.463 ppm immediately following the last methamidophos application. In soil planted with rotational crops at 30 days posttreatment, [¹⁴C]metha-

methamidophos residues declined from 0.403 ppm at 31 days posttreatment to 0.137-0.178 ppm at 187-205 days posttreatment. In soil planted with rotational crops at 120 days posttreatment [¹⁴C]methamidophos residues were 0.241 ppm at 118 days posttreatment, and ranged from 0.130 to 0.398 ppm at 143-436 days posttreatment. In soil planted with rotational crops at 365 days posttreatment, [¹⁴C]methamidophos residues declined from 0.260 ppm at 365 days posttreatment to 0.165 ppm at 499 days posttreatment. For all three rotation intervals, extractable radioactivity was not detected (<0.004 ppm) in soil sampled at crop maturity. Air temperatures ranged from 30 to 98°F over the 499 days of the study.

DISCUSSION:

1. The registrant failed to confirm the application rate; therefore, the extent of pesticide uptake by the rotational crops in relation to the concentration of pesticide in the soil could not be determined. [¹⁴C]Residues in the soil immediately following the last methamidophos treatment were analyzed for total radioactivity only, but were not analyzed for methamidophos and degradates. Soil samples should have been taken after each application, and these soil samples should have been analyzed for methamidophos and degradates.
2. Total methamidophos residues in crop samples comprised up to 0.110 ppm but were not analyzed for methamidophos and degradates. Mature crop samples planted at 30 days posttreatment were extracted, and the registrant stated that all methamidophos "is totally found in the organosoluble fraction"; however, no evidence of this was provided by the registrant.
3. Total methamidophos residues in soil samples comprised up to 0.403 ppm but were not analyzed for methamidophos and degradates. Soil samples taken at crop maturity were extracted, and the registrant stated that all methamidophos "is totally found in the organosoluble fraction"; however, no evidence of this was provided by the registrant.
4. The method of soil sampling, including how deep soils were sampled, was not described.
5. Storage of crop and soil samples after sampling and prior to analysis was not addressed; no storage stability data were provided.
6. It is unclear which parts of the plants were included in samples of stalks and forage. In grasses such as wheat and oats, stalks are not present until the plant nears maturity; however, stalks were reportedly sampled from immature as well as mature plants. Also, the term "forage" usually refers to immature leaves that may be grazed by livestock; however, forage was generally not sampled from immature plants and was sampled from all mature oat and wheat plants. The use of the terms "stalks" and "forage" needs to be clarified by the registrant.
7. Methamidophos was not applied to the soil, but was applied as a foliar spray to the target crop kale.

8. In the text of the original report, it is stated that rotational crops were planted at 30 and 120 days posttreatment; however, according to Table II, these crops were planted at 31 and 118 days posttreatment.
9. The nonradiolabeled methamidophos that was mixed with radiolabeled methamidophos was only 73% chemically pure; the nonlabeled test substance should have been more pure.
10. For many of the immature beet samples, roots were not sampled; only the beet tops were sampled. The beet roots that were not sampled were those that were least mature. The concentration of methamidophos in beet bulbs was greatest in the least mature bulbs sampled.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Methylthio-labeled [^{14}C]methamidophos plus technical grade methamidophos (radiochemical purity >99%, specific activity 2.142 mCi/mole, Chemagro) was sprayed onto five week old kale (2-to 3-inches tall) growing in two tubs of loamy sand soil (84% sand, 11% silt, 5% clay 2.7% organic matter, pH 5.0, CEC 10 meq/100 g) at ≈ 1 lb ai/A. Each application consisted of 1.46 mCi of [^{14}C]methamidophos in 0.2 ml of propylene glycol and 80 ml water. The application was repeated eight times at weekly intervals, for a total application rate of ≈ 8 lb ai/A. The tubs were maintained outdoors under wooden canopy shelters between October 11, 1978 and May 30, 1980.

At 30 and 120 days posttreatment (days after the final treatment), the kale was harvested, and oats (30 days only), wheat (120 days only), sugar beets and kale were each planted in tubs of treated soil. At 365 days after the final treatment, a second crop of wheat, sugar beets, and kale were planted into the same tub of treated soil used for rotational crops planted at 30 days posttreatment (all previously planted crops had been harvested prior to this second planting).

The crops were sampled four times when immature and at maturity. All crops planted at 30 days posttreatment (oats, beets, and kale) were harvested at 87, 108, 122, and 143 days posttreatment; in addition, oats were harvested at 187 days posttreatment, and beets were harvested at 205 days posttreatment. For crops planted at 120 days posttreatment, wheat was harvested at 143, 152, 194, 261, and 436 days posttreatment; beets were harvested at 143, 184, 194, 226, and 282 days posttreatment; and kale was harvested at 143, 254, 261, 273, and 331 days posttreatment. All crops planted at 365 days posttreatment (wheat, beets, and kale) were harvested at 390, 418, 436 and 457 days posttreatment; in addition, wheat was harvested at 471 days posttreatment, and beets and kale were harvested at 499 days posttreatment. Soil samples (depth not specified) were taken at planting and at each crop sampling date.

Total radioactivity in plant (pulverized in liquid nitrogen) and soil samples was quantitated by ISC following combustion. No further analysis of the 120 and 365 day crops were conducted due to the low levels (0.007-0.108 ppm) of total radioactivity. Mature plants from the 30 day rotation (174 days posttreatment for kale, 187 days for oats, and 205 days for beets) and soil samples taken at 177, 331, and 471 day posttreatment were macerated in chloroform/methanol (7:3), and then Soxhlet-extracted with this same solvent. Radioactivity in the organosoluble fraction was quantified by ISC. The method detection limit was 0.004 ppm.