

US EPA ARCHIVE DOCUMENT



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Thru: **Henry Jacoby, Chief**
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Environmental Fate & Effects Division (H7507C)

Attached, please find the EFGWB review of...

Reg./File # :039003
Chemical Name :Metam Sodium
Type Product :Soil Fumigant
Product Name :VAPAM
Company Name :Metam-Sodium Task Force
Purpose :Review studies submitted in support of registration.

Action Code: 627
Date Received: 8/2/91

EFGWB #(s): 91-0715
Time: 7 days

Deferrals to:

EEB/EFED

DEB/HED

OREB/HED

TB1/HED

TB2/HED

RSB/RD

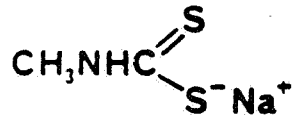
1. CHEMICAL:

chemical name: Sodium Methylthiocarbamate

common name: Metam-Sodium

trade name: VAPAM

structure:



physical/chemical properties:

| | |
|--------------------|--|
| empirical formula: | C ₂ H ₄ NS ₂ Na |
| molecular weight: | 129.2 |
| physical state: | liquid at room temperature |
| boiling point: | 110°C at 763 mm Hg |
| density: | 1.1648 g/ml at 20°C |
| solubility: | 722 g/l at 20°C, pH 7 |
| vapor pressure: | 21.4 torr at 25°C |
| K _{ow} : | <10 at 25°C |

2. TEST MATERIAL:

Metam-Sodium, (sodium methylthiocarbamate)

3. STUDY/ACTION TYPE:

Review studies submitted in support of registration. These include a Hydrolysis, Photodegradation in Water, Photodegradation on Soil, and two Soil Field Dissipation studies.

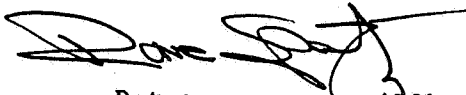
4. STUDY IDENTIFICATION:

- A. Ericson, J.L. 1990. Metam-Sodium - Hydrolysis at pH 5, 7, and 9. Laboratory Project ID No. ENV-017. Report No. RR 90-110B. Unpublished study performed by ICI Americas Inc., Richmond, CA, and submitted by the Metam-Sodium Task Force. Received by EPA on September 19, 1990. MRID #: 416311-01.
- B. Spurgeon, C. 1990. Metam-Sodium - Aqueous Photolysis at 25°C. Laboratory Project ID No. ENV-018. Report No. RR 90-091B. Unpublished study performed by ICI Americas Inc., Richmond, CA, and submitted by the Metam-Sodium Task Force. Received by EPA on June 6, 1990. MRID #: 415177-01.

- C. Haag, W.R., K. Irwin, and T. Mill. 1989. Photolysis of Metam-Sodium on Soil. Laboratory Project ID: SRI 5915-3; ICI ENV-006. Unpublished study performed by SRI International, Menlo Park, CA, and submitted by the Metam-Sodium Task Force. Received by EPA on May 16, 1989. MRID #: 410970-04.
- D. Iwata, Y. 1989b. VAPAM: Field Dissipation Study for Terrestrial Uses, Visalia, California, 1989. Laboratory Project ID: Protocol No. VAPA-89-SD-01; Trial No. US-02-89-221. Report No. RR 89-065B. Unpublished study performed by ICI Americas, Inc., Richmond, CA, and Morse Laboratories, Inc., Sacramento, CA; and submitted by the Metam-Sodium Task Force. Received by EPA on June 6, 1990. MRID #: 415144-01.
- E. Iwata, Y. 1989a. VAPAM: Field Dissipation Study for Terrestrial Uses, Leland, Mississippi, 1989. Laboratory Project ID: Protocol No. VAPA-89-SD-01; Trial No. US-05-89-222. Report No. RR 89-064B. Unpublished study performed by ICI Americas, Inc., Richmond, CA, and Morse Laboratories, Inc., Sacramento CA; and submitted by the Metam-Sodium Task Force. Received by EPA on June 6, 1990. MRID #: 415144-02.
- F. Riggle, B.D. 1991. VAPAM: Cold Storage-Stability Validation for 1,3-Dimethylurea in Soil- Addendum to MRID's 41514401 and 41514402. Laboratory Project ID: VAPA-89-SS-01. Report No. RR 90-413B. Unpublished study performed by ICI Americas, Inc., Richmond, CA; and submitted by the Metam-Sodium Task Force. Received by EPA on February 28, 1991. MRID #: 417986-01.

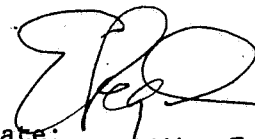
5. REVIEWED BY:

Dana Spatz
Chemist, ECRS #2
EFGWB/EFED/OPP


Date: NOV 4 1991

6. APPROVED BY:

Emil Regelman
Supervisory Chemist, ECRS #2
EFGWB/EFED/OPP


Date: NOV 5 1991

7. CONCLUSIONS:

A. HYDROLYSIS (416311-01)

This study is acceptable and fulfills the Hydrolysis data requirement.

Metam-sodium degraded with a half-life of 2 days at pH 5 and 7, and 4.5 days at pH 9 in buffered aqueous solutions incubated in the dark at

25 ±1°C. The degradates identified in all test solutions were methyl isothiocyanate (MITC), methylamine, 1,3-dimethylthiourea (DMTU), and 1,3-dimethylurea (DMU). The degradate methylcarbamoyl-(dithioperoxy)thioate (MCDT) was identified in the pH 9 test solution. The major degradate formed at pH 5 and 7 was MITC (18% and 60% of initial radioactivity, respectively). At pH 9, two major degradates formed, with MITC accounting for 20% and MCDT accounting for 16% of the initial radioactivity. The formation of methylamine was favored under acidic conditions compared to neutral or alkaline conditions.

B. PHOTODEGRADATION IN WATER (415177-01)

This study is acceptable and fulfills the Photodegradation in Water data requirement.

Metam-sodium degraded with a registrant-calculated half-life of 11.9 minutes, (equivalent to 27.8 minutes of natural California sunlight) in a pH 7 aqueous buffer solution that was irradiated with a filtered xenon arc lamp at 25 ±1°C. The degradates identified were syn- and anti- N-methylthioformamide, methylamine, methyl isothiocyanate (MITC), and sodium methylcarbamoyl-(dithioperoxy)thioate (MCDT). Syn- and anti-N-methylthioformamide were at a maximum concentration of 22.3% by the end of the study interval; methylamine, increased from 14.4 to 17.5%; MITC, increased to 16.0%; and MCDT, increased to 14.1%. Metam-sodium declined from an average concentration of 44.4 mg/L at time zero to 9.5 mg/L by 24.6 minutes posttreatment. The dark control concentration declined to an average of 38.1 mg/L.

Except for syn- and anti- N-methylthioformamide, the degradates identified in this photodegradation study were also identified in the hydrolysis study (41631101).

C. PHOTODEGRADATION ON SOIL (410970-04)

This study provides supplemental information. The following concerns must be satisfactorily addressed by the registrant in order to upgrade this study to acceptable and fulfill the photodegradation on soil data requirement:

- a. The material balances were not provided for the kinetics experiment. This information must be provided along with a clear analysis of identified soil-extracted residues, unidentified soil-extracted residues, soil bound residues, identified trapped volatiles, and unidentified trapped volatiles; comparing the total residues found with the metam-sodium applied. The total sulfur analysis provided for material balance purposes was not adequate. Material balance data must be provided in terms of the amount of each specific residue as well as in terms of percent of applied metam-sodium.

- b. The study authors stated that other than MITC, no carbon-containing degradates were found, although dimethylthiourea had been identified in a previous soil photolysis study (Acc. No. 260468, Project ID: PMS-166, Stauffer Chem. Co.). The current study author reports that dimethylthiourea, carbon disulfide, or methylamine "would have been easily detectable if they had been formed in as little as 1% of the added metam-sodium." Data confirming this statement must be provided. This confirmation should include spectra showing the separation, detection, and identification of metam-sodium and all known degradates by the analytical methods utilized in the study.
- c. A complete set of chromatograms and other relevant raw data including several sample calculations involving the treatment of these data must be submitted.
- d. Humidified air (52% relative humidity) was supplied from a flask containing water saturated with magnesium nitrate. The rationale behind the use of magnesium nitrate was not reported.

Metam-sodium dihydrate (purity 92.6%) at 287 lb ai/A degraded with a registrant-calculated half-life of 70 minutes in loamy sand soil irradiated with a xenon lamp light source at 26°C; while the dark control degraded with a half-life of 63 minutes. Therefore, it was concluded that metam sodium was stable to photodegradation on soil during the course of the study.

Metam-sodium was 119 μMol immediately posttreatment, 92.7 μMol at 60 minutes, 57.7 μMol at 92 minutes and 35.9 μMol at 117 minutes in the irradiated samples. In the dark controls, metam-sodium was 109 μMol immediately posttreatment, 67.5 μMol at 66 minutes, 62.0 μMol at 109 minutes and 15.4 μMol at 157 minutes. The major degradate, methyl isothiocyanate (MITC), was present at 47.5 μMol in irradiated samples at 117 minutes posttreatment, and 66.5 μMol in dark samples at 157 minutes posttreatment. Bisulfide ion was a maximum of 26 μMol in the irradiated samples at 92 minutes, and was a maximum of 10 μMol at 34-66 minutes in the dark controls. Besides MITC, no other carbon-containing degradates were found including methylamine, carbon disulfide and dimethylthiourea.

The degradation in moist soil of metam-sodium to the volatile product MITC was very rapid in both the irradiated samples as well as the dark control, suggesting that photolysis of metam-sodium on soil would not be a significant route of degradation.

D. TERRESTRIAL FIELD DISSIPATION (415144-01, 417986-01)

This study cannot be used to fulfill the Terrestrial Field Dissipation data requirement. This study is unacceptable for the following reasons:

- a. The application rate was not confirmed. The reported 318 lb ai/acre application rate should have yielded an immediate postapplication concentration of approximately 159 ppm Metam-Sodium (equivalent to 90 ppm MITC) at a 0-6" depth. The zero-time sampling interval showed a MITC concentration in soil (0-6" segment) of 49 ppm. This was only 54% recovery of the intended application. No explanation was given for this loss. Spray drift, misapplication, volatilization from the field, analytical error, loss during collection/handling/shipping, etc., could have played a role.
- b. The storage stability data provided in the study report, as well as in the addendum (417986-01: "Cold Storage-Stability Validation for 1,3-Dimethylurea in Soil"), demonstrated that field samples should not have been held in storage for as long as they were before extraction and analysis. Percent recoveries of DMU from sandy loam and silt loam soils (0.50 ppm spike) held in storage at -20°C averaged 80-93% (0, 14, 27 days) until 64 days in storage where the percent recovery dropped to 66-69%. Analysis after 92 days in storage yielded 69-72% recovery. The soil samples from the field dissipation study were held for as long as 130 days before extraction in addition to another 26 days until analysis. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.

For MITC, provided storage stability data included only 3 sampling times; days 0, 87 and 114. These data indicated that MITC samples in soil stored at -20°C could be held for up to 87 days without significant degradation (88-105% recovery). However, after 114 days of storage, recoveries dropped to 78-79%. The soil samples from the field dissipation study were held for as long as 176 days before extraction. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.

- c. The very rapid degradation of Metam-Sodium to MITC in moist soil has been adequately demonstrated in laboratory studies, however, the dissipation of MITC and DMU were not fully tracked in this field dissipation study. Because the major degradate of Metam-Sodium is the highly volatile MITC, attempts should have been made to measure MITC in the air above and around the field plot in order to better define the dissipation of this compound by way of volatilization

from the field. Air samplers should have been placed in and around the field for this purpose.

- d. Several degradates of Metam-Sodium identified in laboratory studies were not looked for in this field dissipation study. These included Methylcarbamodithioperoxothioate (MCDT), Methylamine, and N-methylthioformamide.
- e. Field samples were collected in a predetermined, systematic pattern, not randomly as is recommended.

The Metam-Sodium degradates, methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU), dissipated with registrant-calculated half-lives of 13 hours and 7 days, respectively, from plots of loam soil located in California treated with Metam-Sodium (Vapam, 37% ai) at 318 lb ai/A by an overhead sprinkler. In the 0- to 6-inch soil depth, the degradate methyl isothiocyanate (MITC) was 41-51 ppm immediately posttreatment, 1.2-3.9 ppm at 4 hours, 0.71-1.54 ppm at 8 hours, 0.36-0.98 ppm at 24 hours, and 0.2-0.11 ppm at 4 days posttreatment. MITC was not detected (<0.02 ppm) at 7-14 days posttreatment or at any other soil depth. In the 0- to 6-inch soil depth, the degradate 1,3-dimethylurea (DMU) was 0.22-0.28 ppm immediately posttreatment, 0.21-1.07 ppm at 4 hours to 4 days posttreatment, and 0.17-0.20 at 14 days posttreatment. DMU was not detected (<0.02 ppm) at 32-91 days posttreatment or at any other soil depth.

E. TERRESTRIAL FIELD DISSIPATION (415144-02, 417986-01)

This study cannot be used to fulfill the Terrestrial Field Dissipation data requirement.

This study is unacceptable for the following reasons:

- a. The application rate was not confirmed. The reported 318 lb ai/acre application rate should have yielded an immediate postapplication concentration of approximately 159 ppm Metam-Sodium (equivalent to 90 ppm MITC) at a 0-6" depth. The zero-time sampling interval showed a MITC concentration in soil (0-6" segment) of 22 ppm. This was only 24% recovery of the intended application. No explanation was given for this loss. Spray drift, misapplication, volatilization from the field, analytical error, loss during collection/handling/shipping, etc., could have played a role.
- b. The storage stability data provided in the study report, as well as in the addendum (417986-01: "Cold Storage-Stability Validation for 1,3-Dimethylurea in Soil"), demonstrated that field samples should not have been held in storage for as long as they were before extraction and analysis. Percent

recoveries of DMU from sandy loam and silt loam soils (0.50 ppm spike) held in storage at -20°C averaged 80-93% (0, 14, 27 days) until 64 days in storage where the percent recovery dropped to 66-69%. Analysis after 92 days in storage yielded 69-72% recovery. The soil samples from the field dissipation study were held for as long as 156 days before extraction in addition to another 20 days until analysis. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.

For MITC, provided storage stability data included only 3 sampling times; days 0, 87 and 114. These data indicated that MITC samples in soil stored at -20°C could be held for up to 87 days without significant degradation (88-105% recovery). However, after 114 days of storage, recoveries dropped to 78-79%. The soil samples from the field dissipation study were held for as long as 161 days before extraction. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.

- c. The very rapid degradation of Metam-Sodium to MITC in moist soil has been adequately demonstrated in laboratory studies, however, the dissipation of MITC and DMU were not fully tracked in this field dissipation study. Because the major degradate of Metam-Sodium is the highly volatile MITC, attempts should have been made to measure MITC in the air above and around the field plot in order to better define the dissipation of this compound by way of volatilization from the field. Air samplers should have been placed in and around the field for this purpose.
- d. Several degradates of Metam-Sodium identified in laboratory studies were not looked for in this field dissipation study. These included Methylcarbamo(dithioperoxo)thioate (MCDT), Methylamine, and N-methylthioformamide.
- e. Field samples were collected in a predetermined, systematic pattern, not randomly as is recommended.

The Metam-Sodium degradates, methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU), dissipated with registrant-calculated half-lives of 26 hours and 4 days, respectively, from plots of sandy loam soil located in Mississippi treated with Metam-Sodium (Vapam, 37% ai) at 318 lb ai/A by an overhead sprinkler. In the 0- to 6-inch soil depth, the degradate methyl isothiocyanate (MITC) was 12-22 ppm immediately posttreatment, 7.3-15.0 ppm at 4 hours, 6.3-10.4 ppm at 8 hours, 1.5-10.6 ppm at 24 hours, and 0.07-0.16 ppm at 7 days posttreatment. MITC was not detected (<0.02 ppm) at 14-27 days posttreatment in the 0- to 6-inch soil depth. MITC was detected once in the 6- to 9-inch soil depth at 0.03 ppm at 7

days posttreatment. In the 0- to 6-inch soil depth, the degradate 1,3-dimethylurea (DMU) was 0.11-0.18 ppm immediately posttreatment, 0.09-0.29 ppm at 4 hours to 7 days posttreatment, and ≤ 0.09 ppm at 14 days posttreatment. DMU was not detected (< 0.02 ppm) at 27-91 days posttreatment or at any other soil depth.

8. RECOMMENDATIONS:

The Hydrolysis and Photodegradation in Water data requirements for Metam-Sodium are now satisfied. The Photodegradation in Soil study reviewed in this package was found to provide supplemental information and could possibly be upgraded to acceptable for fulfilling the data requirement if the additional information listed in the Conclusions above are submitted and found to be satisfactory.

As discussed above in the Conclusions, the two Terrestrial Field Dissipation studies were found to have several deficiencies rendering the studies unacceptable. These studies must be repeated. The following recommendations should be taken into account when the new field dissipation studies are conducted:

- a. There was very little rainfall early in the studies and there was no irrigation in one of the studies. These studies would not, therefore, address the situation whereby a heavy rainfall event occurred after application, thus minimizing volatilization and potentially carrying Metam-Sodium and MITC down through the soil profile. Although MITC is volatile, it is also very soluble in water and its Henry's Law constant (2×10^{-4} atm m³/mol) suggests that leaching may be a potential problem under flooded conditions.
- b. The product label for VAPAM (10182-150) suggests that the activity of VAPAM is increased by the use of a tarp spread loosely over the treated area. The label recommends the soil be covered for a minimum period of 48 hours and cultivated seven days after treatment to aerate. A field dissipation study using this regime (tarp) must also be conducted.
- c. The product label also includes a soil injection application method. VAPAM is injected 4 inches deep into the soil. The dissipation of Metam-Sodium and the formation and decline of its degradates following this application method may differ significantly from the dissipation resulting from the sprinkler system application made in the current studies. A field dissipation study with the soil injection application method must also be conducted.

STATUS OF ENVIRONMENTAL FATE DATA REQUIREMENTS FOR
METAM-SODIUM

SATISFIED

161-1 Hydrolysis
161-2 Photodegradation in Water
162-1 Aerobic Soil Metabolism

NOT SATISFIED

161-3 Photodegradation on Soil
161-4 Photodegradation in Air
162-2 Anaerobic Soil Metabolism
162-3 Anaerobic Aquatic Metabolism
162-4 Aerobic Aquatic Metabolism
163-1 Leaching-Adsorption/Desorption
163-2 Laboratory Volatility
164-1 Soil Field Dissipation
164-2 Aquatic (Sediment) Field Dissipation
165-1 Accumulation in Confined Rotational Crops
201-1 Droplet Size Spectrum
202-1 Drift Field Evaluation

RESERVED

163-3 Field Volatility
165-2 Accumulation in Field Rotational Crops
165-4 Accumulation in Fish
166-1 Small-Scale Prospective Ground Water Monitoring

ENVIRONMENTAL FATE SUMMARY

Metam-Sodium is a soil fumigant/wood preservative used primarily as a preplant herbicide to control germinating weed seeds and seedlings in terrestrial food crop, terrestrial nonfood, and aquatic industrial sites. Metam-Sodium is highly unstable in the environment, degrading rapidly to the active soil fumigant, Methyl Isothiocyanate (MITC). In an acceptable Aerobic Soil Metabolism study (401985-02), Metam-Sodium degraded to MITC with a half-life of 23 minutes. MITC was also a major degradate formed in the Hydrolysis (416311-01) and Photodegradation in Water studies (415177-01). A supplemental aged column leaching study (152844) conducted for the metam-sodium DCI demonstrated that MITC is very mobile in soil and has the potential to contaminate ground water. MITC is a Restricted-Use-Pesticide and is on the Ground Water Data Call-In list along with Metam-Sodium.

Insufficient information has been submitted on the fate of Metam-Sodium and its degradate MITC to address a serious concern EFGWB has regarding the fate and transport of these compounds under flooded or anaerobic conditions. Although MITC is volatile, it is also very soluble in water and its Henry's Law constant (2×10^{-4} atm m³/mol) suggests that leaching may be a potential problem under flooded conditions. The potential for either of these compounds to persist and/or move down through the soil as opposed to volatilizing into the atmosphere, must be defined. The required soil field dissipation studies along with the remaining laboratory fate studies should, as discussed above, address this concern.

9. BACKGROUND:

Metam-Sodium is a soil fumigant/wood preservative used primarily as a preplant herbicide to control germinating weed seeds and seedlings in terrestrial food crop, terrestrial nonfood, and aquatic industrial sites. The LUIS report dated 1/21/91 list the following use groups for Metam-Sodium: Terrestrial Food, Terrestrial Feed, Terrestrial Non-Food, Aquatic Non-Food Industrial, Greenhouse Food, Greenhouse Non-Food, and Outdoor Residential. Specific sites include: potato, peanuts, peppermint, agricultural soils, nonagricultural soils, ornamental trees, potting soil, sewage systems, soil preplant indoor, soil preplant outdoor, tobacco, and wood protection treatment.

Metam-Sodium degrades very rapidly to MITC (methyl isothiocyanate) which is the active form of the pesticide. Metam-Sodium has a boiling point of 110°C and a density of 1.165 g/ml at 20°C. Metam-Sodium is readily soluble in water (722 g/L at 20°C). The octanol/water partition coefficient is <10 at 25°C. Metam-Sodium in aqueous solution is volatile with a vapor pressure of 21.4 mm Hg at 25°C. A Ground Water Data Call-In for Metam-Sodium was issued in 1985.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

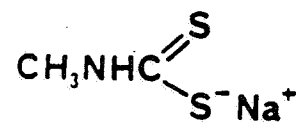
See attached DER's.

11. COMPLETION OF ONE-LINER:

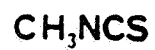
An updated one-liner is attached.

12. CBI APPENDIX:

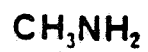
Not applicable.



Sodium N-methyldithiocarbamate
(Metam-sodium)



Methyl isothiocyanate (MITC)



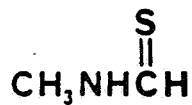
Methylamine



1,3-Dimethylthiourea (DMTU)

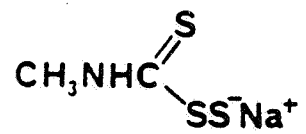


1,3-Dimethylurea (DMU)



N-Methylthioformamide

(syn- and anti-)



Sodium methylcarbamo(dithioperoxo)thioate (MCDT)

Environmental Fate & Effects Division
 PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
 METAM SODIUM

Last Update on November 4, 1991

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

| | | | |
|--------|-----------|---------------|-------|
| LOGOUT | Reviewer: | Section Head: | Date: |
|--------|-----------|---------------|-------|

Common Name: METAM SODIUM

PC Code # : 39003 CAS #: 6734-80-1 Caswell #:

Chem. Name : SODIUM N-METHYLDITHIOCARBAMATE

Action Type: HERBICIDE, NEMATICIDE

Trade Names: METHAM; A7 VAPAM; BUSAN 1020; KARBATION
 (Formul'tn): AQUEOUS SOLUTIONS

Physical State: LIQUID

Use : GENERAL PURPOSE SOIL FUMIGANT, PRE-PLANT HERBICIDE, ACTIVE
 Patterns : AGAINST VARIETY OF INSECTS
 (% Usage) :

Empirical Form: $C_2H_4S_2NNa$
 Molecular Wgt.: 129.20 Vapor Pressure: 21.40E Torr
 Melting Point : °C Boiling Point: 110°C °C
 Log Kow : 0.19 pKa: e °C
 Henry's : E Atm. M3/Mol (Measured) 5.04E -6 (calc'd)

| Solubility in ... | | | | | Comments |
|-------------------|-------|---|-----|----------|----------|
| Water | 7.22E | 5 | ppm | @20.0 °C | |
| Acetone | E | | ppm | e °C | |
| Acetonitrile | E | | ppm | e °C | |
| Benzene | E | | ppm | e °C | |
| Chloroform | E | | ppm | e °C | |
| Ethanol | E | | ppm | e °C | |
| Methanol | E | | ppm | e °C | |
| Toluene | E | | ppm | e °C | |
| Xylene | E | | ppm | e °C | |
| | E | | ppm | e °C | |
| | E | | ppm | e °C | |

Hydrolysis (161-1)

[V] pH 5.0: HALF-LIFE OF 2 DAYS, MAJOR DEGRADATE IS MITC
 [V] pH 7.0: HALF-LIFE OF 2 DAYS, MAJOR DEGRADATE IS MITC
 [V] pH 9.0: HALF-LIFE OF 4.5 DAYS, MAJOR DEGRADATES ARE MITC AND MCDT
 [] pH :
 [] pH :
 [] pH :

15

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
METAM SODIUM

Last Update on November 4, 1991

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Photolysis (161-2, -3, -4)

[V] Water: HALF-LIFE OF 28 MINUTES, MAJOR DEGRADATE IS
[] : SYN- AND ANTI- N-METHYLTHIOFORMAMIDE
[] :
[] :

[S] Soil : STABLE
[] Air :

Aerobic Soil Metabolism (162-1)

[V] T_{1/2} = 23 MINUTES; MITC IS MAJOR DEGRADATE
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Anaerobic Soil Metabolism (162-2)

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Anaerobic Aquatic Metabolism (162-3)

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Aerobic Aquatic Metabolism (162-4)

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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
METAM SODIUM

Last Update on November 4, 1991

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Soil Partition Coefficient (Kd) (163-1)

[S] BASED ON AGED COLUMN LEACHING STUDY, AGED RESIDUES (MITC) WERE
[] VERY MOBILE IN A SANDY CLAY LOAM, LOAMY SAND, AND TWO SAND SOILS
[] AFTER LEACHING, ≈60% OF THE APPLIED WAS IN THE LEACHATES AND ≈12%
[] REMAINED IN THE SOIL COLUMNS.
[]
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Soil Rf Factors (163-1)

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Laboratory Volatility (163-2)

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[]

Field Volatility (163-3)

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Terrestrial Field Dissipation (164-1)

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Aquatic Dissipation (164-2)

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Forestry Dissipation (164-3)

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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
METAM SODIUM

Last Update on November 4, 1991

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Long-Term Soil Dissipation (164-5)

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Accumulation in Rotational Crops, Confined (165-1)

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Accumulation in Rotational Crops, Field (165-2)

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Accumulation in Irrigated Crops (165-3)

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[]

Bioaccumulation in Fish (165-4)

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Bioaccumulation in Non-Target Organisms (165-5)

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Ground Water Monitoring, Prospective (166-1)

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Ground Water Monitoring, Small Scale Retrospective (166-2)

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Ground Water Monitoring, Large Scale Retrospective (166-3)

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Ground Water Monitoring, Miscellaneous Data (158.75)

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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
METAM SODIUM

Last Update on November 4, 1991

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Field Runoff (167-1)

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Surface Water Monitoring (167-2)

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Spray Drift, Droplet Spectrum (201-1)

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Spray Drift, Field Evaluation (202-1)

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Degradation Products

Methylamine

1,3-DIMETHYLUREA (DMU)

1,3-DIMETHYTHIOREA (DMTU)

N-METHYLTHIOFORMAMIDE

METHYL ISOTHIOCYANATE (MITC)

SODIUM METHYLCARBAMO (DITHIOPEROXO) THIOATE (MCDT)

CARBON DISULFIDE

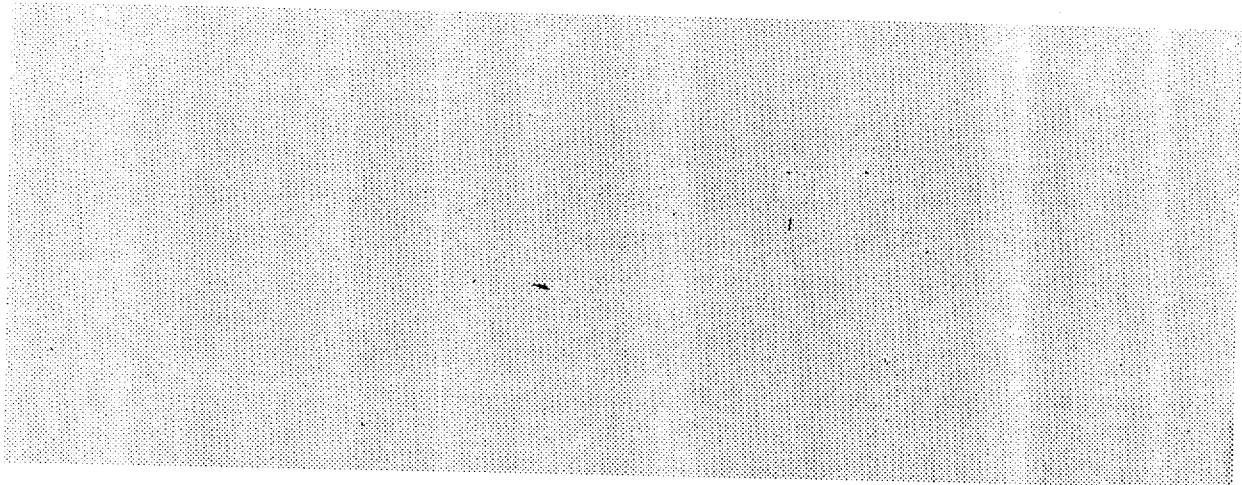
SODIUM HYDROSULFIDE

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
METAM SODIUM

Last Update on November 4, 1991

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Comments



References:

Writer : RJH, DSS

DATA EVALUATION RECORD

STUDY 1

CHEM 039003

Metam-sodium

§161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41631101

Ericson, J.L. 1990. Metam-sodium - hydrolysis at pH 5, 7, and 9. Laboratory Project ID No. ENV-017. Report No. RR 90-110B. Unpublished study performed by ICI Americas Inc., Richmond, CA, and submitted by the Metam-sodium Task Force.

DIRECT REVIEW TIME =16

REVIEWED BY: N. Shishkoff

TITLE: Staff Scientist

EDITED BY: W. Martin
L. Mickley

TITLE: Staff Scientist
Staff Scientist

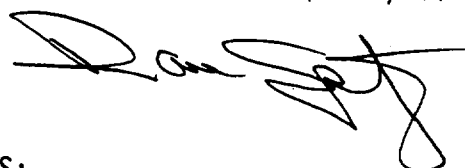
APPROVED BY: W. Spangler

TITLE: Project Manager

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TITLE: Chemist
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NOV 4 1991

CONCLUSIONS:

Degradation - Hydrolysis

This study is acceptable and fulfills the Hydrolysis data requirement.

Metam-sodium degraded with a half-life of 2 days at pH 5 and 7, and 4.5 days at pH 9 in buffered aqueous solutions incubated in the dark at 25 ±1°C. The degradates identified in all test solutions were methyl isothiocyanate (MITC), methylamine, 1,3-dimethylthiourea (DMTU), and 1,3-dimethylurea (DMU). The degradate methylcarbamo-(dithioperoxo)thioate (MCDT) was identified in the pH 9 test solution. The major degradate formed at pH 5 and 7 was MITC (18% and 60% of initial radioactivity, respectively). At pH 9, two major degradates formed, with MITC accounting for 20% and MCDT accounting for 16% of the initial radioactivity. The formation of methylamine was favored under acidic conditions compared to neutral or alkaline conditions.

METHODOLOGY:

Radiolabeled aqueous [methyl-¹⁴C]metam-sodium stock solution had a specific activity of 0.129 Ci/mol and contained 30% metam-sodium by weight. The chemical purity of the stock solution as determined by NMR was >95% and the radiopurity was 78% as determined by HPLC. The major radioimpurities were 1,3-dimethylthiourea (DMTU, 12%) and 1,3-dimethylurea (DMU, 2%). The metam-sodium solutions were prepared by adding 1 μ l of the stock solution to the sterile, buffered aqueous solutions (pH 5, 7 and 9) for every 5 ml of solution prepared. The initial concentrations of metam-sodium in the buffered aqueous solutions were 56-65 mg/L. Aliquots of the treated buffer solutions were transferred to 1-dram sample vials sealed with Teflon-lined caps. The vials were placed in a stainless steel tank with a removable quartz window covered with aluminum foil to exclude light; the temperature was maintained at 25 \pm 1°C with a recirculating water bath. Duplicate vials of the pH 5 test solutions were removed at 0, 0.2, 0.4, 0.8, 1.1, and 1.8 days posttreatment. Duplicate vials of the pH 7 test solutions were removed at 0, 1.0, 1.9, 3.0, 4.1, and 5.1 days posttreatment. Duplicate vials of the pH 9 test solutions were removed at 0, 0.1, 0.2, 0.4, 0.7, 1.0, 1.4, 2.0, 3.0, 3.2, 4.1, and 5.4 days posttreatment.

The test solutions were analyzed immediately after collection. To determine the total radioactivity initially present in the samples, triplicate aliquots of the test solutions were directly injected into an HPLC, the eluant was collected in scintillation vials without passing through a column, and aliquots of the eluant were analyzed by LSC. Additional aliquots of the pH 5 buffer solution were analyzed by reverse-phase HPLC using a cyanopropyl column eluted with methanol:0.02 M pH 7 phosphate buffer (45:55, v:v) containing 0.02 M CTAB (an ion-pair reagent) and 0.015 M EDTA (HPLC Method I). Additional aliquots of the pH 7 and 9 test solutions were analyzed by reverse-phase HPLC using a cyanopropyl column eluted with water:methanol (50:50, v:v) containing 0.02 M CTAB, 0.02 M potassium dihydrogen phosphate, 0.012 M sodium hydroxide, and 0.0003 M EDTA (HPLC Method II). Additional samples from the pH 5 test solution were analyzed by reverse-phase HPLC on a C-18 column eluted with methanol:aqueous 0.035 M phosphate buffer with 0.00033 M hexanesulfonic acid (80:20, v:v; HPLC Method IV). All HPLC columns had UV and radioactive flow detection. Additional aliquots of the test solutions were analyzed by TLC on silica gel plates developed in water:butanol:acetic acid (5:4:1, v:v:v; TLC Method I) or methanol:chloroform (1:10, v:v; TLC Method II). Radioactive areas were located by a quantitative radioimaging system. The retention times and R_f values of the degradates were compared to those of unlabeled reference standards. To confirm tentative identifications from HPLC and TLC, degradates were analyzed by MS (direct-insertion desorption mass spectroscopy and/or negative-ion fast atom bombardment mass spectroscopy) or GC-MS and NMR.

DATA SUMMARY:

Metam-sodium degraded with a half-life of 2 days at pH 5 and 7, and 4.5 days at pH 9 in buffered aqueous solutions incubated in the dark at 25 ±1°C (Table IV). The degradates identified in all test solutions were

methyl isothiocyanate (MITC),
methylamine,
1,3-dimethylthiourea (DMTU), and
1,3-dimethylurea (DMU).

The degradate,

methylcarbamo(dithioperoxo)thioate (MCDT),

was identified in the pH 9 test solutions.

In the pH 5 test solutions, metam-sodium was 78-83% of the applied radioactivity immediately posttreatment, 62-65% at 0.8 days, 53-62% at 1.1 days and 40% at 1.8 days (Table I). MITC increased to 16-19% of the applied radioactivity at 1.8 days; methylamine plus DMTU plus DMU increased from 14% of the applied radioactivity immediately posttreatment to 23-24% at 1.8 days. The increase was attributed to an increase in methylamine. Unassigned radioactivity ("not assigned to a peak") was 1-14% of the applied.

In the pH 7 test solutions, metam-sodium was 76% of the applied radioactivity immediately posttreatment, 61-69% at 1 day, 53-62% at 1.9 days, 27-47% at 3 days, and 13% at 5.1 days (Table II). MITC increased to 55-65% of the applied radioactivity at 5.1 days; methylamine plus DMTU plus DMU were 14-17% at all sampling intervals. An unidentified degradate(s) (Peak 5) was 3-11% of the applied at all sampling intervals; unassigned radioactivity ("not assigned to a peak") was ≤1%.

In the pH 9 test solutions, metam-sodium was 77% of the applied radioactivity immediately posttreatment, 59-61% at 2 days, 47-54% at 3.2 days, and 32-33% at 5.4 days (Table III). MITC increased to 19-20% of the applied radioactivity at 5.4 days; MCDT increased to 16% at 5.4 days, and methylamine plus DMTU plus DMU increased from 14% of the applied radioactivity immediately posttreatment to 20-23% at 5.4 days. The increase was attributed to an increase in methylamine. An unidentified degradate(s) (Peak 5) was 5-9% of the applied at all sampling intervals; unassigned radioactivity ("not assigned to a peak") was 2-7%.

The material balances averaged 94.6%, 93.8%, and 100.9% of applied radioactivity for the pH 5, 7, and 9 experiments, respectively. (Tables I-III).

COMMENTS:

1. The radiopurity of the stock solution was only 78% by HPLC. Attempts to improve the radiopurity of the stock solution were unsuccessful. However, in view of the instability of metam-sodium in dilute aqueous solution and the time required to process the samples, some degradation of metam-sodium would be expected.
2. Three degradates, methylamine, DMTU, and DMU eluted together "under the HPLC conditions employed for the kinetic studies." The study author implied that other methods including MS were used to analyze this peak, however, no data from these analyses were presented. The increase of the peak over time was attributed to an increase in methylamine.

METAM-SODIUM

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 - Description of the product manufacturing process.
 - Description of quality control procedures.
 - Identity of the source of product ingredients.
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DATA EVALUATION RECORD

STUDY 2

CHEM 039003

Metam-sodium

§161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41517701

Spurgeon, C. 1990. Metam-sodium - Aqueous photolysis at 25°C. Laboratory Project ID No. ENV-018. Report No. RR 90-091B. Unpublished study performed by ICI Americas Inc., Richmond, CA, and submitted by the Metam-sodium Task Force.

DIRECT REVIEW TIME = 10

REVIEWED BY: N. Shishkoff

TITLE: Staff Scientist

EDITED BY: W. Martin
L. Mickley

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Staff Scientist


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ORG: Dynamac Corporation
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TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE:



NOV 4 1991

CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is acceptable and fulfills the Photodegradation in Water Data Requirement by providing information on the photodegradation of metam-sodium in aqueous buffered pH 7 solution.
2. Metam-sodium degraded with a registrant-calculated half-life of 11.9 minutes, (equivalent to 27.8 minutes of natural California sunlight) in a pH 7 aqueous buffer solution that was irradiated with a filtered xenon arc lamp at 25 ±1°C. The degradates identified were syn- and anti- N-methylthioformamide, methylamine, methyl isothiocyanate (MITC), and sodium methylcarbamato-(dithioperoxo)thioate (MCDT). Syn- and anti-N-methylthioformamide were at a maximum concentration of 22.3% by the end of the study interval; methylamine, increased from 14.4 to 17.5%; MITC, increased to 16.0%; and MCDT, increased to 14.1%. Metam-sodium declined from an average concentration of 44.4

mg/L at time zero to 9.5 mg/L by 24.6 minutes posttreatment. The dark control concentration declined to an average of 38.1 mg/L.

Except for syn- and anti- N-methylthioformamide, the degradates identified in this photodegradation study were also identified in the hydrolysis study (41631101).

METHODOLOGY:

Methyl-labeled ^{14}C -metam-sodium (radiochemical purity >95%, specific activity 10 mCi/mMol, ICI) plus unlabeled metam-sodium (purity 96.1%) were added at 52.58 mg/L to a sterile (autoclaved) buffer solution adjusted to pH 7 (0.05 M phosphate). Aliquots of the solutions were transferred to sterile quartz photolysis tubes. The filled tubes were flame sealed, and half of the tubes were wrapped in aluminum foil. The tubes were submerged in a recirculating water bath maintained at $25 \pm 1^\circ\text{C}$ in a stainless steel photoreactor with a quartz window. The photoreactor was irradiated with a xenon light source (Heraeus Suntest) filtered to remove wavelengths below 290 nm. Irradiance was measured at the sample location at the beginning and end of the study with a UV/visible spectroradiometer. Duplicate tubes were removed for analysis at 0, 5.4, 12.0, 16.8, and 24.6 minutes for irradiated samples and at 0, 12.0, and 24.6 minutes for dark controls. The samples were either analyzed immediately after sampling by HPLC, or were refrigerated (<13 hr) until analysis.

Aliquots of test solutions were analyzed by HPLC using a cyano column, a mobile phase of methanol:water (50:50, v:v) containing 10 mM phosphate, 10 mM CTAB, and 0.17-0.36 mM EDTA, and with UV detection (220-370 nm; Method I). Additional aliquots of the test solutions were analyzed by HPLC using a cyano column, a mobile phase of methanol:water (40:60, v:v) with 12 mM phosphate, 12 mM CTAB, and 0.10-0.24 mM EDTA, and with radioactive flow detection (Method II). Reference standards were cochromatographed with the aliquots of the test solutions. Aliquots of test solutions were extracted with methylene chloride; the extracts were decanted and evaporated to dryness under nitrogen. The aqueous phase was lyophilized, and the residues were analyzed by GC/MS and NMR.

DATA SUMMARY:

Methyl-labeled ^{14}C -metam-sodium, at 52.58 mg/L, degraded with a half-life of 11.9 minutes (equivalent to 27.8 minutes of natural California sunlight) in a pH 7 aqueous buffered solution irradiated with a filtered xenon arc lamp for up to 24.6 minutes at $25 \pm 1^\circ\text{C}$, corrected for the dark control (Table II, Fig. 4); the average measured light intensity was 487.3 W/m^2 . Metam-sodium declined from

an average concentration of 44.4 mg/L at time zero to 9.5 mg/L by 24.6 minutes posttreatment. The dark control concentration declined to an average of 38.1 mg/L. The degradates identified were:

syn- and anti-N-methylthioformamide,

at a maximum concentration of 22.3% by the end of the study interval;

methylamine,

increased from 14.4 to 17.5%;

methyl isothiocyanate (MITC),

increased to 16.0%; and

sodium methylcarbamodithiothioate (MCDT),

increased to 14.1% (Table VI). The material balances were 90-96% (Table VII).

COMMENTS:

1. The study author stated that metam-sodium has been shown to be most stable "in dilute aqueous solution at pH 7 and 25°C"; however, in the hydrolysis study included in this report (Study 1, MRID 41631101), the half-lives of metam-sodium were 2 days in pH 5 and 7 solutions, and 4.5 days in a pH 9 solution. Although, according to the hydrolysis results, the aqueous photolysis experiment should have been conducted in a pH 9 buffer solution, it is unlikely that there is a significant difference in the photolysis rates of metam-sodium at pH 7 and pH 9.
2. The test solutions were treated with metam-sodium at 52.58 mg/L; the metam-sodium concentration at time 0 was 44.2 mg/L (84% of the applied). The study author reported that "Metam-sodium is unstable in diluted solutions".
3. Metam-sodium and the degradates MITC and MCDT were quantified by HPLC Method I. Syn- and anti-N-methylthioformamide could not be resolved using this solvent system, and could not be reproducibly eluted using Method II; therefore, these degradates were quantified using information derived from both methods.
4. To aid in degradate analysis, metam-sodium was added to water (unbuffered) at 100 mg/L and the solution was irradiated for 1 hour. An aliquot of the test solution was concentrated by rotary evaporation and analyzed by MS. The degradate sodium methylcarbamodithiothioate (MCDT) was identified in the unbuffered solution.

5. The study author calculated that 1 day of irradiation by the xenon light source was equal to 2.33 days of summer sunlight in Richmond, CA.
6. An absorption spectrum of metam-sodium was not provided.

METAN - SODIUM

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 - Description of quality control procedures.
 - Identity of the source of product ingredients.
 - Sales or other commercial/financial information.
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 - The product confidential statement of formula.
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DATA EVALUATION RECORD

STUDY 3

CHEM 039003

Metam-sodium

§161-3

FORMULATION--CO--ACTIVE INGREDIENT

STUDY ID 41097004

Haag, W.R., K. Irwin, and T. Mill. 1989. Photolysis of metam-sodium on soil. Laboratory Project ID: SRI 5915-3; ICI ENV-006. Unpublished study performed by SRI International, Menlo Park, CA, and submitted by the Metam-sodium Task Force.

DIRECT REVIEW TIME =16

REVIEWED BY: N. Shishkoff

TITLE: Staff Scientist

EDITED BY: W. Martin
L. Mickley

TITLE: Staff Scientist
Staff Scientist

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD

SECONDARY REVIEW BY: D. Spatz
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE: 

NOV 4 1991

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study provides supplemental information. The following concerns must be satisfactorily addressed by the registrant in order to upgrade this study to acceptable and fulfill the photodegradation on soil data requirement:
 - a. The material balances were not provided for the kinetics experiment. This information must be provided along with a clear analysis of identified soil-extracted residues, unidentified soil-extracted residues, soil bound residues, identified trapped volatiles, and unidentified trapped volatiles; comparing the total residues found with the metam-sodium applied. The total sulfur analysis provided for material balance purposes was not adequate. Material balance data must be provided in terms of the amount of each specific residue as well as in terms of percent of applied metam-sodium.

- b. The study authors stated that other than MITC, no carbon-containing degradates were found, although dimethylthiourea had been identified in a previous soil photolysis study (Acc. No. 260468, Project ID: PMS-166, Stauffer Chem. Co.). The current study author reports that dimethylthiourea, carbon disulfide, or methylamine "would have been easily detectable if they had been formed in as little as 1% of the added metam-sodium." Data confirming this statement must be provided. This confirmation should include spectra showing the separation, detection, and identification of metam-sodium and all known degradates by the analytical methods utilized in the study.
 - c. A complete set of chromatograms and other relevant raw data including several sample calculations involving the treatment of these data must be submitted.
 - d. Humidified air (52% relative humidity) was supplied from a flask containing water saturated with magnesium nitrate. The rationale behind the use of magnesium nitrate was not reported.
2. Metam-sodium dihydrate (purity 92.6%) at 287 lb ai/A degraded with a registrant-calculated half-life of 70 minutes in loamy sand soil irradiated with a xenon lamp light source at 26°C; while the dark control degraded with a half-life of 63 minutes. Therefore, it was concluded that metam sodium was stable to photodegradation on soil during the course of the study.

Metam-sodium was 119 uMol immediately posttreatment, 92.7 uMol at 60 minutes, 57.7 uMol at 92 minutes and 35.9 uMol at 117 minutes in the irradiated samples. In the dark controls, metam-sodium was 109 uMol immediately posttreatment, 67.5 uMol at 66 minutes, 62.0 uMol at 109 minutes and 15.4 uMol at 157 minutes. The major degradate, methyl isothiocyanate (MITC), was present at 47.5 uMol in irradiated samples at 117 minutes posttreatment, and 66.5 uMol in dark samples at 157 minutes posttreatment. Bisulfide ion was a maximum of 26 uMol in the irradiated samples at 92 minutes, and was a maximum of 10 uMol at 34-66 minutes in the dark controls. Besides MITC, no other carbon-containing degradates were found including methylamine, carbon disulfide and dimethylthiourea.

The degradation in moist soil of metam-sodium to the volatile product MITC was very rapid in both the irradiated samples as well as the dark control, suggesting that photolysis of metam-sodium on soil would not be a significant route of degradation.

METHODOLOGY:

Moistened, sieved (0.246 mm) loamy sand soil (80.2% sand, 14.0% silt, 5.8% clay, 1.9% organic matter, pH 7.8, CEC 12.2 meq/100 g) was spread in a 60 x 10 x 1 mm groove on an aluminum cooling block. Unlabeled metam-sodium dihydrate (purity 92.6%, ICI), dissolved in water (uncharacterized), was applied dropwise to the soil at a rate

equivalent to 287 lb ai/A. The cooling block with the treated soil was placed in a photoreactor with a borosilicate glass cover plate (to filter out wavelengths below 300 nm; Figures 1a,b and 2); the photoreactor was irradiated with a xenon lamp (Varian Eimac R300-3; 300 W) placed 50 cm above the soil surface. A water-filled Pyrex container was placed between the light source and the photoreactor "to remove light below 300 nm and some infrared light"; cooling water was circulated through the block to maintain the temperature at 26°C. Humidified air (52% relative humidity) was drawn through the system at approximately 5 mL/minute and vented sequentially through a tube containing toluene to trap volatile organics and a tube containing a cadmium hydroxide/arabinogalactan solution to trap hydrogen sulfide ("Type I experiment"; designed to measure metam-sodium and "certain products") or dilute HCl to trap methylamine ("Type II experiment"; designed to measure total sulfur). The light intensity was measured using a spectroradiometer and a "laser power meter" with a silicon detector; intensities were compared to noon spring sunlight at 38°N. Samples of the soil were irradiated for up to 136 minutes. After each exposure period, the reactor was disassembled, the soil was removed from the aluminum block for analysis, and the trapping solutions were stored at approximately 3°C in the dark until analysis (<1 day). The dark control samples were placed in the photoreactor; the photoreactor was covered with aluminum foil and placed in the exposure chamber (with the xenon lamp turned off) at 25°C for up to 165 minutes.

The soil from the Type I experiments (to determine decomposition of metam-sodium and formation of "certain products") was rinsed from the cooling plate sequentially with water and toluene into a tube (Figure 5a). The tube was vortexed and centrifuged. An aliquot from the aqueous layer was diluted with deionized water, an aliquot of a cupric chloride in 25% (v:v) acetic acid solution was added to the solution; and the absorbance was determined at 420 nm. An additional aliquot from the aqueous layer was added to a cadmium hydroxide solution; chilled N,N-dimethyl-p-phenylenediamine dihydrochloride in 50% sulfuric acid and 6 M ferric chloride was added to the solution. The mixture was brought to volume (25 mL) with double-distilled water, placed in the dark at room temperature for ≥ 30 minutes, and the absorbance was determined at 670 nm. Aliquots of the aqueous phase, the toluene extract, and the toluene trapping solutions were analyzed by GC with photoionization detection (GC/PID). Aliquots of the cadmium hydroxide trapping solutions were treated and analyzed colorimetrically at 670 nm as previously described.

The soil from the Type II experiments (to determine total sulfur) was scraped from the cooling block into a flask containing 1 N NaOH:30% hydrogen peroxide (2:1, v:v) and shaken on a wrist-action shaker for 10 minutes while "heated briefly with a hot air gun until hot to the touch" (Figure 5b). The flask was then placed in a waterbath at 94°C for ≥ 5 minutes. The slurry was diluted with water and filtered (0.2 μ m). The extract was chromatographed on an AS4A column eluted with 0.75 mM sodium bicarbonate:2.2 mM sodium carbonate with conductivity

detection. Aliquots of the toluene trapping solutions were analyzed by GC/PID; additional aliquots of the toluene trapping solutions were extracted with 24 mM HCl. The HCl extracts of the toluene trapping solutions and aliquots of the HCl trapping solutions were analyzed for methylamine by chromatography on a CS3 column eluted with a 27.5 mM HCl:2.25 mM 2,3-diaminopropionic acid:2.25 mM histidine solution with conductivity detection. The detection limit for methylamine was <0.4% of the applied. The total sulfur recovery was 96-98%. The material balance was calculated by subtraction of sulfur present in the untreated soil from the total sulfur.

DATA SUMMARY:

Metam-sodium dihydrate (purity 92.6%) at 287 lb ai/A degraded with a registrant-calculated half-life of 70 minutes in loamy sand soil irradiated with an artificial light source (xenon lamp) at 26°C; the cumulative intensity of the filtered-light from 300-500 nm was 227 W/m² (Figure 4). Metam-sodium degraded with a registrant-calculated half-life of 63 minutes in the dark controls. Metam-sodium was 119 uMol immediately posttreatment, 92.7 uMol at 60 minutes, 57.7 uMol at 92 minutes and 35.9 uMol at 117 minutes in the irradiated samples (Table I). In the dark controls, metam-sodium was 109 uMol immediately posttreatment, 67.5 uMol at 66 minutes, 62.0 uMol at 109 minutes and 15.4 uMol at 157 minutes. The major degradate,

methyl isothiocyanate (MITC),

was present at 47.5 uMol in irradiated samples at 117 minutes posttreatment, and 66.5 uMol in dark samples at 157 minutes posttreatment (Table II).

Bisulfide ion

was a maximum of 26 uMol in the irradiated samples at 92 minutes, and was a maximum of 10 uMol at 34-66 minutes in the dark controls (Table I).

The material balances in the Type II experiments (total sulfur) ranged from 92.3-100.9% in irradiated samples and 88.9-97.0% in dark controls (Table III).

COMMENTS:

1. The loamy sand soil used in the study was sieved to 0.246 mm which would eliminate medium, coarse and very coarse sands. Standard practice is to use a 2 mm sieve so as to include the complete range of sands. By sieving out the coarser sands, the results could have been biased towards the binding of metam-sodium to the soil by increasing its surface area. However, given the documented rapid degradation of metam-sodium in moist soils, this deficiency in the study is not viewed as having significantly influenced the results.

METAM SODIUM

Page _____ is not included in this copy.

Pages 55 through 68 are not included in this copy.

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- _____ Identity of product inert ingredients.
 - _____ Identity of product inert impurities.
 - _____ Description of the product manufacturing process.
 - _____ Description of quality control procedures.
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 - _____ Sales or other commercial/financial information.
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 - _____ The document is a duplicate of page(s) _____.
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2. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of Metam-Sodium and its degradates.
3. This study is unacceptable for the following reasons:
 - a. The application rate was not confirmed. The reported 318 lb ai/acre application rate should have yielded an immediate postapplication concentration of approximately 159 ppm Metam-Sodium (equivalent to 90 ppm MITC) at a 0-6" depth. The zero-time sampling interval showed a MITC concentration in soil (0-6" segment) of 49 ppm. This was only 54% recovery of the intended application. No explanation was given for this loss. Spray drift, misapplication, volatilization from the field, analytical error, loss during collection/handling/shipping, etc., could have played a role.
 - b. The storage stability data provided in the study report, as well as in the addendum (417986-01: "Cold Storage-Stability Validation for 1,3-Dimethylurea in Soil"), demonstrated that field samples should not have been held in storage for as long as they were before extraction and analysis. Percent recoveries of DMU from sandy loam and silt loam soils (0.50 ppm spike) held in storage at -20°C averaged 80-93% (0, 14, 27 days) until 64 days in storage where the percent recovery dropped to 66-69%. Analysis after 92 days in storage yielded 69-72% recovery. The soil samples from the field dissipation study were held for as long as 130 days before extraction in addition to another 26 days until analysis. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.

For MITC, provided storage stability data included only 3 sampling times; days 0, 87 and 114. These data indicated that MITC samples in soil stored at -20°C could be held for up to 87 days without significant degradation (88-105% recovery). However, after 114 days of storage, recoveries dropped to 78-79%. The soil samples from the field dissipation study were held for as long as 176 days before extraction. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.
 - c. The very rapid degradation of Metam-Sodium to MITC in moist soil has been adequately demonstrated in laboratory studies, however, the dissipation of MITC and DMU were not fully tracked in this field dissipation study. Because the major degradate of Metam-Sodium is the highly volatile MITC, attempts should have been made to measure MITC in the air above and around the field plot in order to better define the dissipation of this compound by way of volatilization from the field. Air samplers

should have been placed in and around the field for this purpose.

- d. Several degradates of Metam-Sodium identified in laboratory studies were not looked for in this field dissipation study. These included Methylcarbam(dithioperoxo)thioate (MCDT), Methylamine, and N-methylthioformamide.
- e. Field samples were collected in a predetermined, systematic pattern, not randomly as is recommended.

METHODOLOGY:

Metam-Sodium (Vapam, 32.7% ai RTU, ICI) was applied by overhead-sprinkler to a bareground plot (90 feet x 150 feet) of loam soil located in Visalia, California, at a rate of 318 lb ai/A on April 13, 1989. The treated plot was subdivided into three subplots (10 feet x 120 feet); a similar plot (10 feet x 120 feet) located 55 feet upwind served as an untreated control. Immediately prior to the Metam-Sodium application, the plot had been irrigated with 434 gallons of water (0.13") to moisten the soil; after application, an additional 371 gallons of water (0.11") were applied to reduce loss due to evaporation. The plots were cultivated to a depth of 1-2 inches and green beans were planted on June 12, 1989. Soil samples were collected from the treated plot immediately posttreatment, at 4, 8, and 24 hours posttreatment, and at 2, 4, 7, and 14 days posttreatment and analyzed for MITC. For DMU analysis, soil samples were collected from the treated plot immediately posttreatment, at 4, 8, and 24 hours posttreatment, and at 2, 4, 7, 14, 32, 60, and 91 days posttreatment. From each subplot, seven soil cores were collected from the 0- to 6-inch depth with a 6.5 inch, zero-contamination corer with a butyrate liner (2-inch diameter), which, when removed, left a stainless steel sleeve in the hole. Seven cores were then collected from the 6- to 30-inch soil depth using a 24-inch zero-contamination corer (1.25-inch diameter) with a butyrate liner, which also, upon removal, left a sleeve in the soil. Three samples were then collected from the 30- to 54-inch soil depth using a 24-inch zero-contamination corer with a butyrate liner (1.25-inch diameter). Soil samples from the untreated plot consisted of collections of ten cores from the 0- to 6-inch depth, ten cores from the 6- to 30-inch depth, and six cores from the 30- to 54-inch depth at the immediately pretreatment sampling interval only. Samples collected at later intervals consisted of ten cores from the 0- to 6-inch depth only. Soil cores were placed in an ice-filled cooler upon collection and were later divided into 0- to 6-, 6- to 9-, 9- to 12-, 12- to 18-, 18- to 30-, 30- to 42-, and 42- to 54-inch segments; soil segments from the same interval, soil depth, and plot were composited. The samples were placed in glass jars, capped, and stored in the freezer

(-10°F) within one hour of processing. The frozen soil samples were shipped to the analytical laboratory, where they were analyzed for methyl isothiocyanate (MITC, 0.02 ppm method detection limit) and 1,3-dimethylurea (DMU, 0.02 ppm method detection limit). Water was added to the jar of soil, and the soil was refrozen and stored (temperature not given). To analyze for MITC, ethyl acetate was added to the frozen soil:water mixture and the slurry was thawed for 12 hours. The thawed slurry was shaken for 2 hours and then centrifuged. An aliquot of the ethyl acetate phase was removed and analyzed by GC. Recoveries from soil fortified with MITC at 0.02-5.0 ppm ranged from 73% to 112% and averaged 95% ±10. To analyze for DMU, methanol was added to the frozen soil:water mixture and the slurry was allowed to thaw. The thawed slurry was shaken for 1 hour and then centrifuged. An aliquot of the aqueous methanol extract was removed and evaporated under vacuum at 45-50°C. The residues were dissolved in ethyl acetate and analyzed by GC. The recoveries from soil fortified with DMU at 0.02-0.2 ppm were 74-113% and averaged 95.5% ±13.8.

DATA SUMMARY:

The Metam-Sodium degradates, methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU), dissipated with registrant-calculated half-lives of 13 hours and 7 days, respectively, from plots of loam soil located in California treated with Metam-Sodium (Vapam, 37% ai) at 318 lb ai/A by an overhead sprinkler.

In the 0- to 6-inch soil depth, the degradate

methyl isothiocyanate (MITC)

was 41-51 ppm immediately posttreatment, 1.2-3.9 ppm at 4 hours, 0.71-1.54 ppm at 8 hours, 0.36-0.98 ppm at 24 hours, and 0.2-0.11 ppm at 4 days posttreatment (Table 4). MITC was not detected (<0.02 ppm) at 7-14 days posttreatment or at any other soil depth. In the 0- to 6-inch soil depth, the degradate

1,3-dimethylurea (DMU)

was 0.22-0.28 ppm immediately posttreatment, 0.21-1.07 ppm at 4 hours to 4 days posttreatment, and 0.17-0.20 at 14 days posttreatment (Table 6). DMU was not detected (<0.02 ppm) at 32-91 days posttreatment or at any other soil depth.

The air temperature during the 6-month study period ranged from 32-104°F. Soil temperatures at the 2-inch depth ranged from 60-100°F. Rainfall over the period totaled 2.77 inches, and approximately 20 inches of irrigation water were applied. Depth to the water table had a yearly range of 10-25 feet, the slope was 0%, and there was no subsurface drainage.

COMMENTS:

1. There was very little rainfall during the course of the study although there was irrigation. This study would not, therefore, address the situation whereby a heavy rainfall event occurred after application, thus minimizing volatilization and potentially carrying Metam-Sodium and MITC down the soil profile. Although MITC is volatile, it is also very soluble in water and its Henry's Law constant (2×10^{-4} atm m³/mol) suggests that leaching may be a potential problem under flooded conditions.
2. The product label for VAPAM (10182-150) suggests that the activity of VAPAM is increased by the use of a tarp spread loosely over the treated area. The label recommends the soil be covered for a minimum period of 48 hours and cultivated seven days after treatment to aerate. A field dissipation study using this regime (tarp) must also be conducted.

The product label also includes a soil injection application method. VAPAM is injected 4 inches deep into the soil. The dissipation of Metam-Sodium and the formation and decline of its degradates following this application method may differ significantly from the dissipation resulting from the sprinkler system application made in this study. A field dissipation study with the soil injection application method must also be conducted.
3. In 1984 and 1988, the trial site was fallow and no chemicals were applied. In 1985, the plots were treated with Benlate, Benomyl, and ICI PP969. In 1986 and 1987, ICI PP993 (FORCE) was applied.

METAM SODIUM

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- Identity of product inert ingredients.
 - Identity of product inert impurities.
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 - Description of quality control procedures.
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DATA EVALUATION RECORD

STUDY 5

CHEM 039003

Metam-Sodium

§164-1

FORMULATION--16--LIQUID-READY TO USE (RTU)

STUDY ID 41514402

Iwata, Y. 1989a. VAPAM: Field dissipation study for terrestrial uses, Leland, Mississippi, 1989. Laboratory Project ID: Protocol No. VAPA-89-SD-01; Trial No. US-05-89-222. Report No. RR 89-064B. Unpublished study performed by ICI Americas, Inc., Richmond, CA, and Morse Laboratories, Inc., Sacramento CA; and submitted by the Metam-Sodium Task Force.

STUDY ID 417986-01

Riggle, B.D. 1991. VAPAM: Cold storage-stability validation for 1,3-Dimethylurea in soil- Addendum to MRID's 41514401 and 41514402. Laboratory Project ID: VAPA-89-SS-01. Report No. RR 90-413B. Unpublished study performed by ICI Americas, Inc., Richmond, CA; and submitted by the Metam-Sodium Task Force.

DIRECT REVIEW TIME = 6

REVIEWED BY: N. Shishkoff

TITLE: Staff Scientist

EDITED BY: W. Martin
L. Mickley

TITLE: Staff Scientist
Staff Scientist

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD

SECONDARY REVIEW BY: D. Spatz

TITLE: Chemist

ORG: EFGWB/EFED/OPP

SIGNATURE: 

NOV 4 1991

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study cannot be used to fulfill the Terrestrial Field Dissipation data requirement.

2. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of Metam Sodium and its degradates.
3. This study is unacceptable for the following reasons:
 - a. The application rate was not confirmed. The reported 318 lb ai/acre application rate should have yielded an immediate postapplication concentration of approximately 159 ppm Metam-Sodium (equivalent to 90 ppm MITC) at a 0-6" depth. The zero-time sampling interval showed a MITC concentration in soil (0-6" segment) of 22 ppm. This was only 24% recovery of the intended application. No explanation was given for this loss. Spray drift, misapplication, volatilization from the field, analytical error, loss during collection/handling/shipping, etc., could have played a role.
 - b. The storage stability data provided in the study report, as well as in the addendum (417986-01: "Cold Storage-Stability Validation for 1,3-Dimethylurea in Soil"), demonstrated that field samples should not have been held in storage for as long as they were before extraction and analysis. Percent recoveries of DMU from sandy loam and silt loam soils (0.50 ppm spike) held in storage at -20°C averaged 80-93% (0, 14, 27 days) until 64 days in storage where the percent recovery dropped to 66-69%. Analysis after 92 days in storage yielded 69-72% recovery. The soil samples from the field dissipation study were held for as long as 156 days before extraction in addition to another 20 days until analysis. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.

For MITC, provided storage stability data included only 3 sampling times; days 0, 87 and 114. These data indicated that MITC samples in soil stored at -20°C could be held for up to 87 days without significant degradation (88-105% recovery). However, after 114 days of storage, recoveries dropped to 78-79%. The soil samples from the field dissipation study were held for as long as 161 days before extraction. The storage stability data do not support this extremely long storage period. Arrangements should have been made to analyze the samples much earlier.
 - c. The very rapid degradation of Metam-Sodium to MITC in moist soil has been adequately demonstrated in laboratory studies, however, the dissipation of MITC and DMU were not fully tracked in this field dissipation study. Because the major degradate of Metam-Sodium is the highly volatile MITC, attempts should have been made to measure MITC in the air above and around the field plot in order to better define the dissipation of this compound by way of volatilization from the field. Air samplers

should have been placed in and around the field for this purpose.

- d. Several degradates of Metam-Sodium identified in laboratory studies were not looked for in this field dissipation study. These included Methylcarbam(dithioperoxo)thioate (MCDT), Methylamine, and N-methylthioformamide.
- e. Field samples were collected in a predetermined, systematic pattern, not randomly as is recommended.

METHODOLOGY:

Metam-Sodium (Vapam, 32.7% ai RTU, ICI) was applied by overhead-sprinkler to a bareground plot (60 feet x 100 feet) of sandy loam soil located in Leland, Mississippi, at a rate of 318 lb ai/A on April 20, 1989. The treated plot was subdivided into three subplots (15 feet x 80 feet); a similar plot (15 feet x 80 feet) located approximately 100 feet upwind served as an untreated control. Immediately prior to the Metam-Sodium application, the plot had been irrigated with 1100 gallons of water (0.17") to moisten the soil; after application, an additional 1050 gallons of water (0.16") were applied to incorporate and reduce evaporative loss. The application of Metam-Sodium involved spraying 2250 gallons of water (0.35"). The plots were rototilled on June 23, and the plots were planted to okra on June 29, 1989. Soil samples were collected from the treated plot immediately posttreatment, at 4, 8, and 24 hours posttreatment, and at 2, 4, 7, 14, and 27 days posttreatment and analyzed for MITC. For DMU analysis, soil samples were collected from the treated plot immediately posttreatment, at 4, 8, and 24 hours posttreatment, and at 2, 4, 7, 14, 27, 63, and 91 days posttreatment. From each subplot, seven soil cores were collected from the 0- to 6-inch depth with a 6.5-inch, zero-contamination corer with a butyrate liner (2-inch diameter), which, when removed, left a stainless steel sleeve in the hole. Seven cores were then collected from the 6- to 30-inch soil depth using a 24-inch zero-contamination corer (1.25-inch diameter) with a butyrate liner, which also, upon removal, left a sleeve in the soil. Three samples were then collected from the 30- to 54-inch soil depth using a 24-inch zero-contamination corer with a butyrate liner (1.25-inch diameter). Soil sampling for the untreated plot consisted of collections of ten cores from the 0- to 6-inch depth, ten cores from the 6- to 30-inch depth and six cores from the 30- to 54-inch depth at the immediately pretreatment sampling interval only. Samples collected at later intervals consisted of ten cores from the 0- to 6-inch depth only. Soil samples were placed in an ice-filled cooler upon collection and were later divided into 0- to 6-, 6- to 9-, 9- to 12-, 12- to 18-, 18- to 30-, 30- to 42-, and 42- to 54-inch segments; soil segments from the same interval, soil depth, and plot were composited. The samples were placed in glass jars, capped, and stored in the freezer (<-4°F) within one hour of processing. The frozen soil samples were shipped to the analytical laboratory where

they were analyzed for methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU). Water was added to the jar of soil, which was refrozen and stored (temperature not given). To analyze for MITC, ethyl acetate was added to the frozen soil:water mixture and the slurry was thawed for 12 hours. The thawed slurry was shaken and then centrifuged. An aliquot of the ethyl acetate phase was removed and analyzed by GC. Recoveries from soil fortified with MITC at 0.02-10.0 ppm ranged from 78% to 112% and averaged 94% ±10. To analyze for DMU, methanol was added to the frozen soil:water mixture and the slurry was allowed to thaw. The thawed slurry was shaken and centrifuged. An aliquot of the aqueous methanol extract was removed and evaporated under vacuum at 45-50°C. The residues were dissolved in ethyl acetate and analyzed by GC. The recoveries from soil fortified with DMU at 0.02-1.0 ppm were 70-116% and averaged 90% ±11.

DATA SUMMARY:

The Metam-Sodium degradates, methyl isothiocyanate (MITC) and 1,3-dimethylurea (DMU), dissipated with registrant-calculated half-lives of 26 hours and 4 days, respectively, from plots of sandy loam soil located in Mississippi treated with Metam-Sodium (Vapam, 37% ai) at 318 lb ai/A by an overhead sprinkler.

In the 0- to 6-inch soil depth, the degradate

methyl isothiocyanate (MITC)

was 12-22 ppm immediately posttreatment, 7.3-15.0 ppm at 4 hours, 6.3-10.4 ppm at 8 hours, 1.5-10.6 ppm at 24 hours, and 0.07-0.16 ppm at 7 days posttreatment (Table 4). MITC was not detected (<0.02 ppm) at 14-27 days posttreatment in the 0- to 6-inch soil depth. MITC was detected once in the 6- to 9-inch soil depth at 0.03 ppm at 7 days posttreatment.

In the 0- to 6-inch soil depth, the degradate

1,3-dimethylurea (DMU)

was 0.11-0.18 ppm immediately posttreatment, 0.09-0.29 ppm at 4 hours to 7 days posttreatment, and ≤0.09 ppm at 14 days posttreatment (Table 6). DMU was not detected (<0.02 ppm) at 27-91 days posttreatment or at any other soil depth.

The air temperature during the 6-month study period ranged from 31-99°F. Soil temperatures at the 2-inch depth ranged from 49-98°F. Rainfall over the period totaled 36.62 inches, and 1.36 inches of irrigation water was applied. Depth to the water table was an average of 6.5 feet and slope was 0.5% toward the North and 2% toward the East.

COMMENTS:

1. There was very little rainfall early in the study and there was no irrigation. This study would not, therefore, address the situation whereby a heavy rainfall event occurred after application, thus minimizing volatilization and potentially carrying Metam-Sodium and MITC down the soil profile. Although MITC is volatile, it is also very soluble in water and its Henry's Law constant (2×10^{-4} atm m³/mol) suggests that leaching may be a potential problem under flooded conditions.
2. The product label for VAPAM (10182-150) suggests that the activity of VAPAM is increased by the use of a tarp spread loosely over the treated area. The label recommends the soil be covered for a minimum period of 48 hours and cultivated seven days after treatment to aerate. A field dissipation study using this regime (tarp) must also be conducted.

The product label also includes a soil injection application method. VAPAM is injected 4 inches deep into the soil. The dissipation of Metam-Sodium and the formation and decline of its degradates following this application method may differ significantly from the dissipation resulting from the sprinkler system application made in this study. A field dissipation study with the soil injection application method must also be conducted.

3. In 1986 and 1987, the trial site was fallow and no chemicals were applied. In 1988, the plots were treated with norflurazon, fluometuran, and ICI R250020. Weeds were controlled during the study period with two applications of ROUNDUP.

METAN SODIUM

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