

EFGWB No.: 91-0193, -0194, -0195, -0196, -0197, -0198, -0283  
Case No.: 2390  
Chemical No.: 039002, 039003  
DP Barcode No.: D158636, 158599, 158620, 158781, 158756, 158739, 158590

## MEMORANDUM

**SUBJECT:** Review of Phase IV Package for Sodium and Potassium Salts of Methylthiocarbamate

**FROM:** Dana S. Spatz, Chemist  
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**THRU:** Henry Jacoby, Chief  
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**TO:** Amy Rispin, Chief  
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Environmental Fate and Effects Division (H7507C)

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 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.

Metam-Sodium appears to be highly unstable in the environment. According to an acceptable Aerobic Soil Metabolism study (401985-02), metam-sodium degrades rapidly ( $t_{1/2}$ : 23 minutes) to the active soil fumigant, methylisothiocyanate (MITC). As such, it is essential that the environmental fate studies conducted using metam-sodium as the test substance include an examination of the formation and degradation of MITC. MITC is a Restricted-Use-Pesticide and is also under a Ground Water Data Call-In. 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.

Potassium N-Methylthiocarbamate is the potassium salt of Metam and should behave identically to Metam-Sodium in the environment. Therefore, studies conducted to satisfy the data requirements for Metam-Sodium may also apply towards fulfilling the data requirements for the potassium salt.

The Phase IV review package for List B chemical Methyldithiocarbamate (case no. 2390) was received by EFGWB on December 3, 1990. The package contained the Phase III response from the Metam-Sodium Task Force; six companies supporting Sodium N-Methyldithiocarbamate, and the Phase III response from Buckman Labs, Inc., supporting Potassium N-Methyldithiocarbamate.

For Metam-Sodium, the Metam-Sodium Task Force has submitted eight summaries and/or studies to satisfy seven data requirements (161-1, 161-2, 161-3, 162-1, 162-2, 163-1, and 164-1). In addition, three waiver requests were submitted (161-4, 162-3, and 165-1).

For Potassium N-Methyldithiocarbamate, Buckman Labs, Inc. has submitted three studies and/or summaries (161-1, 161-2 and 163-1), a commitment to supply two more studies (162-3 and 162-4), and a waiver request for two data requirements (164-2 and 165-4).

The LUIS report dated 1/21/91 lists 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.

A second LUIS report dated 1/21/91 lists the Aquatic Non-Food Industrial use group for Potassium N-Methyldithiocarbamate. Specific sites include: water cooling systems, air washer water systems, evaporative condenser water systems, pulp/paper mill water systems, and secondary oil recovery injection water.

#### Sodium N-Methyldithiocarbamate

The following environmental fate data requirements apply to the above listed use patterns:

Data Requirement	Status
161-1 Hydrolysis	not satisfied
161-2 Photodegradation in Water	not satisfied
161-3 Photodegradation on Soil	not satisfied
161-4 Photodegradation in Air	not satisfied
162-1 Aerobic Soil Metabolism	satisfied
162-2 Anaerobic Soil Metabolism	not satisfied
162-3 Anaerobic Aquatic Metabolism	not satisfied
162-4 Aerobic Aquatic Metabolism	not satisfied
163-1 Leaching-Adsorption/Desorption	not satisfied
163-2 Laboratory Volatility	not satisfied
163-3 Field Volatility	reserved
164-1 Soil Field Dissipation	not satisfied
164-2 Aquatic (Sediment) Field Dissipation	not satisfied
164-5 Long-Term Soil Field Dissipation	reserved
165-1 Accumulation in Confined Rotational Crops	not satisfied
165-2 Accumulation in Field Rotational Crops	reserved
165-4 Accumulation in Fish	reserved
166-1 Small-Scale Prospective Ground Water Monitoring	reserved
166-2 Small-Scale Retrospective Ground Water Monitoring	reserved
166-3 Large-Scale Retrospective Ground Water Monitoring	reserved
201-1 Droplet Size Spectrum	not satisfied
202-1 Drift Field Evaluation	not satisfied

**Potassium N-Methyldithiocarbamate**

The following environmental fate data requirements apply to the Aquatic Non-Food Industrial use pattern:

<b>Data Requirement</b>	<b>Status</b>
161-1 Hydrolysis	not satisfied
161-2 Photodegradation in Water	not satisfied
162-3 Anaerobic Aquatic Metabolism	not satisfied
162-4 Aerobic Aquatic Metabolism	not satisfied
163-1 Leaching-Adsorption/Desorption	not satisfied
164-2 Aquatic (Sediment) Field Dissipation	not satisfied
165-4 Accumulation in Fish	reserved

Attached, please find two Phase IV summary tables listing the environmental fate data requirements for Metam-Sodium and its potassium salt. Also attached is EFGWB's review of the summaries/studies submitted by the registrants.

1. CHEMICAL:

chemical name: Sodium N-methyldithiocarbamate

common name: Metam-Sodium

trade name: Vapam

structure:

physical/chemical properties:

Empirical Formula:	C <sub>2</sub> H <sub>4</sub> NS <sub>2</sub> 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 <sub>ow</sub> :	<10 at 25°C

2. TEST MATERIAL:

Metam-Sodium, (Sodium N-Methyldithiocarbamate)

3. STUDY/ACTION TYPE:

Review summaries/studies for Branch's Phase IV response.

4. STUDY IDENTIFICATION:

Burnett, T.J. "Vapam Aerobic Soil Metabolism". Performed and submitted by Stauffer Chemical Company. Study completed on May 8, 1987. Received by EPA on 5/13/87. Document number: PMS-226; MRC-87-21. MRID #: 401985-02.

Burnett, T.J. "Vapam Anaerobic Soil Metabolism". Performed and submitted by Stauffer Chemical Company. Study completed on May 8, 1987. Received by EPA on 5/13/87. Document number: PMS-194; MRC-87-22. MRID #: 401985-01.

Burnett, T.J. "Vapam Soil Mobility". Performed and submitted by Stauffer Chemical Company. MRC Report No. 85-08. Received by EPA on 12/4/85. Acc. No.: 152844.

Ericson, J.L. "Metam-Sodium - Hydrolysis at pH 5, 7 and 9". Performed by ICI Americas, Inc. Submitted by the Metam-Sodium Task Force: (BASF, Buckman, ICI, Amvac, Or-Cal, UCB). Project ID Number: ENV-017. Received by EPA on 9/19/90. MRID #: 416311-01.

Haag, Werner. "Photolysis of Metam-Sodium on Soil". Performed by SRI International. Sponsored by ICI Americas, Inc. Study completed on January 12, 1989. Received by EPA on 5/16/89. MRID #: 410970-04.

Iwata, Yutaka. "VAPAM: Field Dissipation Study for Terrestrial Uses; Visalia, California, 1989". Performed by ICI Americas and Morse Labs. Study completed on 11/28/89. Received by EPA on 6/6/90. MRID #: 415144-01.

Iwata, Yutaka. "VAPAM: Field Dissipation Study for Terrestrial Uses; Leland, Mississippi, 1989". Performed by ICI Americas and Morse Labs. Study completed on 11/28/89. Received by EPA on 6/6/90. MRID #: 415144-02.

Spurgeon, Colleen. "Metam-Sodium - Aqueous Photolysis at 25°C." Performed by ICI Americas, Inc. Study completed on April 30, 1990. Project ID Number: ENV-018. Received by EPA on 6/6/90. MRID #: 415177-01.

5. REVIEWED BY:

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EFGWB/EFED/OPP

Date:

6. APPROVED BY:

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

Date:

7. CONCLUSIONS:

- A. *Ericson, J.L. "Metam-Sodium - Hydrolysis at pH 5, 7 and 9". Performed by ICI Americas, Inc. Submitted by the Metam-Sodium Task Force: (BASF, Buckman, ICI, Amvac, Or-Cal, UCB). Project ID Number: ENV-017. Received by EPA on 9/19/90. MRID #: 416311-01.*

Based upon a screening of this Hydrolysis study, EFGWB concludes that the study warrants a comprehensive review which will be performed in Phase V.

- B. *Spurgeon, Colleen. "Metam-Sodium - Aqueous Photolysis at 25°C." Performed by ICI Americas, Inc. Study completed on April 30, 1990. Project ID Number: ENV-018. Received by EPA on 6/6/90. MRID #: 415177-01.*

Based upon a review of the summary for this Photodegradation in Water study and a screening of the study itself, EFGWB concludes that the data warrant a comprehensive review which will be performed in Phase V.

- C. Haag, Werner. "Photolysis of Metam-Sodium on Soil". Performed by SRI International. Sponsored by ICI Americas, Inc. Study completed on January 12, 1989. Received by EPA on 5/16/89. MRID #: 410970-04.

Based upon a review of the summary for this Photodegradation on Soil study and a screening of the study itself, EFGWB concludes that the data warrant a comprehensive review which will be performed in Phase V.

- D. Burnett, T.J. "Vapam Aerobic Soil Metabolism". Performed and submitted by Stauffer Chemical Company. Study completed on May 8, 1987. Received by EPA on 5/13/87. Document number: PMS-226; MRC-87-21. MRID #: 401985-02.

This study is acceptable and fulfills the Aerobic Soil Metabolism data requirement.

Metam-sodium degraded with a registrant-calculated half-life of 23 minutes in sand soil that was incubated in the dark at 28°C and 75% of field moisture capacity. At 1 day posttreatment, only 8.7% of the applied radioactivity was recovered from the soil. The majority of the residues had been volatilized: 83% of the applied as methylisothiocyanate (MITC); 0.2% as other organic volatiles, and 0.9% as CO<sub>2</sub>.

See attached DER for complete review.

- E. Burnett, T.J. "Vapam Anaerobic Soil Metabolism". Performed and submitted by Stauffer Chemical Company. Study completed on May 8, 1987. Received by EPA on 5/13/87. Document number: PMS-194; MRC-87-22. MRID #: 401985-01.

This study is not acceptable in fulfilling the Anaerobic Soil Metabolism (162-2) data requirement. The Phase III summary as well as a screening of the submitted study established that it does not satisfy Subdivision N requirements. The design of the study did not permit an adequate determination of the fate of Metam-Sodium in soil under anaerobic conditions. According to the registrant, because Metam-Sodium degrades rapidly to the highly volatile MITC in soil under aerobic conditions ( $t_{1/2}$ =23 minutes), the degradation under anaerobic conditions could not be determined because parent compound was not subjected to anaerobic conditions. Apparently, the degradation of parent went to completion upon initiation of the study. In addition, sampling of the flooded soil and floodwater did not occur until 1 day after anaerobic conditions were initiated and anaerobicity (Eh measurement) was not confirmed. A new study must be conducted in which anaerobic conditions have already been attained before dosing with Metam-Sodium. This study must define the metabolism of Metam-Sodium in soil under anaerobic conditions as well as the fate of the major degradate, MITC.

- F. Burnett, T.J. "Vapam Soil Mobility". Performed and submitted by Stauffer Chemical Company. MRC Report No. 85-08. Received by EPA on 12/4/85. Acc. No.: 152844.

This study cannot be used to fulfill the Leaching-Adsorption/Desorption data requirement. This study provides supplemental information but does not meet Subdivision N guidelines for the following reasons:

- a. The soils were not analyzed after aging and immediately prior to leaching, so that the composition and concentration of the aged residues at the start of leaching was unknown.
- b. Soils were sieved through a 0.5 mm mesh, not the required 2 mm. Increasing the effective surface area of the soil may have served to artificially increase the  $k_d$  values.
- c. Total recovery was only 70 to 78% of the applied radioactivity for the four soil types.
- d. The analytical technique for identifying residues, gas chromatography, does not provide confirmatory identification. MS should have been used to confirm the identification of the residues.
- e. The residues remaining in the aqueous phase after extraction with ethyl acetate (7 to 14% of the activity recovered in the leachate) were not identified.

Metam-sodium residues were very mobile in a sandy clay loam, a loamy sand, and two sand soils. Methyl isothiocyanate (MITC) was identified as the predominant compound ( $\geq 86\%$  of radioactivity) recovered in the leachates. In each soil, approximately 60% of the applied  $^{14}\text{C}$  leached from the 32 cm columns in one peak. The  $k_d$ 's calculated by the author were: Columbia Sand, 0.02; Felton Sand, 0.05; Sorrento Loamy Sand, 0.08; and Sunnyvale Sandy Clay, 0.08.

See attached DER for complete review.

- G. *Iwata, Yutaka. "VAPAM: Field Dissipation Study for Terrestrial Uses; Visalia, California, 1989". Performed by ICI Americas and Morse Labs. Study completed on 11/28/89. Received by EPA on 6/6/90. MRID #: 415144-01.*

Based upon a screening of this Terrestrial Field Soil Dissipation study, EFGWB concludes that the study warrants a comprehensive review which will be performed in Phase V.

- H. *Iwata, Yutaka. "VAPAM: Field Dissipation Study for Terrestrial Uses; Leland, Mississippi, 1989". Performed by ICI Americas and Morse Labs. Study completed on 11/28/89. Received by EPA on 6/6/90. MRID #: 415144-02.*

Based upon a screening of this Terrestrial Field Soil Dissipation study, EFGWB concludes that the study warrants a comprehensive review which will be performed in Phase V.

8. RECOMMENDATIONS:

Metam-Sodium appears to be highly unstable in the environment. According to an acceptable Aerobic Soil Metabolism study (401985-02), metam-sodium degrades rapidly ( $t_{1/2}$ : 23 minutes) to the active soil fumigant, methylisothiocyanate (MITC). As such, it is essential that the environmental fate studies conducted using metam-sodium as the test substance include an examination of the formation and degradation of MITC. MITC is a Restricted-Use-Pesticide and is also under a Ground Water Data Call-In. 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.

STATUS OF ENVIRONMENTAL FATE DATA REQUIREMENTS FOR  
METAM SODIUM

Data Requirement	Status
161-1 Hydrolysis	41631101 to be reviewed in Phase V
161-2 Photodegradation in Water	41517701 to be reviewed in Phase V
161-3 Photodegradation on Soil	41097004 to be reviewed in Phase V
161-4 Photodegradation in Air	not satisfied
162-1 Aerobic Soil Metabolism	satisfied
162-2 Anaerobic Soil Metabolism	not satisfied
162-3 Anaerobic Aquatic Metabolism	not satisfied
162-4 Aerobic Aquatic Metabolism	not satisfied
163-1 Leaching-Adsorption/Desorption	not satisfied
163-2 Laboratory Volatility	not satisfied
163-3 Field Volatility	reserved
164-1 Soil Field Dissipation	41514401, -02 to be reviewed in Phase V
164-2 Aquatic (Sediment) Field Dissipation	not satisfied
164-5 Long-Term Soil Field Dissipation	reserved
165-1 Accumulation in Confined Rotational Crops	not satisfied
165-2 Accumulation in Field Rotational Crops	reserved
165-4 Accumulation in Fish	reserved
166-1 Sm-Scale Prospec. Ground Water Monitoring	reserved
166-2 Sm-Scale Retro. Ground Water Monitoring	reserved
166-3 Lg-Scale Retro. Ground Water Monitoring	reserved
201-1 Droplet Size Spectrum	not satisfied
202-1 Drift Field Evaluation	not satisfied

9. BACKGROUND:

The studies in this package were reviewed as part of the Agency's LIST B Phase IV response.

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 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.

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10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached DER's.

11. COMPLETION OF ONE-LINER:

Amended as applicable.

12. CBI APPENDIX:

Not applicable.

DATA EVALUATION RECORD

CHEM 039003

STUDY 1  
Metam-sodium

\$162-1

STUDY ID 40198502

Burnett, T. 1987a. Vapam aerobic soil metabolism. Document No. PMS-226, MRC-87-21. Unpublished study performed and submitted by Stauffer Chemical Company, Richmond, CA.

REVIEWED BY: E. Hirsh TITLE: Staff Scientist  
EDITED BY: S. Syslo TITLE: Staff Scientist  
K. Patten Task Leader  
APPROVED BY: W. Spangler TITLE: Project Manager

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is acceptable and fulfills the Aerobic Soil Metabolism data requirement.
2. Metam-sodium (analytical grade) degraded with a registrant-calculated half-life of 23 minutes in sand soil that was incubated in the dark at 28°C and 75% of field moisture capacity. The initial concentrations of metam-sodium in two soil samples were 51.3 and 91.4 ppm.

Methyl-labeled [<sup>14</sup>C]metam-sodium (radiochemical purity 96.9%) was applied to a sand soil at a nominal concentration of 126 ppm and incubated at 28°C and 75% of field moisture capacity in the dark. At 1 day posttreatment, only 8.7% of the applied radioactivity was recovered from the soil; 3.4 and 5.3% of the applied were extractable and unextractable, respectively. The majority of the residues had been volatilized: 83% of the applied as methylisothiocyanate (MITC); 0.2% as other organic volatiles, and 0.9% as CO<sub>2</sub>. By the termination of the study at 127 days posttreatment, only 1.9% of the applied radioactivity remained in the soil. During the 127-day study, 79.7-94.3% of the applied radioactivity was accounted for by LSC.

The major nonvolatile degradate,

N,N'-dimethylurea

was a maximum 0.45 ppm at 3 and 7 days posttreatment; the soil also contained

methyl isothiocyanate

at a maximum of 0.22 ppm at 2 days posttreatment. Unidentified extractable [<sup>14</sup>C]residues quantified during HPLC totaled 0.17-0.25 ppm during the study.

#### METHODOLOGY:

##### Half-life determination

Sieved (2-mm) sand soil (91.8% sand, 7% silt, 1.2% clay, 0.2% organic matter, pH 6.9, CEC 6.5 meq/100 g) was weighed into serum vials and the soil moisture content was adjusted to 75% of field capacity. The vials were flushed with oxygen, sealed with a teflon septum, and placed in an incubator at 28°C to acclimate. Then, 10.5 µL of nonlabeled metam-sodium (analytical grade) was injected into each vial through the septum and the soil was analyzed immediately for metam-sodium; the initial concentrations of metam-sodium in two time 0 soil samples were 51.3 and 91.4 ppm. At 16, 17, 30.5, 48, 48.5, and 78 minutes posttreatment, a vial was injected with water. The excess water was decanted, and the decantate was cooled in liquid nitrogen and placed on ice. After all samples were collected, the decantates were filtered, treated with cupric chloride in acetic acid, and analyzed for metam-sodium using spectrophotometry at 420 nm.

##### Degradate determination

Sieved sand soil was weighed into biometer flasks and the soil moisture content was adjusted to 75% of field capacity. A polyurethane foam plug was fitted in the connection to a side arm which was filled with 1.0 N KOH trapping solution. The flasks were attached to an oxygen source through the sidearms and incubated at 28°C for 1 week; then methyl-labeled [<sup>14</sup>C]metam-sodium (radiochemical purity 96.9%, specific activity 0.0835 mCi/mMol), dissolved in ethyl acetate, was applied to the surface of the soil for a final concentration of 126 ppm. Immediately following treatment, a cellulose thimble filled with activated carbon was fitted into the mouth of each flask, and the flasks were sealed. The flasks were reattached to the oxygen source and incubated in the dark at 28°C. The KOH traps were changed at "regular intervals"; the carbon traps were changed at the same intervals as the KOH up to 7 days posttreatment, then the carbon traps in all the remaining flasks were changed at 8 days posttreatment and not changed thereafter. Duplicate flasks of soil were sampled at 0, 1, 2, 3, 7, 14, 21, 30, 60, 92, and 127 days posttreatment.

Immediately after sampling, the soils were extracted three times with water by shaking for 15 minutes. The samples were centrifuged after each extraction, and the aqueous extracts were combined. Aliquots of the extracts and extracted soils were analyzed for total radioactivity by direct LSC and by LSC following combustion, respectively; the remaining extracts and soils were stored frozen. Following frozen storage, the aqueous extracts were filtered and analyzed using reverse-phase HPLC using a methanol:water eluate gradient and photodiode array detection (240 and 215 nm). The samples were cochromatographed with N,N-dimethylurea and methylisothiocyanate; the identity of N,N-dimethylurea was also confirmed by MS.

Additional soil subsamples from 1 and 30 days posttreatment were extracted with acetone followed by methylene chloride, 0.2 N hydrochloric acid in 80% methanol, or 0.2 N sodium hydroxide in 80% methanol. The extracts and extracted soil were analyzed using LSC and LSC following combustion, respectively.

The carbon traps and the cellulose thimbles that held the carbon were extracted with methylene chloride. The thimbles were analyzed for total radioactivity by LSC. Aliquots of the extracts were analyzed for total radioactivity by LSC; the remaining extracts and the extracted carbon were stored at 4°C for an unspecified period. Then, the carbon was exhaustively washed with methylene chloride, dried, and analyzed for unextractable radioactivity by LSC following combustion. The methylene chloride extracts were filtered and analyzed using normal-phase HPLC with a hexane:isopropanol (95:5) to isopropanol:water (99.5:0.5) gradient and photodiode array detection (246 nm). Degradate identification was confirmed using GC/MS.

The KOH trapping solutions were analyzed for total radioactivity by LSC and for CO<sub>2</sub> by barium chloride precipitation.

#### COMMENTS:

1. In the half-life determination experiment, the initial concentrations of metam-sodium in the two time 0 soil samples were 51.3 and 91.4 ppm. Since the samples were treated individually, it is probable that the lack of replication was due to misapplication.
2. The study author stated that although N,N'-dimethylthiourea (a contaminant of Vapam) was not positively identified in the samples, its presence in the soil at early intervals was estimated at a maximum of 0.06 ppm. It is unclear as to how this concentration was determined.
3. An additional experiment was conducted to determine the reason why the extractability of [<sup>14</sup>C]residues in the carbon traps decreased during the course of the study and during storage. It was determined that the MITC bound irreversibly to the carbon. Carbon trap data were corrected based on the binding rates observed in the additional study concerning the characterization of MITC binding to carbon; the study authors stated that corrections for carbon trap recoveries in the individual flasks were made strictly for the purpose of estimating the mass balance.

DATA EVALUATION RECORD

STUDY 2

CHEM 039003

Metam-Sodium

\$163-1

STUDY ID (Acc. No.) 152844

Tambling, D.R., and T.J. Burnett. 1985b. Vapam soil mobility. Laboratory Project ID PMS-167. Unpublished study performed and submitted by Stauffer Chemical Company, Richmond, CA.

REVIEWED BY: N. Glassbrook TITLE: Staff Scientist  
EDITED BY: T. Colvin-Snyder TITLE: Staff Scientist  
K. Patten Task Leader  
APPROVED BY: W. Spangler TITLE: Project Manager

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TITLE: Chemist  
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SIGNATURE:

CONCLUSIONS:

Mobility - Aged Column Leaching

1. This study cannot be used to fulfill the Leaching-Adsorption/Desorption data requirement.
2. Metam-sodium residues were very mobile in a sandy clay loam, a loamy sand, and two sand soils. Methyl isothiocyanate (MITC) was identified as the predominant compound ( $\geq 86\%$  of radioactivity) recovered in the leachates. In each soil, approximately 60% of the applied  $^{14}\text{C}$  leached from the 32 cm columns in one peak. The  $k_d$ 's calculated by the author were: Columbia Sand, 0.02; Felton Sand, 0.05; Sorrento Loamy Sand, 0.08; and Sunnyvale Sandy Clay, 0.08.
3. This study provides supplemental information but does not meet Subdivision N guidelines for the following reasons:
  - a. The soils were not analyzed after aging and immediately prior to leaching, so that the composition and concentration of the aged residues at the start of leaching was unknown.

- b. Soils were sieved through a 0.5 mm mesh, not the required 2 mm. Increasing the effective surface area of the soil may have served to artificially increase the  $k_d$  values.
- c. Total recovery was only 70 to 78% of the applied radioactivity for the four soil types.
- d. The analytical technique for identifying residues, gas chromatography, does not provide confirmatory identification. MS should have been used to confirm the identification of the residues.
- e. The residues remaining in the aqueous phase after extraction with ethyl acetate (7 to 14% of the activity recovered in the leachate) were not identified.

#### METHODOLOGY:

Columbia River Basin sand and Felton sand soils were packed in glass columns (id 11 mm) to depths of 32 to 37 cm and saturated with deionized water. A 0.5 cm layer of chromatography sand was placed on top of each column followed by 8.0 g of dry Columbia sand. The Columbia sand on the columns was then treated with methyl-labeled [ $^{14}\text{C}$ ]metam-sodium (radiochemical purity >96.6%, specific activity 0.0835 mCi/mmol, Stauffer) at a concentration equivalent to 2 qt/100 ft<sup>2</sup> and then the soils were aged for an unspecified period of time. After the aging period, the glass columns were leached with the equivalent of 20 inches of water, and the leachates were collected in 2- to 4-mL fractions.

Aliquots of the leachate fractions were analyzed by LSC immediately on collection; the remainder of each leachate fraction was stored on ice until column leaching was complete. Fractions containing the most radioactivity were pooled and extracted with ethyl acetate. The aqueous phase was analyzed for metam-sodium by spectrophotometry; spectrophotometry measurements consisted of measuring absorbance at 420 nm to detect a complex formed between metam-sodium and the cupric ion in dilute acetic acid. The ethyl acetate phase was analyzed for the degradate methyl isothiocyanate (MITC) by GC with flame ionization detection. The soil from the glass columns was divided into 6-cm sections. The soil sections were frozen for up to one week prior to analysis by LSC following combustion.

In order to determine the rate of degradation of metam-sodium in the aging soils, additional subsamples of Columbia sand soil were placed in glass and stainless steel columns and treated with [ $^{14}\text{C}$ ]metam-sodium as described above. The soils were sampled at unspecified intervals and extracted with 4.0 mL of water. The water extracts were analyzed for total radioactivity by LSC and for metam-sodium by spectrophotometry.

#### DATA SUMMARY:

Based on column leaching experiments, aged methyl-labeled [ $^{14}\text{C}$ ]metam-sodium residues were very mobile in a sandy clay loam, a loamy sand, and two sand soils that were leached with approximately 20 inches of water. After leaching, 57.2-63.4% of the applied radioactivity was in the leachates and 9.7-15.1% remained in the soil columns.

## Methyl Isothiocyanate (MITC)

comprised  $\geq 86\%$  of the radioactivity recovered from the leachates. Total radioactivity in the soils following aging ranged from 60 to 78% of the applied; total radioactivity in the soil and leachate following leaching ranged from 70.5 to 78.2% of the applied.

### COMMENTS:

1. Leachates and soil sections were stored frozen prior to analysis; however, no freezer storage stability data were provided. In addition, the period of time that leachate fractions were stored prior to analysis for MITC was not reported. Since metam-sodium degrades extremely rapidly, freezer storage stability data are necessary for even very short storage intervals.
2. Concentrations of MITC detected by GC were consistently higher than the concentrations obtained by assuming that all the radiolabel detected by LSC was MITC. The authors stated that the LSC data are presumed to be more accurate and that consequently all of the  $^{14}\text{C}$  extracted by ethyl acetate is MITC.
3. Recoveries from soil sub-samples used to determine the extent of degradation of metam-sodium after aging and immediately prior to leaching ranged from 60 to 78% of the applied. Since recoveries of total radioactivity after leaching were approximately 70%, it is probable that the loss of radioactivity took place during aging.
4. Data for the concentrations of MITC and unidentified residues in the extracted aqueous phase in the leachates were not adequately expressed. These data were reported in terms of percent recovered from the pooled leachate fractions; however, all leachate fractions were not pooled, and the study authors did not report which leachate fractions were pooled and analyzed for degradates. These data should have been expressed either in terms of percent of the applied radioactivity or in terms of total radioactivity recovered in the leachates.

PHASE IV  
DATA REQUIREMENTS FOR Sodium N-Methylthiocarbamate

Date: 4/22/91  
Case No: 2390  
Chemical No: 039003

Data Requirement	Composition <sup>1</sup>	Use Pattern <sup>2</sup>	Does EPA Have Data To Satisfy This Requirement? (Yes, No, or Partially)	Bibliographic Citation	Must Additional Data Be Submitted under FIFRA 3(c)(2)(B)?
<b><u>158,290 Environmental Fate</u></b>					
<b><u>DEGRADATION STUDIES-LAB:</u></b>					
161-1 Hydrolysis	TGAI or PAIRA	1,2,3,6,8,9,11	No		No <sup>3</sup>
161-2 Photodegradation In Water	TGAI or PAIRA	1,2,3,6	No		No <sup>4</sup>
161-3 Photodegradation On Soil	TGAI or PAIRA	1,2,3	No		No <sup>5</sup>
161-4 Photodegradation In Air	TGAI or PAIRA	1,2,3,8,9,11	No		Yes <sup>6</sup>
<b><u>METABOLISM STUDIES-LAB:</u></b>					
162-1 Aerobic Soil	TGAI or PAIRA	1,2,3,8,9,11	Yes	40198502	No
162-2 Anaerobic Soil	TGAI or PAIRA	1,2,3	No		Yes <sup>7</sup>
162-3 Anaerobic Aquatic	TGAI or PAIRA	1,2,3,6	No		Yes <sup>8</sup>
162-4 Aerobic Aquatic	TGAI or PAIRA	6	No		Yes
<b><u>MOBILITY STUDIES:</u></b>					
163-1 Leaching-Adsorption/Desorption	TGAI or PAIRA	1,2,3,6,8,9,11	No		Yes <sup>9</sup>
163-2 Volatility (Lab)	TEP	1,2,8,9	No		Yes
163-3 Volatility (Field)	TEP	1,2,8,9	No		Reserved <sup>10</sup>
<b><u>DISSIPATION STUDIES-FIELD:</u></b>					
164-1 Soil	TEP	1,2,3,6,11	No		No <sup>11</sup>
164-2 Aquatic (Sediment)	TEP	6	No		Yes
164-3 Forestry	TEP				
164-5 Soil, Long-term	TEP	1,2,3,6,11	No		Reserved

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Data Requirement	Composition <sup>1</sup>	Use Pattern <sup>2</sup>	Does EPA Have Data To Satisfy This Requirement? (Yes, No, or Partially)	Bibliographic Citation	Must Additional Data Be Submitted under FIFRA 3(c)(2)(B)?
<b>§158.290 Environmental Fate (cont.)</b>					
<b>ACCUMULATION STUDIES:</b>					
165-1 Rotational Crops (Confined)	PAIRA	1,2,3	No		Yes <sup>12</sup>
165-2 Rotational Crops (Field)	TEP	1,2,3	No		Reserved
165-3 Irrigated Crops	TEP	6	No		No
165-4 In Fish	TGAI or PAIRA	1,2,3,6	No		Reserved <sup>13</sup>
165-5 In Aquatic Non-Target Organisms	TEP	1,2,3,6	No		No
<b>SPECIAL GROUND WATER STUDIES:</b>					
166-1 Ground Water Small Prospective	TEP	1,2,3	No		Reserved
166-2 Ground Water Small Retrospective	TEP	1,2,3	No		Reserved
166-3 Ground Water Large Retrospective	TEP	1,2,3	No		Reserved
<b>§158.440 SPRAY DRIFT:</b>					
201-1 Droplet Size Spectrum	TEP	1,2,3	No		Yes <sup>14</sup>
202-1 Drift Field Evaluation	TEP	1,2,3	No		Yes <sup>14</sup>

**FOOTNOTES:**

1. Composition: TGAI= Technical grade of the active ingredient; PAIRA= Pure active ingredient, radiolabeled; TEP= Typical end-use product.
2. Use Patterns: 1= Terrestrial Food; 2= Terrestrial Feed; 3= Aquatic Non-Food (Outdoor); 4= Aquatic Non-Food (Industrial); 5= Aquatic Non-Food (Residential); 6= Greenhouse Food; 7= Greenhouse Non-Food; 8= Residential Outdoor; 9= Residential Indoor; 10= Residential Non-Food; 11= Residential Non-Food; 12= Residential Outdoor; 13= Indoor Non-Food; 14= Indoor Residential.
3. A new Hydrolysis study (41631101) was received by the Agency on September 19, 1990 and will be reviewed in Phase V.
4. A new Photodegradation in Water study (41517701) was received by the Agency on June 6, 1990 and will be reviewed in Phase V.
5. A new Photodegradation on Soil study (41097004) was received by the Agency on May 16, 1990 and will be reviewed in Phase V.
6. Registrant has requested a waiver of this data requirement based upon the reported rapid degradation of Metam Sodium to MITC upon contact with moist soil. This waiver should not be granted because of the extremely high vapor pressure of Metam Sodium in an aqueous solution (21 torr). The study must characterize the photodegradation in air of both Metam Sodium and its major degradate, MITC.
7. The Phase III summary as well as a screening of the submitted study (40198501) established that it does not satisfy Subdivision N requirements.

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8. Waiver request on the grounds that Metam Sodium degrades rapidly to MITC in aerobic soils making it unlikely that parent material will ever be exposed to truly anaerobic conditions is denied. The fate of Metam Sodium in saturated soil conditions where parent may leach through the aerobic soil layer into anaerobic conditions, must be defined. This study may be used to satisfy the Anaerobic Soil Metabolism data requirement (162-2) as well as the Anaerobic Aquatic Metabolism data requirement (162-3).
9. It was concluded that 152844, an aged column leaching study, provided supplemental information but did not meet Subdivision N guidelines. A new study is required. In order to better estimate  $k_d$  values and ultimately the leaching potential of Metam Sodium and MITC, a batch equilibrium study is required. Because of the rapid degradation of Metam Sodium to MITC as shown by the aerobic soil metabolism study ( $t_{1/2}$ : 23 minutes), it is unlikely that equilibrium of Metam Sodium in the batch equilibrium system will be reached. Therefore a separate unaged and aged leaching study will not be required. The required batch equilibrium study must, however, define the leaching potential of the major degradate, MITC, and should attempt to generate a  $k_d$  value for parent Metam Sodium.
10. Reserved pending the results of the laboratory volatility study.
11. Two new soil field dissipation studies (41514401 and 41514402) were received by the Agency on June 6, 1990 and will be reviewed in Phase V.
12. A waiver request was made based upon two major points. The first being that Metam Sodium does not persist in the soil but rapidly degrades to the highly phytotoxic methyl isothiocyanate. The second point was that recent plant metabolism studies have demonstrated that no residues of toxicologic concern were found as a result of the short plant back interval. The plant back interval was not given, however it was certainly governed by the phytotoxicity of MITC. EFGWB cannot evaluate the waiver request because the supporting data have not been submitted to the Branch. The registrants must submit the data on which they are relying to support their waiver request.
13. The reported octanol/water partition coefficient of Metam Sodium is  $<10$ , therefore, it is not expected to bioaccumulate. If the  $<10$   $k_{ow}$  value is confirmed by RSB/RD, then the fish accumulation study will not be required.
14. Triggered by the chemigation application method, the reported phytotoxicity of the degradate MITC, and the risks associated with dermal and inhalation exposure to MITC.

Date: 4/22/91  
 Case No: 2390  
 Chemical No: 039002

PHASE IV  
 DATA REQUIREMENTS FOR Potassium N-Methylthiocarbamate

Data Requirement	Composition <sup>1</sup>	Use Pattern <sup>2</sup>	Does EPA Have Data To Satisfy This Requirement? (Yes, No, or Partially)	Bibliographic Citation	Must Additional Data Be Submitted under FIFRA 3(c)(2)(B)?
<u>§158.290 Environmental Fate</u>					
<u>DEGRADATION STUDIES-LAB:</u>					
161-1 Hydrolysis	TGAI or PAIRA	6	No		No <sup>3</sup>
161-2 Photodegradation In Water	TGAI or PAIRA	6	No		No <sup>4</sup>
161-3 Photodegradation On Soil	TGAI or PAIRA				
161-4 Photodegradation In Air	TGAI or PAIRA				
<u>METABOLISM STUDIES-LAB:</u>					
162-1 Aerobic Soil	TGAI or PAIRA				
162-2 Anaerobic Soil	TGAI or PAIRA				
162-3 Anaerobic Aquatic	TGAI or PAIRA	6	No		Yes
162-4 Aerobic Aquatic	TGAI or PAIRA	6	No		Yes
<u>MOBILITY STUDIES:</u>					
163-1 Leaching	TGAI or PAIRA	6	No		Yes <sup>5</sup>
163-2 Volatility (Lab)	TEP				
163-3 Volatility (Field)	TEP				
<u>DISSIPATION STUDIES-FIELD:</u>					
164-1 Soil	TEP				
164-2 Aquatic (Sediment)	TEP				
164-3 Forestry	TEP				
164-5 Soil, Long-term	TEP	6	No		Yes <sup>6</sup>

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Data Requirement	Composition <sup>1</sup>	Use Pattern <sup>2</sup>	Does EPA Have Data To Satisfy This Requirement? (Yes, No, or Partially)	Bibliographic Citation	Must Additional Data Be Submitted under FIFRA 3(c)(2)(B)?
<b>§158.280 Environmental Fate (cont)</b>					
<b>ACCUMULATION STUDIES:</b>					
165-1 Rotational Crops (Confined)	PAIRA				
165-2 Rotational Crops (Field)	TEP				
165-3 Irrigated Crops	TEP	6	No		No
165-4 In Fish	TGAI or PAIRA	6	No		Reserved <sup>7</sup>
165-5 In Aquatic Non-Target Organisms	TEP	6	No		No
<b>SPECIAL GROUND WATER STUDIES:</b>					
166-1 Ground Water Small Prospective	TEP				
166-2 Ground Water Small Retrospective	TEP				
166-3 Ground Water Large Retrospective	TEP				
<b>§158.440 SPRAY DRIFT:</b>					
201-1 Droplet Size Spectrum	TEP				
202-1 Drift Field Evaluation	TEP				

**FOOTNOTES:**

- Composition: TGAI= Technical grade of the active ingredient; PAIRA= Pure active ingredient, radiolabeled; TEP= Typical end-use product.  
 Use Patterns: 1= Terrestrial Food; 2= Terrestrial Feed; 3= Terrestrial Non-Food; 4= Aquatic Food; 5= Aquatic Non-Food (Outdoor); 6= Aquatic Non-Food (Industrial); 7= Aquatic Non-Food (Residential); 8= Greenhouse Food; 9= Greenhouse Non-Food; 10= Forestry; 11= Residential Outdoor.
- A new Hydrolysis study (41631101) was received by the Agency on September 19, 1980 and will be reviewed in Phase V.
- A new Photodegradation in Water study (41517701) was received by the Agency on June 6, 1980 and will be reviewed in Phase V.
- It was concluded that 152844, an aged column leaching study, provided supplemental information but did not meet Subdivision N guidelines. A new study is required. In order to better estimate  $k_d$  values and ultimately the leaching potential of Potassium N-Methyldithiocarbamate and MITC, a batch equilibrium study is required. The required batch equilibrium study must define the leaching potential of the major degradate, MITC, and should attempt to generate a  $k_d$  value for parent.
- The registrant, Buckman Laboratories, has requested a waiver pending the results/review of the Guideline 161, 162 and 163 studies because "...this (Aquatic Dissipation study) is considered a Tier II study and determination of its need cannot be determined without the Tier I testing." Although the registrant may request a waiver of this data requirement after the laboratory studies have been conducted and reviewed, the Aquatic Dissipation study is considered a core study which will remain a data requirement until such time as the registrant has provided the Agency with sufficient information to waive the data requirement.
- Buckman has requested a waiver based on Potassium N-methyldithiocarbamate having a low octanol/water partition coefficient. The reported  $K_{ow}$  is  $<10$ , therefore, Potassium N-methyldithiocarbamate is not expected to bioaccumulate. If the  $<10$   $k_{ow}$  value is confirmed by RSB/RD, then the fish accumulation data requirement may be waived.

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