1-9-85

HUDSON L. BOYD
CHEMIST
EFB - HED - OPTS
→ LAE 1-9-85

Shaughnessy No.: 090301

EAB logout date: _____

Init: _____

To: J. Ellenberger
Product Manager 12
Registration Division (TS-767C)

From: Dr. Lionel A. Richardson, Chief
Environmental Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of:

Reg./File No.: 352-366

Chemical: Methomyl

Type Product: I

Product Name: _____

Company Name: DuPont

Submission Purpose: Submission of generic data: Kow; Hydrolysis; Anaerobic Soil Metabolism; Field Dissipation; Fish Accumulation

ZBB Code: _____ Action Code: 606

Date In: 11/2/84 (11/15/84) SOC 3 EAB No.: 5082

Date Completed: 12/27/84 TAIS (Level II) Days

44 5.5

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

REGISTRATION DIVISION DATA REVIEW RECORD

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

11/9/84

1. CHEMICAL NAME: McPomny

2. IDENTIFYING NUMBER	3. ACTION CODE	4. ACCESSION NUMBER	TO BE COMPLETED BY PM
372366	606	251424	5. RECORD NUMBER 133716
			6. REFERENCE NUMBER 3
			7. DATE RECEIVED (EPA) 11-2-84
			8. STATUTORY DUE DATE
			9. PRODUCT MANAGER (PM) Ellen/Allen
			10. PM TEAM NUMBER 12

14. CHECK IF APPLICABLE

- ☐ Public Health/Quarantine
- ☐ Minor Use
- ☐ Substitute Chemical
- ☐ Part of IPM
- ☐ Seasonal Concern
- ☐ Review Requires Less Than 4 Hours

AH

TO BE COMPLETED BY PCB

11. DATE SENT TO HED/TSS: 11/2/84

12. PRIORITY NUMBER: 50

13. PROJECTED RETURN DATE: 1/1/85

15. INSTRUCTIONS TO REVIEWER

A. HED: ☐ Total Assessment 3(c)(5)

☐ Incremental Risk Assessment 3(c)(7) and/or E.L. Johnson memo of May 12, 1977.

C. ☐ BFSD

D. ☐ TSS/RD

E. ☐ Other

B. SPRD (Send Copy of Form to SPRD PM)

☐ Chemical Undergoing Active RPAR Review

☐ Chemical Undergoing Active Registration Standards Review

F. INSTRUCTIONS: Hardan Borgol.

16. RELATED ACTIONS

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

☐ Use Any or All Available Information ☐ Use Only Attached Data

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

18. REVIEWS SENT TO

☐ TB ☐ EEB ☐ EF ☐ PL

☐ RCB ☐ EFB ☐ CR ☐ BFSD

	No.	Type of Review	Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
HED		TOXICOLOGY								
		ECOLOGICAL EFFECTS								
		RESIDUE CHEMISTRY								
	1	ENVIRONMENTAL DATE	✓							
RD/TSS		CHEMISTRY								
		EFFICACY								
		PRECAUTIONARY LABELING								
BFSD		ECONOMIC ANALYSIS								

20. ☐ Label Submitted with Application Attached

21. ☐ Confidential Statement of Formula

22. ☐ Representative Labels Showing Accepted Uses Attached

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

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

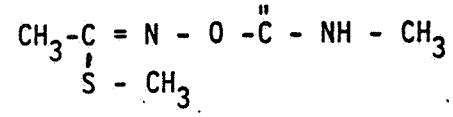
EPA Form 8570-13 (Rev. 11-81) PREVIOUS EDITIONS ARE OBSOLETE.

1.0 INTRODUCTION

Chemical Name: S-Methyl-N-[(methylcarbamoyl) oxy] thioacetimidate

Trade Names: Lannate, Nudrin

Common Name: Methomyl



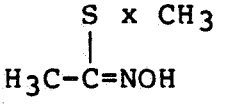
Reference: DuPont Response to EPA Generic Data Requirements, Specifically Environmental Fate "Data Gaps"

Volume II, September, 1983

2.0 DISCUSSION

Exhibit 1 - KOW Methodology: The authors state in their abstract that the report "sets forth conventional methods of measurement and identifies potential sources of measurement error" for octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients. They report a K_{ow} as being 1.08 without describing what they did and without giving any data. THIS REPORT DOES NOT IN ANY WAY SATISFY THE REQUIREMENTS FOR A FISH ACCUMULATION STUDY OR K_{ow} DATA AS REQUESTED IN OUR REPORT DATED 7 Dec. 1982.

Exhibit 2 - Hydrolysis of [1-^{14}C]-Methomyl Doc. No. AMR - 109.83. Following the description of a valid study the author reported no hydrolysis of methomyl after 30 days at pH 5.0 and 7.0 but hydrolysis with a 30-day half-life at pH 9.0. The hydrolysis product was the oximino compound S-methyl N-hydroxythioacetimidate



which increased from about 6% after 3 days of incubation to about 40% after 30 days.

Initial concentrations of 100 and 10ppm methomyl incubated at 25°C dropped to about 50ppm/5ppm respectively after 30 days.

This study fulfills EPA hydrolysis data requirements and is accepted as amended data to DuPont's report #115397 previously criticized but accepted by EPA 7 Dec., 1982.

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Exhibit 3 - "Decomposition of ^{14}C-Methomyl in Flooded Anaerobic Soils. ML/ME 23". The index for the brochure, Accession No 251424, cites this as being an "aerobic soil metabolism" study. However, that is not the case. A data evaluation (DER) of this report is attached.

DATA EVALUATION RECORD

CASE GS 090301 DISC TOPIC GUIDELINE 40 CFR 162-2,3.

CHEM Methomyl

BRANCH EAB DISC-- 30 TOPIC

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID Accession 251424 CONTENT CAT.:
Tab 3

Decomposition of ^{14}C-methomyl in flooded anaerobic soils. Unpublished study by John Harvey. ML/ME-23. Submitted by E.I. duPont in response to registration standard for methomyl.

SUBST. CLASS =

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

REVIEWED BY: H. L. Boyd
TITLE: Chemist
ORG: EAB/HED
LOC/TEL:

SIGNATURE: Herbert Boyd 12/15/84 DATE:

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

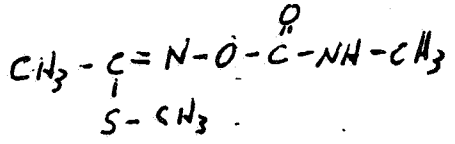
1. This study is scientifically valid.

2. Methomyl decomposes rapidly in flooded anaerobic soils forming volatile products: acetonitrile and finally CO_2.

3. Although acetonitrile is the major anaerobic degradation product of methomyl in the early stages, $^{14}CO_2$ is the end product under flooded conditions. Total conversion of methomyl to CO_2 would likely occur in about 8 days.

4. This study fulfills EPA Data Requirements for Registering Pesticides (1983) by providing data that predict the rate and pattern of methomyl metabolism under anaerobic conditions.

MATERIALS AND METHODS



S-Methyl-N-[(methylcarbamoyl)oxy] thioacetimidate. Methomyl, lannate, nudrin

Into 250ml screw-capped centrifuge tubes was placed 100g moist sediment and 100ml filtrate from backwater/sediment samples obtained from a Maine swamp. Immediately, the bottles were purged with nitrogen, capped, and set aside in the dark to incubate at room temperature for at least 30 days.

Additional bottles were filled with 100g of Fallsington silt loam or Flanagan silt loam (no further description), each having been premixed with 1g powdered alfalfa, 90 ml distilled water and 10 ml water from the Maine impoundment. ("These soils were similar to the ones previously reported on by Harvey for aerobic studies"). These bottles with soil samples were them purged with nitrogen and incubated in the dark as earlier described for water samples. After 30 days all bottles displayed evidence of anaerobic conditions: contents dark in color, foul smelling and filled with gas bubbles.

To bottles of anaerobic soil was quickly added 1.0ml of an aqueous solution of 1-^{14}C-methomyl (0.409 mg, 1.42 u ci, >99% radiochemical purity, source unstated) followed by nitrogen purging and capping. Incubation at room temperature and in the dark was continued.

Several bottles of each soil type, prepared as descibed, were maintained in the light annd agitated daily to effect aerobic conditions. They served as controls.

ANALYSIS

Anaerobic incubation samples were taken at 0, 2, 7, and 14 days after methomyl treatment; aerobic controls were sampled after 0 and 2 days of incubation.

Soil solids were precipitated from the supernatant liquid by centrifugation and extracted 4 times with water and 4 times with methanol. The acidity of the supernatant was checked with a pH meter equipped with a glass electrode.

The 4 aqueous extracts mentioned above were combined and extracted 3 times with 400ml portions of ethyl acetate. A 500ml aliquot of the ethyl acetate extract was dried over magnesium sulfate and concentrated to 10ml, first in a rotary evaporator and finally in a stream of nitrogen. Radioactivity in each liquid fraction was measured by liquid scintillation counting.

After air drying, the extracted soil samples were assayed for radioactivity by combustion and counting.

Ethyl acetate concentrates (extracted from the water extract above) were analyzed for methomyl and/or its metabolite by HPLC. Effluent peaks were detected with a DuPont 410 ultraviolet absorbance detector. Comparisons were made against radioactive standards which had been mixed with the methomyl or the S-methyl N-hydroxy-thioacetimidate prior to injection into the instrument.

Water/sediment samples contained in a narrow mouthed bottle equipped with a septum cap were incubated as room temperature and in the dark until anaerobic conditions existed and then treated with an aqueous solution of ^{14}C-methomyl (0.4 mg, 1.55u Ci). Over a period of 8 days samples of clear supernatant liquid were withdrawn and analyzed for radioactivity (LSC) and pricipitated with excess $BaCl_2$, i.e., the total radioactivity in the aqueous

phase was converted to $^{14}CO_2$. Approximately 100% of the radioactivity had converted to $^{14}CO_2$ by 8 days.

^{14}C-Acetonitrile from ^{14}C-methomyl was identified and measured by collecting samples from the headspace of a bottle prepared with Maine sediment/water/and ^{14}C-methomyl and injecting them into a GC column and then bubbling the effluent from the acetonitrile peak through scintillation counting cocktail.

RESULTS

Aerobic Controls

Extraction of radioactivity from aerobic control soils on Day 0 ranged from 87% for Flanagan soil to 99% for the Fallsington silt loam. It was slightly more difficult to extract residues after 2 days of incubation: only 77% was extractable from Flanagan silt loam and 96% from Fallsington silt loam. The only radioactive species observed, even after 2 days of incubation was ^{14}C-methomyl.

Aerobic Samples

In all cases pH values were near neutral or slightly acidic; pH did not affect hydrolytic stability.

Extraction efficiencies of soil to water and from water to ethyl acetate were lower in anaerobic soils than in the aerobic condition. Excessive loss of radioactive through concentration of extracts indicated very rapid metabolism and the formation of volatile ^{14}C-materials.

Less than 1% methomyl (HPLC analysis) was recoverable from 0-day samples of either of the soils or from the Maine sediment. Loss of radioactivity through the formation of gaseous ^{14}C-products resulted in low (60-81%) recoveries after 2 days of incubation.

It was clearly established that complete breakdown of methomyl to small volatile fragments occurs very rapidly in the presence of active anaerobic microorganisms.

$^{14}CO_2$ was demonstrated to be the end product of ^{14}C-methomyl degradation under flooded soil conditions. However, in the early stages (<5hrs) acetonitrile was the major degradate observed.

DISCUSSION

1. It was unclear just what was done with the incubated, untreated, water/sediment samples. They were supposed to serve as "controls" and it is assumed that they were analyzed by the same methods as were the treated samples.

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Exhibit 4 - Ecosystem Residue Study. Spruce/Fir Forest and Cedar Swamp, Princeton, ME. 1978

This study is captioned, "Terrestial Forest Field Dissipation" in the table of contents.

Whereas, the study may be scientifically valid, there are too few details on the test protocols to permit adequate evaluation. It is described in very general terms almost to the point of being an abstract. Moreover, it would not meet EPA Guidelines for Registration of Pesticides (1983) because there were no preapplication (control) samples nor date of application samples taken; the formulation type (E.C., oil, etc.) was not stated; there were no data given relative to weather, water table, water flow, nor depth of the soil samples examined.

Section 164-3 of the Guidelines requires data from which we can judge the rate of decline of the pesticide from foliage, leaf litter, soil under the litter, standing and moving water, and sediments.

Instead of rejecting the study outright and requiring a new study, this reviewer requests that the registrant be required to give full details of how the study was conducted and of the analytical procedures followed. IT IS NOTED THAT EVEN THE PREPARER OF THE REPORT SUSPECTED SAMPLING ERROR IN THE CEDAR SWAMP STUDY. Naturally we cannot evaluate a study that the researcher considers suspect.

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Exhibit 5 - Continuous exposure of rainbow trout (Salmo gairdneri) to Lannate® in water. A research report by Bionomics, Inc., Wareham, Mass., Nov. 1971.

Rainbow trout were exposed to methomyl at continuous concentrations of 0.075 and 0.75 mg/L for 28 days and then to depuration periods of 21 days.

Analyses of the water in exposure tanks showed that the concentrations of methomyl was almost constantly 0.09 ug/ml for the 0.075 mg/L tank and 0.9-1.0 ug/L in the 0.75 mg/L tank.

Residue results indicated that over a 28 day exposure to even the highest concentration (0.75 ug/L) there was no appreciable methomyl build-up in fish tissue - Values ranged from 0.36 ppm to 0.45 ppm; after 1-day of withdrawal less than 0.02 ppm methomyl were detectible in the fish.

Note: Since the publication of the registration standard for methomyl in October, 1981, we have noted that the octanol/water partition coefficient for methomyl was reported by Metcalf and PO-YUNG LU in August, 1977, to be only 12.

The requirement for fish accumulation studies has been satisfied.

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