4-29-91

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 29 1991

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

APR 29 1991

MEMORANDUM

SUBJECT: **Review of Phase 4 Package** for Thiobencarb (**EFGWB #91-0120, Chemical** #108401, Case #2665, DP **Barcode D157129**)

TO: **Amy Rispin, Chief**
Science Analysis and Coordination Staff
Environmental Fate and Effects Division (H7507C)

FROM: **Herbert L.** Manning, Ph.D. Herbert L. Manning
Section 3, EFGWB/EFED (H7507C)

THRU: Hank Jacoby, Chief Hank Jacoby
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Akiva D. Abramovitch, Ph.D., Chief, Section 3 Akiva Abramovitch
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

The Phase 4 review package for the List B chemical Thiobencarb was reviewed and found to be complete.

The LUIS report (attached, dated 20 Jan 1991) provided the most recent use pattern (Terrestrial Food + Feed Crop and Aquatic Food Crop). The attached table shows the current status of the data requirements for the reported uses.

The registrant's Phase 3 Responses (attached) and the EFGWB's conclusions are as follows:

1. One of the submissions (Hydrolysis, 161-1, MRID #41609012) was a study completed July 1990 and will not be reviewed until Phase 5 is implemented.

2. Photodegradation in Water data (MRID #?) could not be reviewed (retrieved) because the MRID No. was incorrect. The study should be resubmitted.

3. Photodegradation on Soil data (MRID #41215312) were reviewed and found acceptable.

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603

4. Aerobic Soil Metabolism data (MRID #00040925) were reviewed and found unacceptable at this time, but they do provide supplemental information. The study may be made acceptable if the information requested in the DER is supplied.

5. Anaerobic Aquatic Metabolism data (MRID #00040925) were reviewed and found unacceptable. A new study is required.

6. Leaching- Desorption/Desorption data (MRID #41215313) were reviewed and found partially acceptable for <u>unaged</u> parent; however, mobility data on the <u>aged</u> parent are still required.

7. In their Phase 2 Response, the registrant was committed to producing a new Confined Rotational Crop study (165-1) (correspondence attached); however, they now believe their field rotational crop data (4 studies) fulfills the data requirement. They are requesting a waiver of the confined study and are submitting the field studies to satisfy the data requirement. Acceptable field data that determines all accumulated residues and quantifies them will render the confined study satisfied as well.

The field Rotational Crops data (MRID #41609011) were reviewed and found unacceptable at this time, but they do provide supplemental information. The study may be made acceptable if the information requested in the DER is supplied.

8. Accumulation in Aquatic Non-Target Organisms data (MRID #00145833-35 and 00133563) were reviewed and found unacceptable, but they do provide supplemental information. The study may be made acceptable if the information requested in the DER is supplied.

The One-Liner has been updated and is attached.

2665

DP BARCODE: D157129

CASE: 816135
SUBMISSION: S384415

DATA PACKAGE RECORD
BEAN SHEET

DATE: 10/22/90
Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 603 PHASE 3 INITIAL SUB
CHEMICAL: 108401 Thiobencarb
ID#: 108401-000239
COMPANY: 000239 CHEVRON CHEMICAL COMPANY
PRODUCT MANAGER: 50 JAY ELLENBERGER 703-308-8085 ROOM: CST 4J1
PM TEAM REVIEWER: LINDA DELUISE 703-308-8066 ROOM: CST 3N3
RECEIVED DATE: 10/22/90 DUE OUT DATE: / /

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 157129 EXPEDITE: N DATE SENT: 10/22/90 DATE RET.: / /
DP TYPE: 101 Phase IV Review
ADMIN DUE DATE: 11/12/90 CSF: N LABEL: N

ASSIGNED TO	DATE IN	ASSIGNED TO	DATE IN
DIV : EFED	11/07/90	REVR :	/ /
BRAN: EFGB	/ /	CONTR:	/ /
SECT:	/ /		

* * * DATA PACKAGE REVIEW INSTRUCTIONS * * *

For the attached reregistration case, please identify all applicable data requirements and note those for which adaquate data have not been submitted to the Agency.

PRODUCT CHEM INCLUDED

* * * ADDITIONAL DATA PACKAGES FOR THIS SUBMISSION * * *

DP BC	BRANCH	DATE OUT	DUE BACK	INS	CSF	LABEL
157128	EEB	10/22/90	11/12/90	Y	N	N
157130	DEB	10/22/90	11/12/90	Y	N	N
157131	NDEB	10/22/90	11/12/90	Y	N	N
157132	TB-HFAS	10/22/90	11/12/90	Y	N	N

LIST B
Herb 91-0120
11/30

Studies on Hydrolysis & ~~Rotational~~ Crops
Not Be done a part of Phase IV

PHASE IV ENVIRONMENTAL FATE SUMMARY TABLE FOR THIOBENCARB

Chemical Code: 108401
Pesticide Type: Herbicide

Reviewer: H.Manning
Date: 4/17/91

Uses (LUIS report, dated 1/20/91): Terrestrial Food + Feed Crop, Aquatic Food Crop,

	Submitted Studies/ Addendum	DER/Addendum Review/Summary Identification	DER/Addendum Review/Summary Review Conclusions	Additional Data/Info Required?
DEGRADATION-LAB:				
161-1. Hydrolysis	41609012			SWBReviewed[1]
PHOTODEGRADATION:				
161-2. In water	Incorrect ID			Yes[2]
161-3. On soil	41215312	DER(910120/4-5-91)	Satisfied	No
161-4. In Air	None			No[3]
METABOLISM-LAB:				
162-1. Aerobic Soil	00040925	DER(910120/4-5-91)	DNS/Sal/Supp	Yes[4]
162-2. Anaerobic Soil	None			No[5]
162-3. Anaerobic Aquat	00040925	DER(910120/4/5/91)	DNS/NSal/NSupp	Yes[5]
162-4. Aerobic Aquat	None			SWBSubmitted[6]

DYNAMAC
CORPORATION

THIOBENCARB

PHASE IV

TASK 1: REVIEW AND EVALUATION OF INDIVIDUAL STUDIES

April 5, 1991

Final Report

Contract No. 68D90058

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
2275 Research Boulevard
Rockville, MD 20850-3262

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THIOBENCARB

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2. Aerobic and anaerobic soil metabolism. (Pack, 040925) 2.1

3. Mobility (batch equilibrium). (Pack, 41215313) 3.1

4. Field rotational crop. (Chevron Chemical Company, 41609011-B, 41609011-C, 41609011-D; Leary, 41609011-A) 4.1

5. Bioaccumulation in aquatic non-target organisms. (Fujie, 00145834, Acc. No. 247109, Acc. No. 256967; Kennedy, 1984, No Study ID; 00133563, 00145833, 00145835, Acc. No. 256967) 5.1

Appendix 6.3

DATA EVALUATION RECORD

STUDY 1

CHEM 108401 Thiobencarb §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41215312
McGovern, P.A., K. Shepler, and L.O. Ruzo. 1988. Soil surface photolysis of ^{14}C-thiobencarb in natural sunlight. PTRL Report No. 129W-1. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Richmond, CA; and submitted by Chevron Chemical Company, Richmond, CA.

DIRECT REVIEW TIME - 16

REVIEWED BY: S. Syslo TITLE: Staff Scientist

EDITED BY: W. Martin TITLE: Staff Scientist

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
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APPROVED BY: H. Manning H. Manning
TITLE: Microbiologist
ORG: EFGWB/EFED/OPP
TEL: 703-557-7323

SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study can be used to fulfill data requirements.

2. Thiobencarb photodegraded with a calculated half-life of 168 days on sandy loam soil irradiated outdoors at Richmond, California, for 30 days; in contrast, thiobencarb degraded with a half-life of 280 days in the dark controls. The major non-volatile degradate was 4-chlorobenzoic acid.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of thiobencarb on sandy loam soil.

INTRODUCTION

Thiobencarb is a herbicide registered for use to control grasses and broadleaf weeds in direct seeded and transplanted rice. Thiobencarb is applied as a preemergence or early postemergence treatment. Single active ingredient formulations include emulsifiable concentrates and granular. Thiobencarb can be formulated with propanil. Some or all applications of thiobencarb may be classified as RUP.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of thiobencarb on sandy loam soil.

4. No additional data on the photodegradation of thiobencarb on soil are needed at this time.

METHODOLOGY:

Portions (approximately 3.1 g) of non-sterile, sieved (<2 mm) sandy loam soil (50.2% sand, 46.1% silt, 3.7% clay, 2.5% organic carbon, CEC 59 meq/100 g) were placed in petri dishes (50-mm diameter) to a depth of approximately 0.5 mm. Uniformly phenyl ring-labeled [^{14}C]thiobencarb (radiochemical purity 99.3%, specific activity 41.7 mCi/mM, Chevron), fortified with unlabeled thiobencarb (purity not specified) and dissolved in acetone, was applied at approximately 6 lb ai/A evenly to the soil surfaces using a syringe. The dishes were placed in photolysis chambers (Figure 3) located outdoors in Richmond, California (37.45 N), and were oriented so that the chambers were perpendicular to the ecliptic. The photolysis chambers for the irradiated samples consisted of a stainless steel chamber covered with a quartz lid and equipped with a circulating jacket in which circulated a temperature-controlled glycol:water solution; dark control samples were incubated in similar chambers in which the covers were glass plates covered with dark material. The soil temperature was monitored by thermocouples attached to the soil surface; the maximum measured temperatures were 40.9 C in the irradiated soil and 38.3 C in the dark controls. Air (uncharacterized) was drawn through the chamber (flow rate not specified); the exiting air was drawn sequentially through one trap of ethylene glycol and two traps of 10% aqueous sodium hydroxide. Samples were exposed to natural sunlight for 30 days during September and October, 1988. Sunlight intensity and cumulative sunlight energy were measured using a photodetector. The cumulative energy received by the samples was 246.56 W min/cm^2; the maximum light intensity measured during the study was 23650 uW/cm^2 (Table V). Duplicate dishes of irradiated and control soil were analyzed at time 0 and at 2, 9, 15, 21, 26, and 30 days posttreatment; gas traps were assayed at "regular intervals."

The soil from each sample was transferred to an Erlenmeyer flask and extracted with acetone by sonication (duration not specified). The soil:acetone slurry was suction-filtered, and the soil was rinsed twice with acetone and three times with water. The extract and rinsates were combined, and aliquots of the resulting solution were analyzed by LSC, one-dimensional TLC, and HPLC. TLC was done using silica gel plates developed twice in hexane:ether (4:1, v:v); [^{14}C]residues on the plates were located by autoradiography and identified by comparison to unlabeled reference standards chromatographed on the same plates. [^{14}C]Residues were scraped from the plates and quantified by LSC. Reverse-phase HPLC (C-18 column)

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was done using an eluant gradient of acetonitrile:water:20% acetic acid (30:65:5, v:v:v) to acetonitrile:20% acetic acid (95:5, v:v) and UV (255 nm) detection. Peaks were identified by comparison of retention times to those of unlabeled reference standards chromatographed under the same conditions. Fractions of eluate were collected from the column and analyzed for total radioactivity by LSC; radiochromatograms were constructed to determine retention times and peak areas of radioactive residues. Recoveries of radioactivity applied to the column averaged 95.1%. The detection limit was 0.1% of the applied; the quantitation limit was 0.5%.

The extracted soil was air-dried, and portions were analyzed for total radioactivity by LSC following combustion. Triplicate aliquots of the trapping solutions were analyzed for total radioactivity by LSC.

DATA SUMMARY:

Phenyl ring-labeled [^{14}C]thiobencarb (radiochemical purity 99.3%), at approximately 6 lb ai/A, degraded with a registrant-calculated half-life of 168 days on sandy loam soil that was irradiated outdoors for 30 days at Richmond, California (37.45 N), during September and October, 1988. The cumulative energy received by the samples was 246.56 W min/cm^2; the maximum light intensity measured during the study was 23650 uW/cm^2 (Table V). In contrast, thiobencarb degraded with a half-life of 280 days in dark controls incubated adjacent to the irradiated samples. The concentration of thiobencarb in the irradiated soil declined from 100.3-102.2% of the applied radioactivity immediately posttreatment to 83.2-88.1% at 15 days and 86.5-89.1% at 30 days. The major degradate was

4-chlorobenzoic acid,

which was present only in the irradiated samples at a maximum of 1.3% of the applied at 9 days posttreatment. Unidentified radioactivity comprised a maximum of 2.9% in the irradiated samples at 9 days posttreatment and 1.3% at 30 days in the dark control (Table VI). The major volatile degradate was $^{14}CO_2$, which comprised 0.2% of the applied radioactivity in the irradiated samples by 30 days posttreatment; it was not present in the dark controls (Table I). Other volatile residues were <0.01%. Unextracted radioactivity comprised 0.3-0.5% of the applied at time 0; and was a maximum of 8.7% in the irradiated samples and 5.7% in the dark controls at 26 days posttreatment (Table I). Material balances during the study ranged from 89.9 to 102.5% in the irradiated samples and 91.6 to 100.1% in the dark controls (Table I).

COMMENTS:

1. The pH of the soil was not reported.

2. It was not specified whether the data for thiobencarb and 4-chlorobenzoic acid were derived from the HPLC method or the TLC method.

3. The statistical estimation of the photodegradation half-life of thiobencarb reported in this experiment is of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

4. There were a number of differences between the study protocol and the analytical methods as described by the study authors. The study authors did not explicitly state if the soil was dried before use; however, in the study protocol, it was specified that the soil would be air-dried before use. The study method stated that loose dry soil was treated; the protocol specified that the soil be made into a slurry that was dried before application. The study authors did not specify the method used for application of the pesticide solution to the soil; the protocol specified application by syringe. The study authors did not report the depth of soil in the petri dish; the protocol specified a soil depth of approximately 0.5 mm.

Thiobencarb

Page_____ is not included in this copy.

Pages 12 through 19 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

[✓ FIFRA registration data.]

____ The document is a duplicate of page(s) __________.

____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

STUDY 2

CHEM 108401 Thiobencarb §162-1 and 162-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 00040925

Pack, D.E. 1975. The soil metabolism of [ring-U-^{14}C] benthiocarb. File No. 773.21. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA.

DIRECT REVIEW TIME - 36

REVIEWED BY: S. Syslo TITLE: Staff Scientist

EDITED BY: T. Colvin-Snyder TITLE: Staff Scientist
K. Ferguson Task Leader

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SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study cannot be used to fulfill data requirements.
2. Thiobencarb degraded with an observed half-life of 15-28 days in clay and silty clay loam soils incubated at room temperature. The degradates thiobencarb sulfoxide, 4-chlorobenzyl methyl sulfone, 4-chlorobenzoic acid, desethyl thiobencarb, and 4-chlorobenzyl methyl sulfoxide were isolated.

3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reasons:

   [^{14}C]thiobencarb residues in the water extracts of the soils, which comprised a maximum of 11% of the applied radioactivity (approximately 0.7 ug/g), were not characterized;

   several areas of radioactivity on the TLC plates that each contained up to 0.50-0.59% of the applied radioactivity (approximately 0.03 ug/g) were not identified; and

   soil incubation conditions, such as moisture, temperature, and light exposure, were not adequately detailed.

4. In order for this study to fulfill the aerobic soil metabolism data requirement, [^{14}C]residues in the water must be characterized and all [^{14}C]residues isolated at $\geq$0.01 ug/g must be identified, and details of the aerobic incubation conditions must be provided.

Metabolism - Anaerobic Aquatic

1. This study cannot be used to fulfill data requirements.

2. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of thiobencarb and its degradates.

3. This study is unacceptable for the following reason:

   material balances were incomplete; up to 21.4% of the applied radioactivity in the clay soil and up to 60.9% in the silty clay loam soil was not accounted for.

4. Since the material balances were incomplete, the problems with this study cannot be resolved with the submission of additional data. A new study is required.

METHODOLOGY:

Metabolism - Aerobic Soil

Portions of clay (California soil; 18% sand, 26% silt, 56% clay, 1.95% organic matter, pH 4.6, CEC 32.5 meq/100 g) and silty clay loam (Louisiana soil; 3% sand, 69% silt, 28% clay, 1.36% organic matter, pH 5.8, CEC 14.5 meq/100 g) soils were placed in jars and treated with at approximately 6 ug/g with uniformly ring-labeled [^{14}C]thiobencarb (radiochemical purity 99.8%, specific activity 3.83 mCi/mM, Chevron Chemical), dissolved in acetone. The jars were covered with polyethylene film, and the treated soils were incubated at room temperature under unspecified light conditions; water was added to the soil "as needed to facilitate microbial activity, but to avoid excess". Soils were sampled at intervals up to 365 days posttreatment.

A portion of each soil sample was analyzed for total radioactivity by LSC following combustion. Additional soil subsamples were analyzed using the procedure presented in Figure 1. The soil was acidified to pH 2 with 1 M $NaHSO_4$:water (4.5:10), and the resulting soil slurry was extracted by mixing with ethyl acetate. The extraction was repeated five times; after each extraction, the solution was removed by filtering. Then, the soil was extracted three times with water; after each extraction, the sample was centrifuged and the supernatant decanted and filtered. The combined ethyl acetate extracts and the combined water extracts were analyzed for total radioactivity by LSC; the water extracts were not further analyzed. The ethyl acetate extracts were stored frozen at -20 C (length of storage unspecified), then thawed and concentrated to dryness by rotary evaporation. The residue was redissolved in ethyl acetate; aliquots were analyzed for total radioactivity by LSC, and for thiobencarb and its degradates by two-dimensional TLC on silica gel plates developed in the first direction with benzene saturated with formic acid:ether (3:1) and in the second direction with ether:diethylamine (10:1). To analyze for alpha-(4-chlorotoluene) sulfonic acid, additional aliquots were analyzed by two-dimensional TLC on silica gel plates developed in the first direction with benzene saturated with formic acid:ether (3:1) and in the second direction with n-propanol:-concentrated ammonium hydroxide (4:1). To analyze for several possible degradates that had the same Rf value as thiobencarb using the two-dimensional TLC systems, the extracts were also analyzed by one-dimensional TLC using benzene. The sample extracts were cochromatographed with reference standards. Radioactive zones were visualized by autoradiography and identified by comparison to nonlabeled reference standards that were visualized under UV light. Radioactive areas were scraped from the TLC plates and quantified by LSC. Recoveries of thiobencarb from fortified soil ranged from 78 to 96%; recoveries of 4-chlorobenzoic acid averaged 94%. Unextracted [^{14}C]residues in the soil were determined by LSC following combustion. All extracts and extracted soil samples were stored at -20 C when not in use (duration of storage not specified).

In order to determine the extent of volatilization of thiobencarb residues, additional portions of the two soils were treated at approximately 6 ug/g with uniformly ring-labeled [^{14}C]thiobencarb dissolved in acetone. Humidified, compressed air (air-flow rate not specified) was passed over the soil, through Drierite to remove water vapor, and then sequentially through solutions of methoxyethanol:ethanolamine (6:4) and saturated aqueous barium hydroxide. The methoxyethanol:ethanolamine trapping solution was changed 1-2 times per week for up to 365 days posttreatment; aliquots of the solutions were analyzed for total radioactivity by LSC. Duplicate samples of each soil were removed for analysis at intervals up to 365 days posttreatment. Soil samples were extracted as described above and analyzed for parent thiobencarb by GC.

Metabolism - Anaerobic Aquatic

Portions (approximately 20 g) of the clay and silty clay loam soils described above were placed in glass jars and moistened with water (30 mL, not further characterized). The jars were then flushed with nitrogen and tightly capped, and the samples were incubated for 1 week at an unspecified temperature. After 1 week, uniformly ring-labeled [^{14}C]thiobencarb, dissolved in acetone, was added to each sample at approximately 6 ug/g. The jars were again flushed with nitrogen and tightly sealed, and the soil:water systems were incubated at room temperature. The samples were collected at intervals up to 365 days posttreatment, and acidified, extracted, and analyzed as described.

In order to determine the extent of volatilization of thiobencarb residues, additional portions of the two soils treated with uniformly ring-labeled [^{14}C]thiobencarb dissolved in acetone at approximately 6 ug/g. The soils were not flooded with water. Humidified, compressed nitrogen (air-flow rate not specified) was passed over the soil, through Drierite to remove water vapor, and then sequentially through solutions of methoxyethanol:ethanolamine (6:4) and saturated aqueous barium hydroxide. The methoxyethanol:ethanolamine trapping solution was changed 1-2 times per week for up to 365 days posttreatment; aliquots of the solutions were analyzed for total radioactivity by LSC. Duplicate samples of each soil were removed for analysis at intervals up to 365 days posttreatment. Soil samples were extracted as described above and analyzed for parent thiobencarb by GC.

DATA SUMMARY:

Metabolism - Aerobic Soil

Ring-labeled [^{14}C]thiobencarb (radiochemical purity 99.3%), at approximately 6 ug/g, degraded with an observed half-life of 15-28 days in clay and silty clay loam soils incubated aerobically at room temperature. [^{14}C]Thiobencarb declined from 5.27-5.40 ug/g immediately posttreatment to 3.61-3.78 ug/g at 15 days, 1.43-1.99 ug/g at 28 days, and 0.04-0.26 ug/g at 245 days (Tables 14 and 15). The degradates

thiobencarb sulfoxide (compound 56, S-oxy-S-[(4-chlorophenyl)methyl] diethylcarbamothioate, maximum 0.249 ug/g at 28 days posttreatment);

4-chlorobenzyl methyl sulfone (compound 59, maximum 0.240 ug/g at 56 days);

4-chlorobenzoic acid (compound 10, maximum 0.156 ug/g at 7 days);

desethyl thiobencarb (compound 1, S-[(4-chlorophenyl)methyl] ethylcarbamothioate, maximum 0.078 ug/g at 28 days); and

4-chlorobenzyl methyl sulfoxide (compound 58, maximum 0.054 ug/g at 28 days)

were isolated. Uncharacterized [^{14}C]residues in the water extracts of the soils comprised a maximum of 9.12-11.00% of the applied radioactivity (Tables 6 and 8). Unextracted [^{14}C]residues in the soils increased to a maximum of 29.7-39.4% of the applied at 28 days posttreatment and decreased to 17.0-22.0% by 365 days posttreatment (Tables 6 and 8). $^{14}CO_2$, collected from separate samples of the same soils, totaled 54.5-77.4% of the applied radioactivity at 365 days posttreatment; concentrations of parent thiobencarb in these soils were similar to concentrations in the soils used to determine concentrations of thiobencarb degradates (Tables 5, 6, 8, 14, and 15). Material balances for the clay soil were 91.2-116.5%, and material balances for the silty clay loam soil were 68.1-100.2% (Table 6 and 8).

Metabolism - Anaerobic Aquatic

Ring-labeled [^{14}C]thiobencarb (radiochemical purity 99.3%), at approximately 6 ug/g, degraded with an observed half-life of approximately 243 days and >181 days in flooded clay and silty clay loam soils (20 g soil:30 mL water), respectively, that were incubated anaerobically (nitrogen atmosphere) at room temperature. In order to establish anaerobic conditions, the soils were flooded and maintained under a nitrogen atmosphere 7 days prior to treatment. In the soil:water systems, [^{14}C]thiobencarb decreased from 5.98-6.51 ug/g immediately posttreatment to 3.02-3.62 ug/g at 181 days (Tables 14 and 15). Thiobencarb was 3.17 ug/g in the clay soil at 243 days. The degradates

4-chlorobenzoic acid (compound 10, maximum 0.101 ug/g at 181 days posttreatment);

thiobencarb sulfoxide (compound 56, maximum 0.067 ug/g at 7 days);

desethyl thiobencarb (compound 1, maximum 0.032 ug/g at 56 days);

4-chlorobenzyl methyl sulfone (compound 59, maximum 0.017 ug/g at 28 days); and

4-chlorobenzyl methyl sulfoxide (compound 58, maximum 0.012 ug/g at 28 days)

were isolated in both soil:water systems. Degradates found only in the silty clay loam soil:water system were:

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2-hydroxy thiobencarb (compound 38, S-[(4-chloro-2-hydroxyphenyl)methyl] diethylcarbamothioate, maximum 0.031 at 119 days posttreatment) and

3-hydroxy thiobencarb (compound 43, S-[(4-chloro-3-hydroxyphenyl)methyl] diethylcarbamothioate, maximum 0.023 ug/g at 119 days posttreatment).

Uncharacterized [^{14}C]residues in the water extracts of the soil:water systems comprised a maximum of 2.84-7.88% of the applied radioactivity (Tables 7 and 9). Unextracted [^{14}C]residues in the soil:water systems increased to a maximum of 27.8-42.8% of the applied at 364 days posttreatment.

In a separate experiment conducted to determine volatilization under anaerobic conditions, in which samples of the same soils that were treated with thiobencarb and incubated under a nitrogen atmosphere but were not flooded, $^{14}CO_2$ totaled 1.52-2.56% of the applied radioactivity at 364 days posttreatment (Tables 7 and 9). Concentrations of parent thiobencarb in the clay soil were similar to concentrations in the clay soil used to determine concentrations of thiobencarb degradates; the decline of parent thiobencarb in the silty clay loam soil for the two experiments appeared to be similar, although actual thiobencarb concentrations differed due to different application rates (Tables 5, 7, 9, 14, and 15).

Material balances, determined by combining data for $^{14}CO_2$ with data from the first experiment were 78.6-95.0 for the clay soil and were 39.1-96.6% for the silty clay loam soil (Tables 7 and 9).

COMMENTS:

General

1. The potential degradate alpha-(4-chlorotoluene) sulfonic acid was not quantified because it did not migrate from the TLC origin in the solvent systems used. The study author considered the amount of thiobencarb residues remaining at the TLC origin to be maximum concentration values of alpha-(4-chlorotoluene) sulfonic acid present in the soils.

2. In the volatilization experiments, an additional trap containing methoxyethanol was initially placed ahead of the methoxyethanol:ethanolamine trap in order to trap any volatile non-CO_2 radioactivity. Since no radioactivity was detected in the methoxyethanol trap, the use of this trap was discontinued after the first few sampling intervals.

3. EFGWB prefers that [^{14}C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least

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three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison with the R_f of reference standards.

In this study, the sample extracts were analyzed using one-dimensional and two-dimensional TLC. Radioactive areas on the TLC plates were identified only by comparison with the location of known reference standards chromatographed on the same plates.

4. The following potential degradates were not detected (detection limit 0.005-0.01 ug/g) in any soil or soil:water sample: 4-chlorobenzyl sulfide, 4-chlorobenzyl mercaptan, 4-chlorobenzyl alcohol, S-[(4-chlorophenyl)methyl] N-ethyl-N-(2-hydroxyethyl)-carbamothioate, 4-chloro-2-hydroxybenzyl alcohol, 4-chlorobenzyl disulfide, S-[4-chloro-2-hydroxyphenyl)methyl] ethylcarbamothioate, 4-chloro-3-hydroxybenzyl acid, 4-chloro-3-hydroxybenzyl alcohol, 4-chlorobenzaldehyde, S-[4-chloro-3-hydroxyphenyl)methyl] ethylcarbamothioate, and 4-chlorobenzyl methyl sulfide.

Metabolism - Aerobic Soil

1. [^{14}C]Thiobencarb residues in the water extracts of the soils, which comprised a maximum of 11% of the applied radioactivity, were not analyzed for thiobencarb and its degradates. Several radioactive areas on the TLC plates that contained >0.01 ug/g of thiobencarb residues were not identified: spot G (maximum 0.59% of the applied); spot E (maximum 0.56%); and spot I (maximum 0.50%) (Tables 10 and 12).

2. Incubation conditions were not adequately described. The soil moisture content during the study was not reported. The exact incubation temperatures were not reported; the study author stated only that soils were incubated at room temperature. It was not specified whether samples were incubated in the dark.

3. Material balances for the silty clay loam soil were incomplete, declining significantly towards the end of the study (Table 8). Declining material balances may confound determination of the degradation half-life of a pesticide; however, the results for the silty clay loam soil were similar to those of the clay soil, for which material balances were acceptable (Table 6). Therefore, the problems with material balances for the silty clay loam soil are not considered to interfere with the interpretation of the data for this soil.

4. The extracted soils were further analyzed to determine the percentages of unextracted radioactivity in fulvic acid, humic acid, and humin soil organic matter fractions. The fulvic acid, humic acid, and humin fractions each contained a maximum of 19.89%, 3.01%, and 21.92% of the applied radioactivity, respectively.

Metabolism - Anaerobic Aquatic

1. Material balances, determined by combining data for thiobencarb residues in soil with data for $^{14}CO_2$ determined in a separate experiment, were incomplete. Up to 21.4% and 60.9% of the applied radioactivity was unaccounted for in the clay and silty clay loam soils, respectively.

2. Data for concentrations of thiobencarb and its degradates at 364 days posttreatment were not provided. In addition, for the silty clay loam soil, the value for the concentration of thiobencarb at the last sampling interval provided (245 days posttreatment) was illegible.

3. [^{14}C]Thiobencarb residues in the water extracts of the soils, which comprised a maximum of 7.88% of the applied radioactivity, were not analyzed for thiobencarb and its degradates. Several spots on the TLC plates that contained >0.01 ug/g of thiobencarb residues were not identified: spot G (maximum 0.49% of the applied); spot E (maximum 0.90%); and spot I (maximum 0.22%) (Tables 11 and 13).

4. Incubation conditions were not adequately described. The exact incubation temperatures were not reported; the study author stated only that soils were incubated at room temperature. It was not specified whether samples were incubated in the dark.

5. In the experiments used to quantify volatilized $^{14}CO_2$, the soil samples were incubated anaerobically (nitrogen atmosphere) but were not flooded with water as were the soils in the rate determination experiment. The study author stated that flooding does not affect the rate of degradation of thiobencarb in soils incubated under a nitrogen atmosphere; however, while the data appear to support this statement, no evidence was provided to suggest that the rate of breakdown of thiobencarb degradates to CO_2 is similar under flooded and nonflooded conditions.

6. The extracted soils were further analyzed to determine the percentages of unextracted radioactivity in fulvic acid, humic acid, and humin soil organic matter fractions. The fulvic acid, humic acid, and humin fractions each contained a maximum of 3.97%, 1.53%, and 39.3% of the applied radioactivity, respectively.

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Thiobencarb

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DATA EVALUATION RECORD

STUDY 3

CHEM 108401 Thiobencarb §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41215313
Pack, D.E. 1988. Freundlich soil adsorption/desorption coefficients of thiobencarb. Laboratory Project ID MEF-0097/8814700. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA.

DIRECT REVIEW TIME = 8

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CONCLUSIONS:

Mobility - Leaching and Adsorption/desorption Studies

1. This study can be used to fulfill data requirements.

2. Thiobencarb was marginally mobile to immobile in sandy loam, loam, silt loam, clay loam and silty clay soils. Specifically, Freundlich constants for the soils were: sandy loam (K_{ads}= 5.42, 1/n= 1.22), loam (K_{ads}= 7.30, 1/n= 0.95), silty clay (K_{ads}= 9.28, 1/n= 0.95), clay loam (K_{ads}= 11.3, 1/n= 0.86), and silt loam (K_{ads}= 20.1, 1/n= 1.01).

3. This study is acceptable and partially fulfills EPA Data Requirements for registering pesticides by providing information on the mobility (batch equilibrium) of <u>unaged</u> thiobencarb in sandy loam, loam, silt loam, clay loam and silty clay soils.

4. No additional information is required at this time on the mobility of unaged thiobencarb in soil. Data are needed on the mobility of aged thiobencarb residues in soil.

METHODOLOGY:

Sandy loam, loam, silty clay, silt loam, and clay loam soils (Table 1) were air-dried at room temperature and sieved (16 mesh). Based on the results of preliminary experiments using the sandy loam soil, an equilibration time of 1 hour was selected for the definitive study.

For the definitive adsorption study, duplicate portions (1 g) of each test soil were mixed with 5 mL of a 0.01 M calcium sulfate solution containing 0.1, 0.2, 0.5, or 1.0 ug/mL uniformly ring-labeled [^{14}C]thiobencarb (radiochemical purity >99.8%, specific activity 41.7 mCi/mMol, Wizard Laboratories) in glass tubes. The soil:solution slurries were equilibrated with shaking for 1 hour at 25 C in the dark. Following the equilibration period, the soil:solution slurries were centrifuged and the supernatants were decanted; aliquots (1 mL) of the supernatants were analyzed by LSC. The amount of thiobencarb adsorbed to the soil was determined by subtraction.

Desorption of thiobencarb was determined by replacing the supernatant with an equal volume of pesticide-free 0.01 M calcium sulfate solution. The soil:solution slurries were shaken for 44 hours at 25 C in the dark, and then the slurries were centrifuged. The supernatants were decanted and aliquots were analyzed by LSC. The amount of thiobencarb remaining adsorbed to the soil was determined by subtraction.

DATA SUMMARY:

Based on batch equilibrium experiments, uniformly ring-labeled [^{14}C] thiobencarb (radiochemical purity >99.8%), at 0.1, 0.2, 0.5, or 1.0 ug/mL, was determined to be mobile in sandy loam, loam, silty clay, silt loam, and clay loam soil:0.01 M calcium sulfate solution slurries that were equilibrated for 1 hour at 25 C. Freundlich K_{ads} values were 5.42 for the sandy loam soil, 7.30 for the loam soil, 9.28 for the silty clay soil, 11.3 for the clay loam soil, and 20.1 for the silt loam soil (Table XIII). Adsorption was not related to CEC or organic matter content of the soils.

Following desorption in pesticide-free calcium sulfate solution for 44 hours, <1-22% of the radioactivity that had been adsorbed to the soils was desorbed (Tables III-XII). Freundlich K_{des} values were 14.3 for the sandy loam soil, 21.7 for the loam soil, 28.8 for the silty clay soil, 46.7 for the clay loam soil, and 94.5 for the silt loam soil (Table XIII).

COMMENTS:

1. The study author was unable to analyze the soil to confirm adsorption and to provide a material balance. The method used to determine the amount of radioactivity remaining on the soil after desorption was air-drying the soil "for several days", grinding the soil, and analyzing for total radioactivity by LSC following combustion. The study author stated that "the amounts of radioactivity found in the combustion of every soil were much less than expected", and further stated that "whenever a dilute aqueous solution of thiobencarb is evaporated (even at ambient temperature), most of the thiobencarb also evaporates." Therefore, it was not possible to dry the soil before combustion without loss of thiobencarb, and it was not possible to combust the wet soil.

2. Although the study author stated that Freundlich K_{ads} values of 5-20 indicate that "Thiobencarb is fairly strongly absorbed", it is generally accepted that these Freundlich K_{ads} values are indicitive of mobile compounds.

3. The soil was oversieved. A "16 Mesh" screen has a opening of 1.0-1.19 mm. Although Subdivision N guidelines state that a 2-mm mesh screen should be used to sieve the soil, the effect of oversieving appears to have been minimal.

4. The K_{oc} values were not reported. However, adsorption did not appear to be related to soil organic material, CEC or pH.

THIOBENCARB

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