DP Barcode : D171009, D177514, D175733
PC Code No. : 101101
EFGWB Out : 12/7/92

TO: Walter Waldrop
Product Manager PM 71
Special Review and Reregistration Division (H7508W)

FROM: Akiva D. Abramovitch, Ph.D., Head
Environmental Chemistry Review Section #3
Environmental Fate & Ground Water Branch/EFED (H7507C)

A

THRU: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Henry Jacoby

Attached, please find the EFGWB review of...

Reg./File # :3125-314, 3125-325

Common Name :Metribuzin

Product Name :Sencor, Lexone

Company Name :Mobay

Purpose :Review of 161-1,2,3, 162-1,2, 163-1, 164-1, and 165-1 studies.

Type Product :Herbicide Action Code: 627, 660 EFGWB #(s): 92-0177, -0806, -0609, -0624

Review Time: 10.0 days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

161-1	TRID 470173-008	Y	162-4			164-4			166-1		
161-2	TRID 470173-007	Y	163-1	ACC. # 93110, MRID 42283001	P	164-5			166-2		
161-3	TRID 470173-009	Y	163-2			165-1	MRID 40838402	S	166-3		
161-4			163-3			165-2			167-1		
162-1	MRID 40367602	Y	164-1	MRID 40380901 MRID 42236101	S, S	165-3			167-2		
162-2	MRID 40367603	Y	164-2			165-4			201-1		
162-3			164-3			165-5			202-1		

Y = Acceptable (Study satisfied the Guideline)/Concur P = Partial (Study partially satisfied the Guideline, but additional information is still needed)
S = Supplemental (Study provided useful information, but Guideline was not satisfied) N = Unacceptable (Study was rejected)/Non-Concur

1. CHEMICAL: Common name:

Metribuzin

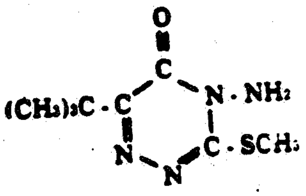
Chemical name:

4-amino-6-(1,1-dimethylethyl)-3-methylthio)-1,2,4-triazin-5(4H)-one.

Trade name(s):

Sencor, Lexone

Structure:



Formulations:

Lexone 4L, Lexone DF, Sencor 4, Sencor DF.

Physical/Chemical properties:

Molecular formula: $C_8H_{14}N_4OS$
Molecular weight: 214.3.
Physical state: White crystalline solid.
Melting Point: 125-126.5°C.
Solubility: (20°C): 1.2 g/l water; 820 g/kg acetone; 220 g/kg benzene; 850 g/kg chloroform; 1 kg/kg cyclohexanone; 190 g/kg ethanol; 2 g/kg hexane; 120 g/kg toluene.

2. TEST MATERIAL: See Attached DER's.

3. STUDY/ACTION TYPE:

Review of 161-1,2,3, 162-1,2, 163-1, 164-1, and 165-1 studies.

4. STUDY IDENTIFICATION:

Christopher, R.J, J.B. Lane, and G.D. Parker. 1988. Residues of Metribuzin (Sencor) in Rotational Crops and Soils. Laboratory Project ID: SE 052301. Report No. 98324. Performed and submitted by Mobay Corporation, Stillwell, Kansas (MRID 40838402).

Daly, D. October 7, 1988. Soil Adsorption-Desorption with ^{14}C-Sencor. Unpulished study conducted by ABC Laboratories and submitted by Miles Corporation. ABC Report # 36997 (MRID 42283001).

Delk, J.L. 1987. Dissipation of Sencor and its Oxidative Metabolites in Field Soil. Laboratory Project ID: SE 8300-87. Unpublished study performed by Morse Laboratories, Inc., and submitted by Mobay Corporation, Kansas City, Missouri (MRID 40380901).

Detra, R.L., J.B. Lane, and M.D. Thyssen. 1987. Degradation of Sencor in aerobic sandy loam. Laboratory Project ID 94880. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO (MRID 40367602).

Detra, R.L., and M.D. Thyssen. 1987. Degradation of Sencor in anaerobic sandy loam. Laboratory Project ID Report Number 94881. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO (MRID 40367603).

Grace, T.J. and T.S. Cain. 1990. Dissipation of Metribuzin in California Soils. Unpublished study performed by Plant Sciences, Inc., Watsonville, CA, Siemer and Associates, Fresno, CA, NET Atlantic, Inc., Bedford, MA and submitted by Mobay Chemical, Kansas City, MO (MRID 42236101).

Lane, J.B. 1986. Sencor aged soil residue leaching. Report No. 93110. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO (ACC 263702).

Morgan, J.G. 1986a. The aqueous photolysis of Sencor-5-^{14}C. Report No. 91763. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

Morgan, J.G. 1986b. The hydrolysis of Sencor-5-^{14}C. Report No. 91764. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

Morgan, J.G. 1986c. The photodecomposition of Sencor-5-^{14}C on soil. Report No. 91765. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

5. REVIEWED BY:

James Breithaupt, Agronomist
EFGWB/EFED/OPP
Review Section #3

Signature: James Breithaupt
Date: 10/27/92

6. APPROVED BY:

Akiva Abramovitch, Chief
EFGWB/EFED/OPP
Review Section #3

Signature: Akiva Abramovitch
Date: NOV 9 1992

7. CONCLUSION:

161-1 (TRID 470173-008, DER 1, Acceptable)

Metribuzin was stable in sterile aqueous buffer solutions (pH 5, 7, and 9) that were incubated in darkness at 25 °C.

161-2 (TRID 470173-007, DER 2, Acceptable)

Metribuzin photodegraded with a half-life of 4.3 hours in pH 6.6 water irradiated with natural sunlight in Kansas City, MO at 26-29 °C. In contrast, metribuzin was stable in dark control samples during the 6-hour study period. After 6 hours of irradiation, metribuzin comprised 33.3% of the applied radioactivity, the degradate deaminated metribuzin (DA) comprised 55%, and three unidentified degradates each comprised $\leq$5.2%. During the study, material balances in the irradiated and dark control solutions ranged from 95.4 to 102.3% of the applied. The structures of metribuzin and its degradates can be seen in DER 4.

161-3 (TRID 470173-009, DER 3, Acceptable)

Metribuzin degraded with a half-life of 2.5 days on sandy loam soil irradiated outdoors in Kansas City, Missouri at temperatures up to 31 °C. The concentration of metribuzin on the irradiated soil declined to 48.4% of the applied radioactivity by 4 days posttreatment, in contrast to 95.9% undegraded after 4 days in the dark control. The major degradates were deaminated metribuzin (DA) with a maximum of 16.1 % of applied dose, and the distinct photoproducts pentylidene metribuzin (maximum 8.6%), and hexylidene metribuzin (maximum 9.5%); During the study, the material balances ranged from 98.2% to 101.5% of the applied radioactivity (Tables II and IV).

162-1 (MRID 40367602, DER 4, Acceptable)

Metribuzin degraded with a half-life of 106 days in sandy loam soil (series not specified) that was incubated at 26 °C and 75% of 0.33 bar moisture capacity in darkness. Two major degradates identified were deaminated, diketo metribuzin (DADK) and diketo metribuzin (DK). Four minor degradates identified were deaminated metribuzin (DA), 2-methyl-DADK, 4-methyl-DADK,and 3-amino-DA). The structures of metribuzin and its metabolic degradates may be seen in DER 4.

162-2 (MRID 40367603, DER 5, Acceptable)

Metribuzin degraded with a half-life of 112 days in sandy loam that was flooded and incubated at 24 ± 2 °C in the dark for 60 days following 30 days of aerobic incubation. During the anaerobic portion of the study, the degradates identified were DADK, DA, DK, and 2-methyl-DADK. Seventy-eight to 88 % of all radioactivity was in the organic phase from the methanol extrations of soil and <5 % was in the aqueous phase.

A

163-1 (MRID 42283001, DER 6, Acceptable)

Metribuzin was determined to be very mobile in sandy, sandy loam, silt loam, and clay loam soil:calcium chloride solution slurries (3:10, w:v). Freundlich Kd_{ads} values were 0.25 for the sandy soil, 0.02 for the sandy loam soil, 0.22 for the silt loam soil, and 0.20 for the clay loam soil; 1/n values ranged from 1.06-1.68. Kd_{des} values were 0.56 for the sand, 0.141 for the sandy loam, 0.51 for the silt loam, and 0.41 for the clay loam soil. Koc_{ads} values were 47, 3.1, 15, and 17 for sand, sandy loam, silt loam, and clay loam soils, respectively. Koc_{des} values were 106, 24.3, 33, and 36, respectively. The soils contained 0.58, 0.64, 1.68, and 1.28 % OC, respectively.

163-1 (ACC. 263702, DER 7, Acceptable)

The aged leaching study is acceptable and partially satisfies the aged portion of the 163-1 data requirement. For complete satisfaction of the 163-1 data requirement, the registrant should conduct either batch equilibrium or soil column leaching using the degradates DK and DADK.

Metribuzin and its oxidation degradates were very mobile in an aged soil column leaching study. Kansas sandy loam soil spiked with 7.4 ppm of metribuzin was added to sandy loam, silt loam, and silty clay soils packed in 30-cm columns and leached with 50.8 cm of water. The amount of applied radioactivity in the leachate was 23, 42, 28, and 55 % in the silt loam, silty clay, Kansas sandy loam, and California sandy loam. Most of the radioactivity in the leachate was parent metribuzin, and the degradates DA, DADK, and DK ranged from 1-3.1 % of the applied amount (See DER 4 for degradate identification).

164-1 (MRID 40380901, DER 8, Supplemental Data)

The terrestrial field dissipation study provides good estimates of persistence under field conditions in Michigan, Maine, and California, but does not satisfy the data requirement since it did not address leaching. The soils were only sampled to 12 inches of depth and did not address the leaching potential of metribuzin at the sites studied in Michigan, Maine, California, Indiana, and Florida. Also, the day=0 recoveries were ≤ 50 % of the nominal rate in Mississippi and Texas.

The half-lives at the Michigan, Maine, and California sites were 58 to 107 days in silty clay loam, muck sandy loam, muck clay loam, and sandy clay loam soils.

(MRID 42236101, DER 9, Presently Unacceptable)

The 164-1 study is unacceptable at this time but may be upgraded to acceptable. The registrant should clarify the rate of application at the Fresno site (See Comment 1 in COMMENTS section) and verify that the application rate was 2 lbs ai/A. If the California studies are upgraded to acceptable, then the 164-1 data requirement is considered to be satisfied with the combination of the terrestrial field dissipation studies in this review and the current ground water monitoring data.

The EFGWB reviewer calculated the application rates for the Watsonville and Fresno sites from the calibration information on p. 15 of the study. The application rate appears to be correct at the Watsonville site. However, the calibration information indicates that the application rate at the Fresno site was 1.05 lbs ai/A instead of the nominal rate of 2 lbs ai/A. This is in contrast to the day=0 soil data (p. 64 of study) that indicates an application rate of approximately 2 lbs ai/A.

The estimated half-lives of metribuzin (Sencor 75 DF) in sandy loam soils in California were 128 and 40 days at Watsonville and Fresno, respectively. The difference in the half-lives of metribuzin can be readily explained by the cooler soil and air temperatures at Watsonville. No leaching of metribuzin or its oxidative degradate DADK were observed below 12 inches of depth at either site except for some detections that were probable contamination or sampling error in the Fresno site. The other oxidation degradates of interest in the study, DA and DK, were not found below 6 inches of depth and not past 7 and 361 days in Watsonville and 60 and 179 days in Fresno, respectively.

165-1 (MRID 40838402, DER 10, supplemental data)

The 165-1 study provides only supplemental data and cannot be upgraded because only a half-rate of compound was applied and phytotoxicity problems were observed with kale and red beets at the 32-day sampling interval. Also, no storage stability data for compounds in plant parts were provided, extremely-sensitive rotational crops were used, and no explanation was given for the occurrence of the degradate DADK in kale at up to 5.9 times the soil concentration. DADK was the only compound that significantly accumulated and accumulated with higher concentrations in the plant than in soil.

Metribuzin residues accumulated in confined rotational crops (kale, red beets, and wheat) planted 32, 122, and 270 days postapplication in sandy loam soil sprayed with ^{14}C-metribuzin at 0.19 lb ai/A. The major degradate identified in the crops and soil was DADK, which was the only compound that accumulated significantly and with higher plant concentrations than soil concentrations.

EFGWB (9/24/90 and 5/20/92) only dealt with reducing the rotational interval for peanuts from 12 to 8 months. Since small grains such as wheat and barley and root crops such as potatoes and beets are also rotated into treated areas, the 165-1 data requirement was not satisfied. Also, the 165-1 study in this review provides only supplemental data, and a new 165-1 study is therefore necessary for satisfying the data requirement.

ENVIRONMENTAL FATE ASSESSMENT

Metribuzin is hydrolytically stable for at least 30 days and to aerobic and anaerobic soil metabolism (half-lives of 106 and 112 days, respectively). Direct photolysis is the principal means of degradation with half-lives of 4.3 hours in water (pH 6.6) and 2.5 days on sandy loam soil. Metribuzin is very mobile in soils with Freundlich K values ranging from 0.02 to 0.51 in sandy, sandy loam, silt loam, and clay loam soils with 0.58 to 1.68 % OC. K_{oc} values ranged from 3.1 to 106 in the tested soils. Terrestrial field dissipation half-lives were 128 and 40 days in California and 58 to 107 days in other studies conducted in Michigan, Maine, and California that were considered to contain only supplemental data.

The major degradates identified in acceptable soil metabolism studies are deaminated metribuzin (DA), diketo metribuzin (DK), and deaminated diketo metribuzin (DADK). The distinctive photolytic degradates on soil are pentylidene metribuzin and hexylidene metribuzin.

Metribuzin is a known leacher and has been detected in ground water in 12 states with concentrations of trace levels to 25.10 ug/L. Metribuzin and its degradates DK and DADK were also detected in a required retrospective ground-water monitoring study conducted for EFGWB on potatoes (minor-use crop) in Portage County, Wisconsin (90-0479).

All labels of metribuzin currently contain a GROUND WATER ADVISORY on the label of all formulations. The label advisory reads: "Metribuzin is a chemical which can travel (seep or leach) through soil and can contaminate ground water which may be used as drinking water. Metribuzin has been found in ground water as a result of agricultural use. Users are advised not to apply metribuzin where the water table (ground water) is close to the soil surface, and where the soils are very permeable, i.e., well-drained soils such as loamy sands. Your local agricultural agencies can provide further information on the type of soil in your area and the location of ground water."

8. RECOMMENDATIONS:

Inform the Registrant that:

(1) The hydrolysis (161-1), aqueous (161-2) and soil photolysis (161-3), and aerobic (162-1) and anaerobic (162-2) soil metabolism data requirements are satisfied in this review.

(2) Soil column leaching or batch equilibrium studies using the degradates DK and DADK should be conducted to satisfy the 163-1 data requirement for metribuzin, since the degradates have been detected in ground water with parent metribuzin,

(3) If the California field dissipation studies are upgraded to acceptable, then the 164-1 data requirement is considered to be satisfied with the combination of the terrestrial field dissipation studies in this review and the current ground water monitoring data. MRID 40380901 (DER 8,

supplemental data) provides good estimates for persistence of metribuzin under field conditions in Michigan, Maine, and California, but does not address mobility since the soils were sampled to only 12 inches of depth. MRID 42236101 (DER 9) is presently unacceptable but may possibly be upgraded to acceptable, as indicated in the CONCLUSIONS section of this review.

(4) MRID 40838402 contains supplemental data and does not satisfy the 165-1 data requirement (DER 10). The 165-1 and 165-2 data requirements remain unsatisfied in this review.

(5) The 165-4 data requirement was waived by EFGWB 90-0130, 2/7/89.

(6) Because the registrant is a member of the Spray Drift Task Force, EFGWB concurs with the request that droplet size spectrum and field drift data submission be delayed until the final report of the Task Force is to be submitted (December 1994). EFGWB agrees that this data requirement may be satisfied through the work of the Spray Drift Task Force, provided that HED or EEB has no need of these data in advance of the Task Force's final report. This recommendation is in accordance with PR Notice 90-3 (4/10/90), which allows registrants to fulfill the spray drift (201-1 and 201-1) data requirements through the Task Force.

9. BACKGROUND:

A. Introduction

The Registration Standard dated June 1985 stated that the Environmental Fate Data Requirements for terrestrial food/feed uses of metribuzin are hydrolysis (161-1), aqueous (161-2) and soil (161-3) photolysis, aerobic (162-1) and anaerobic (162-2) soil metabolism, leaching-adsorption-desorption (163-1), laboratory volatility (163-2), terrestrial field dissipation (164-1), confined (165-1) and field (165-2) rotational crops, accumumulation in fish (165-4), and ground water monitoring.

B. Directions for Use

Metribuzin is a selective triazine herbicide registered for use on terrestrial food crop (field and vegetable crops) and terrestrial non-crop (turf, rights-of-way) sites. Application rates range from 0.13 to 2.0 lb ai/A on most field and vegetable crops, 2 to 6 lb ai/A on sugarcane, and 1.0 to 7.5 lb ai/A on noncrop sites. Metribuzin is formulated only as a single active ingredient pesticide. Single active ingredient formulations consist of 35-75% WP and 4 lb/gal FlC. Metribuzin may be applied to the foliage or soil surface using ground equipment, aircraft, or sprinkler irrigation systems (potatoes). It may be soil-incorporated. Metribuzin exhibits some toxicity to fish (rainbow trout 76 mg/L and goldfish >10 mg/L).

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Refer to attached reviews.

11. COMPLETION OF ONE-LINER:

One-liner was updated.

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12. <u>CBI APPENDIX</u>:

All data reviewed here are considered "company confidential" by the registrant and must be treated as such.

DP BARCODE: D175733 REREG CASE #

CASE: 819350
SUBMISSION: S414191

DATA PACKAGE RECORD
BEAN SHEET

DATE: 03/17/92
Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 627 GENERIC DATA SUBMISSION
CHEMICALS: 101101 1,2,4-Triazin-5(4H)-one, 4-amino-6-(1,1-dimethylet %

ID#: 101101-
COMPANY:
PRODUCT MANAGER: 71 WALTER WALDROP 703-308-8062 ROOM: CS1 3B3
PM TEAM REVIEWER: ERIC FERIS 703-308-8048 ROOM: CS1 3G5
RECEIVED DATE: 01/31/92 DUE OUT DATE: 04/30/92

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 175733 EXPEDITE: Y DATE SENT: 03/17/92 DATE RET.: / /
CHEMICAL: 101101 1,2,4-Triazin-5(4H)-one, 4-amino-6-(1,1-dimethylethyl)-3-(m
DP TYPE: 001 Submission Related Data Package
ADMIN DUE DATE: 06/15/92 CSF: N LABEL: N

ASSIGNED TO	DATE IN	DATE OUT
DIV : EFED	03 /19/92	/ /
BRAN: EFGB	/ /	/ /
SECT: IO	/ /	/ /
REVR :	/ /	/ /
CONTR:	/ /	/ /

* * * DATA REVIEW INSTRUCTIONS * * *

LIST A REREGISTRATION CHEMICAL

IMPORTANT NOTE:
This study is for gln 164-1. An expedited review request for another 164-1 study was forwarded to Anne Barton. You may want to include this study in the review of the previously submitted, expedited review study (DP Barcode D171009).

Thank you

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

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

DP BARCODE: D171009

RE REG CASE #

CASE: 819350
SUBMISSION: S406682

DATA PACKAGE RECORD
BEAN SHEET

DATE: 11/12/91
Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 627 GENERIC DATA SUBMISSION
CHEMICALS: 101101 1,2,4-Triazin-5(4H)-one, 4-amino-6-(1,1-dimethylet %

ID#: 101101
COMPANY:
PRODUCT MANAGER: 71 WALTER WALDROP 703-308-8062 ROOM: CS1 3B3
PM TEAM REVIEWER: ERIC FERIS 703-308-8048 ROOM: CS1 3G5
RECEIVED DATE: 10/30/91 DUE OUT DATE: 11/29/91

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 171009 EXPEDITE: Y DATE SENT: 11/12/91 DATE RET.: / /
CHEMICAL: 101101 1,2,4-Triazin-5(4H)-one, 4-amino-6-(1,1-dimethylethyl)-3-(m
DP TYPE: 001 Submission Related Data Package
ADMIN DUE DATE: 12/12/91 CSF: N LABEL: N

ASSIGNED TO		DATE IN	DATE OUT
DIV :	EFED	11/12/91	/ /
BRAN:	EFGB	/ /	/ /
SECT:	IO	/ /	/ /
REVR :		/ /	/ /
CONTR:		/ /	/ /

* * * DATA REVIEW INSTRUCTIONS * * *

LIST A CHEMICAL

A DCI was issued on July 31, 1991. Registrant cited the following in response to the respective guideline requirements:

163-1	accession # 263702
164-1	MRID 40380901
165-1	MRID 40838402

These studies were covered by the July 2, 1990 in-depth review screen. It deemed each of these studies as not meeting guideline requirements, however no explanation was provided. We need to be able to provide the registrant with a valid reason for rejection of these studies. Please provide me with one ASAP so I can get us some good data.

- THANKS!

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

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

DATA EVALUATION RECORD

STUDY 1

CHEM 101101 Metribuzin §161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID (TRID 470173-008)
Morgan, J.G. 1986b. The hydrolysis of Sencor-5-^{14}C. Report No. 91764. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 12

REVIEWED BY: W. Martin
TITLE: Staff Scientist
ORG: Dynamac Corporation
TEL: 301-468-2500

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: EFGWB/EFED/OPP
TEL: 305-5925

J. Breithaupt

SIGNATURE:

CONCLUSIONS:

Degradation - Hydrolysis

1. The hydrolysis study is acceptable and fulfills the 161-1 data requirement for metribuzin.
2. Metribuzin was stable in sterile, aqueous pH 5, 7, and 9 buffer solutions that were incubated in darkness at 25 °C.

METHODOLOGY:

Triazine ring-labeled ^{14}C-metribuzin (labeled in the number 5 position with a radiopurity of >99 % and specific activity of 21.9 mci/mMol was put into acetonitrile. The acetonitrile was transferred to a flask, the solvent evaporated under a nitrogen stream, and the residues were redissolved into "HPLC-grade" water with shaking and sonication. Aliquots of the metribuzin stock solution were added to approximately 22 ppm to aqueous 0.01 M buffer solutions adjusted to pH 5 (sodium acetate), pH 6 and 7 (potassium phosphate), and pH 9 (sodium borate). The treated buffer solutions were than filter-sterilized (0.45 um), dispensed into autoclaved glass vials, capped with teflon seals, and incubated in darkness at approximately 25 °C.

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Duplicate vials were removed for analysis at 0, 3, 8, 14, 20, 27, and 34 days after treatment.

The samples were analyzed for total radioactivity using LSC and for specific compounds using reverse phase (C_8 column) HPLC eluted with acetonitrile:water:acetic acid (35:65:0.4, v/v/v) with UV and radioactivity detection. The retention times of the residues were compared to reference standards of metribuzin, 6-tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)-one (DA), 6-tert-butyl-3-(methylthio)-1,2,4-triazin-3,5(2H,4H)-dione (DK), and 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) chromatographed in the same system.

In order to confirm the HPLC results, the 34-day samples and a metribuzin standard were partitioned with methyl-t-butyl ether and analyzed by GLC.

DATA SUMMARY:

Triazine ring-labeled ^{14}C-metribuzin (radiochemical purity >99 %), at approximately 22 ppm, did not hydrolyze in sterile aqueous pH 5, 7, and 9 buffer solutions incubated in darkness at 24.5-24.9 °C for 34 days. At 34 days after treatment, metribuzin comprised 97.1-100.2 % of the applied radioactivity (Table 1). Material balances ranged from 94.3-100.2 % of applied radioactivity.

COMMENTS:

The alkalinity of the pH 9 buffer solution declined to 8.42 at 34 days after treatment in both the control and test solutions. However, the results do not appear to be affected and therefore repeating the study is not necessary. The study author suggested that the 0.01 M buffer solution may have been too dilute to maintain the desired pH.

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METRIBUZIN

Page_____ is not included in this copy.

Pages 14 through 17 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.

X FIFRA registration data.

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

____ The document is not responsive to the request.

DATA EVALUATION RECORD

STUDY 2

CHEM 101101 Metribuzin §161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID (TRID Number 470173-0007)
Morgan, J.G. 1986a. The aqueous photolysis of Sencor-5-^{14}C. Report No. 91763. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 12

REVIEWED BY: W. Martin
TITLE: Staff Scientist
ORG: Dynamac Corporation
TEL: 301-468-2500

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: EFGWB/EFED/OPP
TEL: 305-5925

J. Breithaupt

SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation in Water

1. The aqueous photolysis study is acceptable and satisfies the 161-2 data requirement for metribuzin.

2. Metribuzin photodegraded with a half-life of 4.34 hours in "HPLC" water (pH 6.6) that was irradiated with sunlight at 26-29 °C. The only major degradate formed in the study was deaminated metribuzin (DA) which increased to 55 % of the applied dose by the end of the study.

METHODOLOGY:

An aqueous stock solution of triazine ring-labeled ^{14}C-metribuzin (labeled in the 5 position; radiochemical purity >99%, specific activity 21.9 mCi/mMol, Mobay) was diluted with "HPLC grade" water to produce a final metribuzin concentration of 20.33 ppm. Aliquots of the solution were filter-sterilized (0.45 um) into two autoclaved quartz photolysis cells that were fitted with two syringe ports and a thermocouple (Figure 2). The cells were covered with aluminum foil, then mounted on brackets within a photolysis apparatus, which con-

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sisted of a double-walled stainless steel tray covered with a quartz plate (Figure 3). The photolysis chamber was equipped with both a thermometer and radiometer which gave 10-minute averaged readings; a water/glycol solution was circulated through the heat jacket of the chamber to maintain the temperature at approximately 27 °C. When the setup was complete, the foil was removed from around one of the two photolysis cells and the treated solutions were exposed to sunlight in Kansas City, MO, on December 22, 1985. Samples were collected at 0, 0.5, 1, 2, 3, 4, 5, and 6 hours posttreatment. During the study period, the temperatures of the irradiated and dark control solutions ranged from 26.1 to 29.0 °C and 26.1 to 26.9 °C, respectively.

The samples were analyzed for total radioactivity using LSC and for specific compounds using reverse phase (C_8 column) HPLC eluted with acetonitrile:water:acetic acid (35:65:0.4, v:v:v), with UV and radioactivity detection. The retention times of the residues were compared to reference standards of metribuzin, 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA), 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK), and 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK).

DATA SUMMARY:

Triazine ring-labeled ^{14}C-metribuzin (radiochemical purity >99%), at 20.33 ppm, photodegraded with a registrant-calculated half-life of 4.34 hours in water irradiated with sunlight in Kansas City, MO (Table II). In contrast, ^{14}C-metribuzin was stable in the dark control during the 6-hour study period (Table I). After 6 hours of irradiation, ^{14}C-metribuzin comprised 33.3% of the applied radioactivity,

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA)

comprised 55%, and three unidentified degradates each comprised ≤5.2% (Table II). During the study, material balances in the irradiated and dark control solutions ranged from 95.4 to 102.3% of the applied (Tables I and II).

COMMENTS:

The study author stated that the photolysis solutions were not buffered because metribuzin was known to be stable to hydrolysis over a wide pH range. The pH of the solutions during the course of the study ranged from 6.57 to 6.69.

METRIBUZIN

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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.

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DATA EVALUATION RECORD

STUDY 3

CHEM 101101 Metribuzin §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID (TRID 470173-009)
Morgan, J.G. 1986c. The photodecomposition of Sencor-5-^{14}C on soil. Report No. 91765. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 12

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SIGNATURE: J. Breithaupt

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. The soil photolysis study is acceptable and satisfies the 161-3 data requirement for metribuzin.

2. Metribuzin photodegraded with a half-life of 2.5 days on sandy loam soil irradiated outdoors in Kansas City, Missouri at ≤31 °C. In contrast, metribuzin was relatively stable in the dark control. The major degradates were deaminated metribuzin (DA), pentylidene metribuzin, and hexylidene metribuzin.

METHODOLOGY:

A slurry of sieved (420 um) sandy loam soil (70% sand, 26% silt, 4% clay, 2.8% organic matter, pH 5.2, CEC 21 meq/100 g) was spread in Petri dishes to a depth of approximately 1 mm. The soils were air-dried overnight, then treated at 11.21 ug/cm^2 with triazine ring-labeled ^{14}C-metribuzin (labeled in the 5 position; radiochemical purity 99.14%, specific activity 21.9 mCi/mM, Mobay) in acetonitrile and air-dried for an additional hour. Half of the dishes were covered with aluminum foil, and all dishes of treated soil were placed in a photolysis apparatus. The photolysis apparatus consisted of a stainless steel tray containing a photodetector and covered with a quartz plate (Figure 2). A glycol:water solution (15 °C) circulating through a cooling jacket surrounding the tray controlled the soil temperature, which was monitored by a thermocouple thermometer placed in a dish of untreated soil inside the chamber. The maximum measured temperatures were 31.1 °C in the irradiated soil and 30.9 °C in the dark controls. Compressed air (ultra-pure grade) was passed through the chamber and exhausted through an Amberlite XAD-4 resin column and a 1 N sodium hydroxide trapping solution. The photolysis apparatus, located outdoors in Kansas City, Missouri, was oriented at a 45° angle to vertical and faced due south. Duplicate dishes of irradiated and dark control soil were removed for analysis after 0, 0.5, 1, 2, and 4 days of irradiation.

Each soil sample was transferred to a fritted glass filter funnel. The Petri dish was rinsed with acetonitrile and acetonitrile:water (1:1, v:v), and the rinse solution was poured into the funnel. The soil in the funnel was then extracted by rinsing three times with acetonitrile. An aliquot of the extract was concentrated under vacuum, and the resulting residues were redissolved in acetonitrile:-water (1:1, v:v). The solution was filtered (0.45 u), and the concentration flask was rinsed with acetonitrile. Both solutions were analyzed for total radioactivity using LSC. Aliquots of the acetonitrile:water solutions were analyzed by reverse phase (C_8 column) HPLC with gradient elution from acetonitrile:water:acetic acid (35:65:0.4, v:v:v) to acetonitrile with UV and radioactivity detection. The radioactive peaks were quantified by LSC and the retention times compared to reference standards of metribuzin, 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA), 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK), and 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) chromatographed in the same system. Subsamples of the extracted soil were analyzed for unextractable radioactivity using LSC following combustion.

The 4-day posttreatment extract was also analyzed by HPLC eluted with acetonitrile:water:acetic acid (67.5:32.5:0.2, v:v:v). The "major peaks" (designated compounds V and VI) from this HPLC reanalysis were further analyzed by TLC using silica gel plates developed in chloroform:ethyl acetate (9:1, v:v). The "major bands" were scraped from the plates, eluted in methyl tert-butyl ether and analyzed by GLC/MS with reference standards.

The Amberlite resin and sodium hydroxide trapping solutions were analyzed by LSC.

DATA SUMMARY:

Triazine ring-labeled ^{14}C-metribuzin (radiochemical purity 99.14%), at 94.4 ppm, degraded with a half-life of 2.5 days on sandy loam soil irradiated outdoors in Kansas City, Missouri. The concentration of metribuzin on the irradiated soil declined to 48.4% of the applied

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radioactivity by 4 days posttreatment, in contrast to 95.9% undegraded after 4 days in the dark control. The major degradates were

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA; maximum 16.1% of the applied),

pentylidene metribuzin (maximum 8.6%), and

hexylidene metribuzin (maximum 9.5%);

the maximum concentrations of all three compounds occurred at 4 days posttreatment. Unidentified apolar degradate(s) were a maximum 9.4% of the applied at 4 days posttreatment; two unidentified degradates and other uncharacterized residues were each ≤3.9% (Table IV). During the study, the material balances ranged from 98.2% to 101.5% of the applied radioactivity (Tables II and IV).

COMMENTS:

1. The methods description was incomplete. For example, the study author described the method to identify Compound VI, but the methodology used to identify Compound V was not reported.

2. Although the exact dates of the study were not reported, the study apparently was conducted on November 4-7, 1985. The study author noted that on November 6 the sky was heavily overcast.

3. The study author reported that the amount of test material used per sample was the equivalent of an application rate of 0.995 lb/A. The reviewer estimated that the application rate was 94.4 ppm, based on 219 ug metribuzin applied to 2.32 g of soil in each dish.

4. The study author stated that the half-life was calculated from the UV absorbance measurements during HPLC rather than the radioactivity measurements "due to the fewer measurements and manipulations necessary to obtain the former data". The concentration of metribuzin as determined by UV absorbance was approximately 7% less than the concentration determined by radiocarbon detection.

5. X-ray film was placed on the surface of the soil in a treated plate and exposed in a darkroom overnight. The films showed that the radioactivity was "evenly distributed" with "localized concentrations" on what appeared to be organic material in the soil.

METRIBUZIN

Page_____ is not included in this copy.

Pages 32 through 40 are not included.

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____ 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.

X FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 4

CHEM 101101 Metribuzin §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40367602
Detra, R.L., J.B. Lane, and M.D. Thyssen. 1987. Degradation of Sencor in aerobic sandy loam. Laboratory Project ID 94880. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 10

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SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. The aerobic soil metabolism study is acceptable and satisfies the 162-1 data requirement for metribuzin.

2. Metribuzin degraded with a half-life of 106 days in sandy loam soil that was incubated at 26 °C and 75% of 0.33 bar moisture capacity in darkness. Two major degradates identified were 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) and 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK). Four minor degradates identified were 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA); 2-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (2-methyl-DADK); 4-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (4-methyl-DADK); and, 3-amino-6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (3-NH_2-DA).

METHODOLOGY:

Air-dried, sieved (2 mm) sandy loam (67% sand, 27% silt, 6% clay, 2.4% organic matter content, pH 5.2, CEC 2.2 meq/100 g) was weighed (50 g) into 32 Erlenmeyer flasks and treated at 7.6 ppm with ring-labeled [^{14}C]metribuzin (labeled in the 5 position; radiochemical purity 98.7%, specific activity 20.8 mCi/mM, Mobay) dissolved in

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acetonitrile. The solvent was evaporated and the soil was manually mixed by rotating the sample flask at an angle. The soil was moistened to 75% of 0.33 bar with distilled water. Each sample flask was wrapped in aluminum foil to prevent photolysis and connected to a flow-through apparatus as shown in Figure 2. Humidified, CO_2-free air (20-30 mL/minute) was drawn through individual flasks and into separate 10% sodium hydroxide trapping solutions. The treated soil was incubated on a laboratory bench at 26 ± 2 C. Duplicate soil samples were collected at 0, 1, 3, 7, 14, 30, 59, 92, 122, 184, 273, and 365 days posttreatment. The trapping solutions were sampled at each sampling interval.

The soil samples were analyzed as shown in Figure 3. A portion of each soil sample was extracted with methanol at room temperature by stirring for 2 hours, then the extract was filtered. The extracted soil was further extracted by refluxing for 2 hours in methanol:water (7:3, v:v); the extract was cooled, filtered, and combined with the first methanol extract. The methanol was evaporated from the extracts, and the resulting aqueous solution was partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The aqueous fraction resulting from the partitioning was analyzed for total radioactivity by LSC. The organic fraction was evaporated to dryness and redissolved in methylene chloride:methanol (1:1, v:v). Aliquots of the organic extracts were analyzed for total radioactivity by LSC; additional aliquots were analyzed for metribuzin and its degradates using TLC on silica gel plates developed in the following solvent systems: chloroform:ethyl acetate (1:1, v:v; solvent system A); benzene:ethyl acetate:acetic acid (50:10:1, v:v; solvent system B); hexane:ethylene glycol dimethylether:methylene chloride: acetic acid (60:40:10:1, v:v; solvent system C). Unlabeled reference standards were cochromatographed with the extracts and, following development, visualized using UV fluorescence quenching. Radioactive areas on the plates were located using autoradiography, then scraped from the plates and analyzed for total radioactivity by LSC.

The twice-extracted soil was refluxed for 4 hours in 1 N hydrochloric acid, and the extract was filtered and partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The resulting organic fraction was rotary evaporated to dryness; the resulting residues were dissolved in methylene chloride:methanol (1:1, v:v), and aliquots were analyzed by LSC and TLC as described above. The aqueous fraction was analyzed by LSC only. $[^{14}C]$Residues remaining in the extracted soil were quantified by LSC following combustion. The identities of the degradates were confirmed using one or more of the following analytical methods: HPLC with linear gradient elution from water:acetic acid (249:1, v:v) to acetonitrile:water:acetic acid (149.4:99.6:1, v:v:v); GC with electron capture detection; GC/MS or MS-direct probe. Method detection limits were not provided.

In order to characterize polar material that remained at the origin of the TLC plates in solvent system A, three 0.5 mL-aliquots of the extract were developed on separate TLC plates. Radioactivity remaining at the origin was collected and eluted from the silica gel with methanol. The solution was dried under a stream of nitrogen, and the residue was redissolved in water and extracted three times with methyl-t-butyl ether (MtBE). The MtBE was evaporated under a stream of nitrogen, the residue was redissolved in methanol, and then analyzed using solvent system B. An aliquot of sample was dissolved in distilled water and refluxed for 2 hours. The refluxate was extracted three times with methylene chloride:acetonitrile (2:1, v:v), and the extract was evaporated to dryness under a stream of nitrogen. The residue was dissolved in methanol, and aliquots were analyzed using solvent system B. The aqueous fraction of the refluxate was divided into two portions; one portion was acidified with 5% sodium acetate (pH 4.2) and the remaining portion was alkalinized with 5% sodium borate (pH 9.2). Each portion was then extracted three times with methylene chloride:acetonitrile (2:1, v:v); the organic and aqueous extracts were then analyzed by LSC.

Aliquots of the trapping solutions were analyzed for total radioactivity using LSC.

DATA SUMMARY:

Ring-labeled [^{14}C]metribuzin (radiochemical purity 98.7%), at 7.6 ppm, degraded with a registrant-calculated half-life of 106 days in sandy loam that was incubated in darkness at 26 ± 2 °C and 75% of 0.33 bar moisture capacity. Metribuzin decreased from 98.9% of the applied at 0 days to 53.1% at 59 days, 33.1% at 92 days, and 13.6% at 365 days (Table V). Six degradates were identified in the soil extracts.

6-Tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) comprised a maximum of 33.6% of the applied (2.55 ppm) at 365 days posttreatment;

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK) comprised a maximum of 12.2% (0.93 ppm) at 92 days; and

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA) comprised a maximum of 6.8% (0.52 ppm) at 122 days.

2-Methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (2-methyl-DADK),

4-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (4-methyl-DADK), and

3-amino-6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (3-NH_2-DA)

each comprised ≤2.2% of the applied during the course of the study. In addition, eight unidentified [^{14}C]compounds (Unknowns I-VIII) were each isolated at maximum concentrations ranging from 0.3 to 9.3% of the applied (0.02-0.71 ppm) (Table IV). [^{14}C]Residues remaining at the origin comprised up to 11.9% of the applied, diffuse radioactivity comprised up to 5.3%, uncharacterized water-soluble residues comprised up to 5.7%, and unextractable [^{14}C]residues comprised up to

23.2% (Tables III and V). Cumulative volatiles totalled up to 7.6% of the applied (0.58 ppm) by 273 days posttreatment. During the study, the material balances ranged from 92.6 to 110.3% of the applied.

COMMENTS:

1. The data were variable, especially at the later sampling intervals (Table III, Figure 11). This variability may have had an effect on the estimation of the half-life of metribuzin.

2. Method detection limits and recovery efficiencies from fortified soil samples were not provided.

METRIBUZIN

Page_____ is not included in this copy.

Pages 45 through 60 are not included.

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____ 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.

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DATA EVALUATION RECORD

STUDY 5

CHEM 101101 Metribuzin §162-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40367603

Detra, R.L., and M.D. Thyssen. 1987. Degradation of Sencor in anaerobic sandy loam. Laboratory Project ID Report Number 94881. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Metabolism - Anaerobic Soil

1. The anaerobic soil metabolism study is acceptable and satisfies the 162-2 data requirement for metribuzin.

2. Metribuzin degraded with a half-life of 112 days in sandy loam that was flooded and incubated at 24 ± 2 °C in darkness for 60 days following 30 days of aerobic incubation. During the anaerobic portion of the study, the degradates identified were: 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK); 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA); 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK); and 2-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)dione (2-methyl-DADK). Seventy-eight to 88 % of all radioactivity was in the organic phase from the methanol extrations of soil and <5 % was in the aqueous phase.

METHODOLOGY:

Air-dried, sieved (2 mm) sandy loam (67% sand, 27% silt, 6% clay, 2.4% organic matter content, pH 5.2, CEC 2.2 meq/100 g) was weighed (50 g) into eight Erlenmeyer flasks and treated at 6 ppm with ring-labeled [^{14}C]metribuzin (labeled in the 5 position, radiochemical purity 97%, specific activity 20.8 mCi/mM, Mobay) dissolved in acetonitrile. The solvent was evaporated and the soil was manually mixed by rotating the flask at an angle. The soil was moistened to 75% of 0.33 bar with distilled water. Each sample flask was wrapped in aluminum foil to prevent photolysis and connected to a flow-through apparatus. Humidified, CO_2-free air (20-30 mL/minute) was drawn through individual flasks and into separate 10% sodium hydroxide trapping solutions. The treated soil was incubated on a laboratory bench at 26 ± 2 °C.

Following a 30-day aerobic incubation, the soil samples were flooded with 50 mL of HPLC-grade water and the air flow was terminated. The samples were then incubated at 24 ± 1 °C for 60 days. Duplicate soil samples were collected immediately after flooding and on days 31 and 60 of the anaerobic incubation period. To trap evolved $^{14}CO_2$, the flasks were reconnected to the flow-through system and purged with air for 1 hour; the trapping solutions were sampled at each sampling interval.

The anaerobic soil samples were analyzed as shown in Figure 2. The samples were filtered to separate the soil and water. The resulting water fraction was extracted three times with methylene chloride:acetonitrile (2:1, v:v). The aqueous phase was analyzed for total radioactivity by LSC; the organic phase was collected in a boiling flask.

Portions of each soil fraction were extracted by stirring with methanol for 2 hours. The mixture was filtered under vacuum, and the methanol filtrate was pooled with the organosolubles from the water fraction. The extracted soil was further extracted by refluxing for 2 hours in methanol:water (7:3, v:v); the extract was cooled, filtered, and combined with the first methanol extract. The methanol was removed by rotary evaporation from the extracts, and the resulting aqueous solution was partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The aqueous fraction resulting from the partitioning was analyzed for total radioactivity by LSC. The organic fraction was evaporated to dryness and redissolved in methylene chloride:methanol (1:1, v:v). Aliquots of the organic extracts were analyzed for total radioactivity by LSC; additional aliquots were analyzed for metribuzin and its degradates using TLC on silica gel plates developed in the following solvent systems: chloroform:ethyl acetate (1:1, v:v; solvent system A); benzene:ethyl acetate:acetic acid (50:10:1, v:v; solvent system B); and, hexane:ethylene glycol dimethyl ether:methylene chloride: acetic acid (60:40:10:1, v:v; solvent system C). Unlabeled reference standards were cochromatographed with the extracts and, following development, visualized using UV fluorescence quenching. Radioactive areas on the plates were located using autoradiography, then scraped from the plates and analyzed for total radioactivity by LSC.

The twice-extracted soil was refluxed for 4 hours in 1 N hydrochloric acid, and the extract was filtered and partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The resulting organic fraction was rotary evaporated to dryness; the resulting residues

Water Preparation

The test water was sterilized using a 0.22 micron filter.

Preliminary Study

Duplicate 1-g samples of sandy, sandy loam, silt loam, and clay loam soils and 10 ml of 25 ug/ml test solutions were added to sterilized tubes and shaken for 4, 6, 8, 16, 24, 36, and 48 hours. The radioactivity in solution at each time was analyzed by LSC.

Adsorption

Sand, sandy loam, silt loam, and clay loam soils were mixed with 0.01 M calcium chloride solutions containing triazine-labeled ^{14}-metribuzin) (Metribuzin; radiochemical purity 99.4 %, specific activity 20.8 uCi/mg, Mobay) at nominal concentrations of 0, 250, 187.5, 125, and 5 ug/mL (3 g soil:10 mL solution). The soil:solution slurries were shaken at 25 ± 1 °C for 4 hours and then centrifuged. Triplicate 1 ml volumes of the supernatant were removed and analyzed by LSC.

Desorption

The removed supernatant was replaced by 0.01 M $CaNO_3$ and the tubes were again shaken for 24 hours. After centrifuging, triplicate 1-ml aliquots were again removed and analyzed by LSC.

Soil Analysis

The wet soil pellets combusted in triplicate for radioanalysis to determine mass balance of metribuzin.

DATA SUMMARY:

Based on batch equilibrium studies, triazine-labeled ^{14}C-metribuzin (radiochemical purity 99.4 %), at 0, 250, 187.5, 125, and 25 ug/ml, was determined to be very mobile in sandy, sandy loam, silt loam, and clay loam soil:calcium chloride solution slurries (3:10, w:v) that were equilibrated by shaking for 4 hours in darkness at room temperature. The actual concentrations of metribuzin in solution were 210, 157, 103, and 20 ug/ml. Freundlich Kd_{ads} values were 0.25 for the sandy soil, 0.02 for the sandy loam soil, 0.22 for the silt loam soil, and 0.20 for the clay loam soil; 1/n values ranged from 1.06-1.68. Kd_{des} values were 0.56 for the sand, 0.141 for the sandy loam, 0.51 for the silt loam, and 0.41 for the clay loam soil. Koc_{ads} values were 47, 3.1, 15, and 17 for sand, sandy loam, silt loam, and clay loam soils, respectively. Koc_{des} values were 106, 24.3, 33, and 36, respectively. The soils contained 0.58, 0.64, 1.68, and 1.28 % OC, respectively.

DATA EVALUATION RECORD

STUDY 6

CHEM 046301 METRIBUZIN §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42283001
Daly, D. October 7, 1988. Soil Adsorption-Desorption with ^{14}C-Sencor. Unpulished study conducted by ABC Laboratories and submitted by Miles Corporation. ABC Report # 36997 (MRID 42283001).

DIRECT REVIEW TIME = 2 Days

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SIGNATURE: B Conerly-Perks for ADA

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption (163-1)

1. The leaching-adsorption-desorption study is acceptable and satisfies the unaged portion of the 163-1 data requirement.

2. Metribuzin is very mobile in soil with Freundlich K_{ads} values of 0.02-0.25 for the adsorption phase and 0.14-0.56 for the desorption phase in soils with 0.58-1.68 % OC. K_{oc} values ranged from 3 to 46 for adsorption and 24 to 106 for desorption.

METHODOLOGY:

Soil Preparation

Sand, sandy loam, silt loam, and clay loam soils (series not specified) from California were ground to pass a 2-mm diameter size sieve, air dried, and characterized. The protocol deviation stated that the soils were sterilized using 1 % (w/w) sodium azide because conducting the study with both sterilized and non-sterilized soils would "exceed the time allowed for the study."

METRIBUZIN

Page 65 is not included in this copy.

Pages ____ through ____ are not included.

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____ 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.

X FIFRA registration data.

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

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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.

COMMENTS:

1. Information about the source of soils was not provided. The registrant stated that ABC Laboratories provided the soils, and that the study was conducted for CALIFORNIA registration of metribuzin. Therefore, the EFGWB reviewer assumed that all four soils were from California. EFGWB generally requires soils from different geographical use regions, but the mobility of metribuzin is very evident in this study. Therefore, the study will satisfy the unaged portion of the 163-1 guideline.

2. The registrant sterilized the soil using sodium azide to stabilize the metribuzin and EFGWB does not normally recommend sterilization of soils for mobility studies. However, the mobility of metribuzin was highly evident and repeating the study is not warranted.

METRIBUZIN

Page_____ is not included in this copy.

Pages 67 through 82 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.
- __X__ FIFRA registration data.
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DATA EVALUATION RECORD

STUDY 3

CHEM 101101 Metribuzin §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID (TRID 470173-009)
Morgan, J.G. 1986c. The photodecomposition of Sencor-5-^{14}C on soil. Report No. 91765. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 12

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APPROVED BY: J. Breithaupt
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J. Breithaupt

SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. The soil photolysis study is acceptable and satisfies the 161-3 data requirement for metribuzin.

2. Metribuzin photodegraded with a half-life of 2.5 days on sandy loam soil irradiated outdoors in Kansas City, Missouri at ≤31 °C. In contrast, metribuzin was relatively stable in the dark control. The major degradates were deaminated metribuzin (DA), pentylidene metribuzin, and hexylidene metribuzin.

METHODOLOGY:

A slurry of sieved (420 um) sandy loam soil (70% sand, 26% silt, 4% clay, 2.8% organic matter, pH 5.2, CEC 21 meq/100 g) was spread in Petri dishes to a depth of approximately 1 mm. The soils were air-dried overnight, then treated at 11.21 ug/cm^2 with triazine ring-labeled ^{14}C-metribuzin (labeled in the 5 position; radiochemical purity 99.14%, specific activity 21.9 mCi/mM, Mobay) in acetonitrile and air-dried for an additional hour. Half of the dishes were covered with aluminum foil, and all dishes of treated soil were placed in a photolysis apparatus. The photolysis apparatus consisted of a stainless steel tray containing a photodetector and covered with a quartz plate (Figure 2). A glycol:water solution (15 °C) circulating through a cooling jacket surrounding the tray controlled the soil temperature, which was monitored by a thermocouple thermometer placed in a dish of untreated soil inside the chamber. The maximum measured temperatures were 31.1 °C in the irradiated soil and 30.9 °C in the dark controls. Compressed air (ultra-pure grade) was passed through the chamber and exhausted through an Amberlite XAD-4 resin column and a 1 N sodium hydroxide trapping solution. The photolysis apparatus, located outdoors in Kansas City, Missouri, was oriented at a 45° angle to vertical and faced due south. Duplicate dishes of irradiated and dark control soil were removed for analysis after 0, 0.5, 1, 2, and 4 days of irradiation.

Each soil sample was transferred to a fritted glass filter funnel. The Petri dish was rinsed with acetonitrile and acetonitrile:water (1:1, v:v), and the rinse solution was poured into the funnel. The soil in the funnel was then extracted by rinsing three times with acetonitrile. An aliquot of the extract was concentrated under vacuum, and the resulting residues were redissolved in acetonitrile:-water (1:1, v:v). The solution was filtered (0.45 u), and the concentration flask was rinsed with acetonitrile. Both solutions were analyzed for total radioactivity using LSC. Aliquots of the acetonitrile:water solutions were analyzed by reverse phase (C_8 column) HPLC with gradient elution from acetonitrile:water:acetic acid (35:65:0.4, v:v:v) to acetonitrile with UV and radioactivity detection. The radioactive peaks were quantified by LSC and the retention times compared to reference standards of metribuzin, 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA), 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK), and 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) chromatographed in the same system. Subsamples of the extracted soil were analyzed for unextractable radioactivity using LSC following combustion.

The 4-day posttreatment extract was also analyzed by HPLC eluted with acetonitrile:water:acetic acid (67.5:32.5:0.2, v:v:v). The "major peaks" (designated compounds V and VI) from this HPLC reanalysis were further analyzed by TLC using silica gel plates developed in chloroform:ethyl acetate (9:1, v:v). The "major bands" were scraped from the plates, eluted in methyl tert-butyl ether and analyzed by GLC/MS with reference standards.

The Amberlite resin and sodium hydroxide trapping solutions were analyzed by LSC.

DATA SUMMARY:

Triazine ring-labeled ^{14}C-metribuzin (radiochemical purity 99.14%), at 94.4 ppm, degraded with a half-life of 2.5 days on sandy loam soil irradiated outdoors in Kansas City, Missouri. The concentration of metribuzin on the irradiated soil declined to 48.4% of the applied

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radioactivity by 4 days posttreatment, in contrast to 95.9% undegraded after 4 days in the dark control. The major degradates were

> 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA; maximum 16.1% of the applied),
>
> pentylidene metribuzin (maximum 8.6%), and
>
> hexylidene metribuzin (maximum 9.5%);

the maximum concentrations of all three compounds occurred at 4 days posttreatment. Unidentified apolar degradate(s) were a maximum 9.4% of the applied at 4 days posttreatment; two unidentified degradates and other uncharacterized residues were each ≤3.9% (Table IV). During the study, the material balances ranged from 98.2% to 101.5% of the applied radioactivity (Tables II and IV).

COMMENTS:

1. The methods description was incomplete. For example, the study author described the method to identify Compound VI, but the methodology used to identify Compound V was not reported.

2. Although the exact dates of the study were not reported, the study apparently was conducted on November 4-7, 1985. The study author noted that on November 6 the sky was heavily overcast.

3. The study author reported that the amount of test material used per sample was the equivalent of an application rate of 0.995 lb/A. The reviewer estimated that the application rate was 94.4 ppm, based on 219 ug metribuzin applied to 2.32 g of soil in each dish.

4. The study author stated that the half-life was calculated from the UV absorbance measurements during HPLC rather than the radioactivity measurements "due to the fewer measurements and manipulations necessary to obtain the former data". The concentration of metribuzin as determined by UV absorbance was approximately 7% less than the concentration determined by radiocarbon detection.

5. X-ray film was placed on the surface of the soil in a treated plate and exposed in a darkroom overnight. The films showed that the radioactivity was "evenly distributed" with "localized concentrations" on what appeared to be organic material in the soil.

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METRIBUZIN

Page_____ is not included in this copy.

Pages 86 through 94 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.

X FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 4

CHEM 101101 Metribuzin §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40367602
Detra, R.L., J.B. Lane, and M.D. Thyssen. 1987. Degradation of Sencor in aerobic sandy loam. Laboratory Project ID 94880. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 10

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J. Breithaupt

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. The aerobic soil metabolism study is acceptable and satisfies the 162-1 data requirement for metribuzin.

2. Metribuzin degraded with a half-life of 106 days in sandy loam soil that was incubated at 26 °C and 75% of 0.33 bar moisture capacity in darkness. Two major degradates identified were 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) and 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK). Four minor degradates identified were 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA); 2-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (2-methyl-DADK); 4-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (4-methyl-DADK); and, 3-amino-6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (3-NH_2-DA).

METHODOLOGY:

Air-dried, sieved (2 mm) sandy loam (67% sand, 27% silt, 6% clay, 2.4% organic matter content, pH 5.2, CEC 2.2 meq/100 g) was weighed (50 g) into 32 Erlenmeyer flasks and treated at 7.6 ppm with ring-labeled [^{14}C]metribuzin (labeled in the 5 position; radiochemical purity 98.7%, specific activity 20.8 mCi/mM, Mobay) dissolved in acetonitrile. The solvent was evaporated and the soil was manually mixed by rotating the sample flask at an angle. The soil was moistened to 75% of 0.33 bar with distilled water. Each sample flask was wrapped in aluminum foil to prevent photolysis and connected to a flow-through apparatus as shown in Figure 2. Humidified, CO_2-free air (20-30 mL/minute) was drawn through individual flasks and into separate 10% sodium hydroxide trapping solutions. The treated soil was incubated on a laboratory bench at 26 ± 2 C. Duplicate soil samples were collected at 0, 1, 3, 7, 14, 30, 59, 92, 122, 184, 273, and 365 days posttreatment. The trapping solutions were sampled at each sampling interval.

The soil samples were analyzed as shown in Figure 3. A portion of each soil sample was extracted with methanol at room temperature by stirring for 2 hours, then the extract was filtered. The extracted soil was further extracted by refluxing for 2 hours in methanol:water (7:3, v:v); the extract was cooled, filtered, and combined with the first methanol extract. The methanol was evaporated from the extracts, and the resulting aqueous solution was partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The aqueous fraction resulting from the partitioning was analyzed for total radioactivity by LSC. The organic fraction was evaporated to dryness and redissolved in methylene chloride:methanol (1:1, v:v). Aliquots of the organic extracts were analyzed for total radioactivity by LSC; additional aliquots were analyzed for metribuzin and its degradates using TLC on silica gel plates developed in the following solvent systems: chloroform:ethyl acetate (1:1, v:v; solvent system A); benzene:ethyl acetate:acetic acid (50:10:1, v:v; solvent system B); hexane:ethylene glycol dimethylether:methylene chloride: acetic acid (60:40:10:1, v:v; solvent system C). Unlabeled reference standards were cochromatographed with the extracts and, following development, visualized using UV fluorescence quenching. Radioactive areas on the plates were located using autoradiography, then scraped from the plates and analyzed for total radioactivity by LSC.

The twice-extracted soil was refluxed for 4 hours in 1 N hydrochloric acid, and the extract was filtered and partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The resulting organic fraction was rotary evaporated to dryness; the resulting residues were dissolved in methylene chloride:methanol (1:1, v:v), and aliquots were analyzed by LSC and TLC as described above. The aqueous fraction was analyzed by LSC only. [^{14}C]Residues remaining in the extracted soil were quantified by LSC following combustion. The identities of the degradates were confirmed using one or more of the following analytical methods: HPLC with linear gradient elution from water:acetic acid (249:1, v:v) to acetonitrile:water:acetic acid (149.4:99.6:1, v:v:v); GC with electron capture detection; GC/MS or MS-direct probe. Method detection limits were not provided.

In order to characterize polar material that remained at the origin of the TLC plates in solvent system A, three 0.5 mL-aliquots of the extract were developed on separate TLC plates. Radioactivity remaining at the origin was collected and eluted from the silica gel with methanol. The solution was dried under a stream of nitrogen, and the residue was redissolved in water and extracted three times with methyl-t-butyl ether (MtBE). The MtBE was evaporated under a stream of nitrogen, the residue was redissolved in methanol, and then analyzed using solvent system B. An aliquot of sample was dissolved in distilled water and refluxed for 2 hours. The refluxate was extracted three times with methylene chloride:acetonitrile (2:1, v:v), and the extract was evaporated to dryness under a stream of nitrogen. The residue was dissolved in methanol, and aliquots were analyzed using solvent system B. The aqueous fraction of the refluxate was divided into two portions; one portion was acidified with 5% sodium acetate (pH 4.2) and the remaining portion was alkalinized with 5% sodium borate (pH 9.2). Each portion was then extracted three times with methylene chloride:acetonitrile (2:1, v:v); the organic and aqueous extracts were then analyzed by LSC.

Aliquots of the trapping solutions were analyzed for total radioactivity using LSC.

DATA SUMMARY:

Ring-labeled [^{14}C]metribuzin (radiochemical purity 98.7%), at 7.6 ppm, degraded with a registrant-calculated half-life of 106 days in sandy loam that was incubated in darkness at 26 ± 2 °C and 75% of 0.33 bar moisture capacity. Metribuzin decreased from 98.9% of the applied at 0 days to 53.1% at 59 days, 33.1% at 92 days, and 13.6% at 365 days (Table V). Six degradates were identified in the soil extracts.

6-Tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) comprised a maximum of 33.6% of the applied (2.55 ppm) at 365 days posttreatment;

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK) comprised a maximum of 12.2% (0.93 ppm) at 92 days; and

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA) comprised a maximum of 6.8% (0.52 ppm) at 122 days.

2-Methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (2-methyl-DADK),

4-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (4-methyl-DADK), and

3-amino-6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (3-NH_2-DA)

each comprised ≤2.2% of the applied during the course of the study. In addition, eight unidentified [^{14}C]compounds (Unknowns I-VIII) were each isolated at maximum concentrations ranging from 0.3 to 9.3% of the applied (0.02-0.71 ppm) (Table IV). [^{14}C]Residues remaining at the origin comprised up to 11.9% of the applied, diffuse radioactivity comprised up to 5.3%, uncharacterized water-soluble residues comprised up to 5.7%, and unextractable [^{14}C]residues comprised up to

23.2% (Tables III and V). Cumulative volatiles totalled up to 7.6% of the applied (0.58 ppm) by 273 days posttreatment. During the study, the material balances ranged from 92.6 to 110.3% of the applied.

COMMENTS:

1. The data were variable, especially at the later sampling intervals (Table III, Figure 11). This variability may have had an effect on the estimation of the half-life of metribuzin.

2. Method detection limits and recovery efficiencies from fortified soil samples were not provided.

METRIBUZIN

Page_____ is not included in this copy.

Pages 99 through 114 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.

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DATA EVALUATION RECORD

STUDY 5

CHEM 101101 Metribuzin §162-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40367603

Detra, R.L., and M.D. Thyssen. 1987. Degradation of Sencor in anaerobic sandy loam. Laboratory Project ID Report Number 94881. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Metabolism - Anaerobic Soil

1. The anaerobic soil metabolism study is acceptable and satisfies the 162-2 data requirement for metribuzin.

2. Metribuzin degraded with a half-life of 112 days in sandy loam that was flooded and incubated at 24 ± 2 °C in darkness for 60 days following 30 days of aerobic incubation. During the anaerobic portion of the study, the degradates identified were: 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK); 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA); 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK); and 2-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)dione (2-methyl-DADK). Seventy-eight to 88 % of all radioactivity was in the organic phase from the methanol extrations of soil and <5 % was in the aqueous phase.

METHODOLOGY:

Air-dried, sieved (2 mm) sandy loam (67% sand, 27% silt, 6% clay, 2.4% organic matter content, pH 5.2, CEC 2.2 meq/100 g) was weighed (50 g) into eight Erlenmeyer flasks and treated at 6 ppm with ring-labeled [^{14}C]metribuzin (labeled in the 5 position, radiochemical

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purity 97%, specific activity 20.8 mCi/mM, Mobay) dissolved in acetonitrile. The solvent was evaporated and the soil was manually mixed by rotating the flask at an angle. The soil was moistened to 75% of 0.33 bar with distilled water. Each sample flask was wrapped in aluminum foil to prevent photolysis and connected to a flow-through apparatus. Humidified, CO_2-free air (20-30 mL/minute) was drawn through individual flasks and into separate 10% sodium hydroxide trapping solutions. The treated soil was incubated on a laboratory bench at 26 ± 2 °C.

Following a 30-day aerobic incubation, the soil samples were flooded with 50 mL of HPLC-grade water and the air flow was terminated. The samples were then incubated at 24 ± 1 °C for 60 days. Duplicate soil samples were collected immediately after flooding and on days 31 and 60 of the anaerobic incubation period. To trap evolved $^{14}CO_2$, the flasks were reconnected to the flow-through system and purged with air for 1 hour; the trapping solutions were sampled at each sampling interval.

The anaerobic soil samples were analyzed as shown in Figure 2. The samples were filtered to separate the soil and water. The resulting water fraction was extracted three times with methylene chloride:acetonitrile (2:1, v:v). The aqueous phase was analyzed for total radioactivity by LSC; the organic phase was collected in a boiling flask.

Portions of each soil fraction were extracted by stirring with methanol for 2 hours. The mixture was filtered under vacuum, and the methanol filtrate was pooled with the organosolubles from the water fraction. The extracted soil was further extracted by refluxing for 2 hours in methanol:water (7:3, v:v); the extract was cooled, filtered, and combined with the first methanol extract. The methanol was removed by rotary evaporation from the extracts, and the resulting aqueous solution was partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The aqueous fraction resulting from the partitioning was analyzed for total radioactivity by LSC. The organic fraction was evaporated to dryness and redissolved in methylene chloride:methanol (1:1, v:v). Aliquots of the organic extracts were analyzed for total radioactivity by LSC; additional aliquots were analyzed for metribuzin and its degradates using TLC on silica gel plates developed in the following solvent systems: chloroform:ethyl acetate (1:1, v:v; solvent system A); benzene:ethyl acetate:acetic acid (50:10:1, v:v; solvent system B); and, hexane:ethylene glycol dimethyl ether:methylene chloride: acetic acid (60:40:10:1, v:v; solvent system C). Unlabeled reference standards were cochromatographed with the extracts and, following development, visualized using UV fluorescence quenching. Radioactive areas on the plates were located using autoradiography, then scraped from the plates and analyzed for total radioactivity by LSC.

The twice-extracted soil was refluxed for 4 hours in 1 N hydrochloric acid, and the extract was filtered and partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The resulting organic fraction was rotary evaporated to dryness; the resulting residues

Water Preparation

The test water was sterilized using a 0.22 micron filter.

Preliminary Study

Duplicate 1-g samples of sandy, sandy loam, silt loam, and clay loam soils and 10 ml of 25 ug/ml test solutions were added to sterilized tubes and shaken for 4, 6, 8, 16, 24, 36, and 48 hours. The radioactivity in solution at each time was analyzed by LSC.

Adsorption

Sand, sandy loam, silt loam, and clay loam soils were mixed with 0.01 M calcium chloride solutions containing triazine-labeled ^{14}-metribuzin) (Metribuzin; radiochemical purity 99.4 %, specific activity 20.8 uCi/mg, Mobay) at nominal concentrations of 0, 250, 187.5, 125, and 5 ug/mL (3 g soil:10 mL solution). The soil:solution slurries were shaken at 25 ± 1 °C for 4 hours and then centrifuged. Triplicate 1 ml volumes of the supernatant were removed and analyzed by LSC.

Desorption

The removed supernatant was replaced by 0.01 M $CaNO_3$ and the tubes were again shaken for 24 hours. After centrifuging, triplicate 1-ml aliquots were again removed and analyzed by LSC.

Soil Analysis

The wet soil pellets combusted in triplicate for radioanalysis to determine mass balance of metribuzin.

DATA SUMMARY:

Based on batch equilibrium studies, triazine-labeled ^{14}C-metribuzin (radiochemical purity 99.4 %), at 0, 250, 187.5, 125, and 25 ug/ml, was determined to be very mobile in sandy, sandy loam, silt loam, and clay loam soil:calcium chloride solution slurries (3:10, w:v) that were equilibrated by shaking for 4 hours in darkness at room temperature. The actual concentrations of metribuzin in solution were 210, 157, 103, and 20 ug/ml. Freundlich Kd_{ads} values were 0.25 for the sandy soil, 0.02 for the sandy loam soil, 0.22 for the silt loam soil, and 0.20 for the clay loam soil; 1/n values ranged from 1.06-1.68. Kd_{des} values were 0.56 for the sand, 0.141 for the sandy loam, 0.51 for the silt loam, and 0.41 for the clay loam soil. Koc_{ads} values were 47, 3.1, 15, and 17 for sand, sandy loam, silt loam, and clay loam soils, respectively. Koc_{des} values were 106, 24.3, 33, and 36, respectively. The soils contained 0.58, 0.64, 1.68, and 1.28 % OC, respectively.

DATA EVALUATION RECORD

STUDY 6

CHEM 046301 METRIBUZIN §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42283001
Daly, D. October 7, 1988. Soil Adsorption-Desorption with ^{14}C-Sencor. Unpulished study conducted by ABC Laboratories and submitted by Miles Corporation. ABC Report # 36997 (MRID 42283001).

DIRECT REVIEW TIME = 2 Days

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SIGNATURE: B Conerly-Parks for ADA

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption (163-1)

1. The leaching-adsorption-desorption study is acceptable and satisfies the unaged portion of the 163-1 data requirement.
2. Metribuzin is very mobile in soil with Freundlich K_{ads} values of 0.02-0.25 for the adsorption phase and 0.14-0.56 for the desorption phase in soils with 0.58-1.68 % OC. K_{oc} values ranged from 3 to 46 for adsorption and 24 to 106 for desorption.

METHODOLOGY:

Soil Preparation

Sand, sandy loam, silt loam, and clay loam soils (series not specified) from California were ground to pass a 2-mm diameter size sieve, air dried, and characterized. The protocol deviation stated that the soils were sterilized using 1 % (w/w) sodium azide because conducting the study with both sterilized and non-sterilized soils would "exceed the time allowed for the study."

METRIBUZIN

Page 119 is not included in this copy.

Pages _____ through _____ 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.

X FIFRA registration data.

_____ The document is a duplicate of page(s) _____.

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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.

COMMENTS:

1. Information about the source of soils was not provided. The registrant stated that ABC Laboratories provided the soils, and that the study was conducted for CALIFORNIA registration of metribuzin. Therefore, the EFGWB reviewer assumed that all four soils were from California. EFGWB generally requires soils from different geographical use regions, but the mobility of metribuzin is very evident in this study. Therefore, the study will satisfy the unaged portion of the 163-1 guideline.

2. The registrant sterilized the soil using sodium azide to stabilize the metribuzin and EFGWB does not normally recommend sterilization of soils for mobility studies. However, the mobility of metribuzin was highly evident and repeating the study is not warranted.

METRIBUZIN

Page _____ is not included in this copy.

Pages 121 through 132 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.
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- X 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.

Duplicate glass columns were packed to a depth of approximately 30 cm with air-dried, sieved sandy loam, silt loam, and silty clay soils (Table II) and saturated with 0.01 M calcium chloride solution. The soil columns were drained and wrapped in aluminum foil. The aged treated soil subsamples were placed on top of each column, and the treated layers were stabilized with a glass fiber filter. The columns were leached with 1120 mL (20 inches) of 0.01 M calcium chloride solution over a 2-day period. The leachate was collected continuously in 100 mL fractions. After leaching, the soil columns were frozen (-5 C) for 24-48 hours, then sectioned into 6-cm segments. The glass columns were rinsed with water and methanol, and the rinses were analyzed for residual radioactivity using LSC.

Aliquots of individual leachate fractions were analyzed for total radioactivity using LSC. The remaining leachate was pooled, concentrated (method not reported), and partitioned with methylene chloride:acetonitrile (2:1, v:v). The aqueous and organic phases were analyzed for total radioactivity using LSC; the organic phase was analyzed by one-dimensional TLC on silica gel plates developed in chloroform:ethyl acetate (1:1, v:v) or chloroform:ethylene glycol dimethyl ether:dioxane:acetic acid (95:5:5:1, v:v:v:v).]Residues on the plates were identified by comparison to reference standards of metribuzin, 6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA), 4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK) and 6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK). The organic phase was also analyzed using reverse phase HPLC using a water:acetonitrile:acetic acid (325:175:2, v:v:v) mobile phase and radioactivity detection.

The soil segments were air-dried and pulverized, and portions of each segment were analyzed for total radioactivity using LSC following combustion. A subsample of the 0- to 6-cm section was extracted by stirring with methanol and then refluxed with methanol:water (7:3, v:v); each extraction was for 2 hours (Figure 2). The extracts were pooled, the methanol was evaporated, and the aqueous phase partitioned with methylene chloride:acetonitrile (2:1, v:v). Both phases were analyzed by LSC, and the organic phase was also analyzed by TLC. The extracted soil was then refluxed with 1 N hydrochloric acid, and the extract was filtered and partitioned with methylene chloride:acetonitrile (2:1, v:v). Both phases were analyzed by LSC; the organic phase was also analyzed by TLC as previously described. The residual radioactivity in the extracted soil was determined using LSC following combustion.

DATA SUMMARY:

Based on column leaching studies, aged (30 days) ^{14}C-metribuzin residues were mobile to very mobile (22.8-54.8% of the applied in the leachate) in two sandy loam, silt loam and silty clay soils that were leached with 20 inches of 0.01 M calcium chloride solution over a 2-day period (Table III). Following leaching, the leachate from the silt loam soil contained 22.8% of the applied radioactivity, the leachate from the high organic matter (2.4%) sandy loam soil contained 28.0%, the leachate from the silty clay loam soil contained 42.2%, and the leachate from the low organic matter (1.2%) sandy loam soil contained 54.8%. In the 0- to 6-cm soil column segments, total radioactivity ranged from 30% to 37.3% of the applied (Table III, Figure 3). Each of the remaining 4- to 6-cm-thick soil segments contained ≤9.5% of the applied. The material balances for the columns were 91-96.5%.

DATA EVALUATION RECORD

CHEM 101101 STUDY 7

FORMULATION--00--ACTIVE INGREDIENT Metribuzin

STUDY ID (ACC 263702) §163-1

Lane, J.B. 1986. Sencor aged soil residue leaching. Report No. 93110. Unpublished study performed and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is acceptable and partially satisfies the aged portion of the 163-1 data requirement. The aged mobility data requirement may be satisfied with submission of batch equilibrium or soil column leaching data for the degradates DK and DADK.

2. Based on column leaching studies, aged metribuzin residues were mobile to very mobile in sandy loam, silt loam, and silty clay soils. Twenty-three to 55 % of applied radioactivity was found in the leachate, and 16-48 % of the radioactivity in the leachate was metribuzin. The degradates DA, DK, and DADK were found in the leachate at ≤ 3.1 % of applied.

METHODOLOGY:

Triazine ring-labeled ^{14}C-metribuzin (labeled in the 5 position; radiochemical purity 98.7%, specific activity 21.9 mCi/mM, Mobay), dissolved in acetonitrile, was applied at 7.4 ppm to air-dried, sieved (2 mm) sandy loam soil in an amber glass jar. The solvent was evaporated, then the soil was mixed, moistened to 75% of field capacity with distilled water, and mixed again. The treated soil was incubated for 30 days at 22-24 °C. Humidified, CO$_2$-free air was drawn through the jar and exhausted through a sodium hydroxide trapping solution. After the aging period, the soil was divided into 25.5-g subsamples. Two of the subsamples were transferred immediately to the top of previously-made soil columns; the remaining subsamples were frozen (-5 C) for up to 8 days before being used in the leaching experiments. A portion of each subsample was analyzed for total radioactivity using LSC.

METRIBUZIN

Page 135 is not included in this copy.

Pages _____ through _____ are not included.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

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_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

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_____ The product confidential statement of formula.

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In the leachate from the columns, metribuzin averaged 15.9%-48.4% of the applied radioactivity,

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA) was 0.4-3.1%,

6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK) was 0.8-1.6%, and

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK) was 0.9-2.3%

(Table VI). Unidentified organosoluble ^{14}C-residues and water-soluble ^{14}C-residues in the leachate comprised $\leq$0.6 and 0.7-1.1% of the applied radioactivity, respectively.

^{14}C-Residues identified in the 0- to 6-cm soil segments were metribuzin (10.4-13.6% of the applied radioactivity), DADK (5.0-8.4%), DA (1.2-1.9%), and DK (1.6-3.0%; Table V).

COMMENTS:

1. Although the residues in the aged soil were not characterized before application to the soil columns, leaching occurred over a period of only 2 days. Since the half-life of metribuzin under anaerobic conditions appears to be 112 days (Study 5), it is unlikely that significant changes in the nature of the ^{14}C-residues occurred during the leaching period.

2. The distribution of ^{14}C-compounds in soil segments deeper than 6 cm was not addressed.

were dissolved in methylene chloride:methanol (1:1, v:v), and aliquots were analyzed by LSC and TLC as described above. The aqueous fraction was analyzed by LSC only. $[^{14}C]$Residues remaining in the extracted soil were quantified by LSC following combustion. The identities of the degradates were confirmed using at least two techniques such as: cochromatography using TLC in solvent systems A and B; HPLC with linear gradient elution from water:acetic acid (249:1, v:v) to acetonitrile:water:acetic acid (747:498:5, v:v:v); GC with electron capture detection; and, GC/MS or MS-direct probe. Method detection limits were not provided.

Trapping solutions were analyzed for total radioactivity by LSC.

DATA SUMMARY:

Ring-labeled $[^{14}C]$metribuzin (radiochemical purity 97%), at 6.0 ppm, degraded with a registrant-calculated half-life of 112 days in sandy loam that was flooded and incubated at 24 ± 2 °C in darkness for 60 days following 30 days of aerobic incubation (Figure 12). During the anaerobic period, $[^{14}C]$metribuzin declined from 63.6% of the applied (3.82 ppm) immediately prior to flooding to 44.3% (2.66 ppm) after 60 days of anaerobic incubation (Table V). During the anaerobic portion of the study, the degradates identified were:

6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK), at a maximum of 9.4% of the applied (0.56 ppm) on day 60;

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA), at a maximum of 7.5% (0.45 ppm) on day 31;

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK), at a maximum of 3.4% (0.20 ppm) on day 60; and

2-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (2-methyl-DADK), at a maximum of 2.4% (0.14 ppm) on day 31.

In addition, six unidentified $[^{14}C]$compounds (Unknowns I-VI) were each isolated at maximum concentrations ranging from 0.4 to 4.4% of the applied (0.02-0.44 ppm) (Table IV). $[^{14}C]$Residues remaining at the origin comprised up to 1.2% of the applied, diffuse radioactivity comprised up to 0.6%, uncharacterized water-soluble residues comprised up to 5.7%, and unextractable $[^{14}C]$residues comprised up to 8.2% (Tables III-V). Cumulative $[^{14}C]$volatiles totalled up to 0.2% of the applied (0.58 ppm) by 273 days posttreatment. During the study, the material balances ranged from 99.0 to 103.1% of the applied.

COMMENTS:

1. Although it appears that the concentration of metribuzin in the soil systems increased between days 31 and 60, the low average value of 34.7% obtained on day 31 was, according to the study author, "probably an artifact based on a poor replicate for that day". The data

tables present only averaged metribuzin concentrations; however, as presented in Figure 12, it is apparent that one of the two samples analyzed on day 31 is in disagreement with other data points. The half-life estimate (112 days) was calculated excluding that replicate.

2. A complete description of the test water, including pH and dissolved oxygen content, was not provided.

3. Method detection limits and recovery efficiencies from fortified soil and water samples were not provided.

METRIBUZIN

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Pages 139 through 160 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.

X FIFRA registration data.

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DATA EVALUATION RECORD

STUDY 8

CHEM 101101 Metribuzin §164-1

FORMULATION--06--WETTABLE POWDER
FORMULATION--12--EMULSIFIABLE CONCENTRATE

STUDY ID 40380901
Delk, J.L. 1987. Dissipation of Sencor and its oxidative metabolites in field soil. Laboratory Project ID SE-8300-87. Mobay Project ID No. Sencor Objective No. 8300. Unpublished study performed by Morse Laboratories Inc. Sacramento, CA, and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 40

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CONCLUSIONS:

Field Dissipation - Terrestrial

1. The terrestrial field dissipation study provides good estimates of persistence under field conditions in Michigan, Maine, and California, but does not satisfy the data requirement since it did not address leaching. The soils were sampled to only 12 inches of depth and did not address the leaching potential of metribuzin at the sites studied in Michigan, Maine, California, Indiana, and Florida. Also, the day-0 recoveries were ≤50 % of the nominal rate in Mississippi and Texas.

2. The half-lives at the Michigan, Maine, and California sites were 58 to 107 days in silty clay loam, muck sandy loam, muck clay loam, and sandy clay loam soils.

METHODOLOGY:

Metribuzin (Sencor 50% WP or Sencor 4 lb ai/gal EC) was incorporated at either 32 or 96 oz ai/A into various soil types in eleven field plots located at nine sites in eight states in 1973 and 1987.

Two methods were used to incorporate metribuzin into the soil. In the mixing method (post hole), the upper 3 inches of soil was excavated from a hole 18 inches in diameter, metribuzin was added to the excavated soil, and the soil was mixed in a cement mixer for approximately 15 minutes. The soil was then returned to the hole and tamped to restore the original surface level. The alternate method was that metribuzin was broadcast on the soil surface and the soil was subsequently tilled to incorporate the metribuzin.

<u>Kalamazoo, Michigan</u>: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of silty clay loam soil (Table 14-a) on July 7, 1973. Soil samples were collected at 0, 29, 58, 114, 257, 380, 483, and 730 days posttreatment.

<u>Mentha, Michigan</u>: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of sandy loam (muck) soil (Table 14-b) on July 11, 1973. Soil samples were collected at 0, 28, 57, 113, 362, 482, and 730 days posttreatment.

<u>Presque Isle, Maine</u>: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of clay loam (muck) soil (Table 14-c) on July 2, 1973. Soil samples were collected at 0, 30, 67, 122, 308, 364, 487, and 729 days posttreatment.

<u>Presque Isle, Maine</u>: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of sandy clay loam (muck) soil (Table 14-d) on July 2, 1973. Soil samples were collected at 0, 30, 67, 122, 308, 364, 487, and 729 days posttreatment.

<u>Holtville, California</u>: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 96 oz ai/A into sandy clay loam soil (CA, Table 15) in a desert field plot on June 28, 1987. Soil samples were collected at 0, 28, 48, 62, and 77 days posttreatment.

<u>Benoit, Mississippi</u>: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 32 oz ai/A into loamy sand soil (MS-32, Table 15) and at 96 oz ai/A into sandy loam soil (MS-96, Table 15) in a field plot on August 4, 1987. Soil samples were collected from both plots at 0, 14, 31, and 42 days posttreatment.

<u>Howe, Indiana</u>: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 32 oz ai/A into sandy loam soil (IN, Table 15) in a field plot on July 6, 1987. Soil samples were collected at 0, 28, and 45 days posttreatment.

<u>Adams Gardens, Texas</u>: Metribuzin (4 lb ai/gal EC or 75% dry flowable) was broadcast-incorporated at 32 oz ai/A and 96 oz ai/A into unvegetated plots (6.6 m x 30 m) of sandy loam soils (TX-32 and TX-96, respectively; Table 15) on June 22, 1987. Soil samples were collected at 0, 30, 44, 60, and 74 days posttreatment.

<u>Vero Beach, Florida</u>: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 32 oz ai/A into sand soil (FL, Table 15) in a field plot on June 28, 1987. Soil samples were collected at 0, 30, 44, and 61 days posttreatment.

The soil was analyzed by the method described in Mobay report 40468. This method involves refluxing of the soil and chromatography of the soil extract on silica gel and Floricil columns followed by GC. The limits of determination were 0.01 ppm for metribuzin, DA, DK, and DADK. Recoveries from soil fortified with 0.01-1.0 ppm were 81-142% for metribuzin, 88-110% for DADK, 70-151% for DK and 70-91% for DA.

The soil samples were stored frozen a maximum of 758 days.

<u>DATA SUMMARY</u>:

Metribuzin dissipated with registrant-calculated half-lives of 9 to 107 days in the upper 6 inches of soil in eleven field plots located at nine sites in eight states treated with metribuzin (50% WP or 4 lb ai/gal EC) at either 32 or 96 oz ai/A (Table 13). The individual experiments were conducted in 1973 and 1987. The dissipation rate of metribuzin appeared to have been affected by both the formulation and the rate of application. The EC formulation of metribuzin applied at 32 oz ai/A dissipated with half-lives of 9 to 42 days; in contrast, the EC formulation applied at 96 oz ai/A dissipated with half-lives of 37 to 68 days. Detection of metribuzin residues from the EC application was generally limited to the 0- to 6-inch soil layer. The WP formulation of metribuzin applied at 32 oz ai/A dissipated with half-lives of 50 to 104 days, and residues in WP-treated soils were detected in the 6- to 12-inch soil layer (the maximum depth of sampling). The metribuzin degradates recovered from the field plots were

6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK),

6-tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)-one (DA), and

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK).

Kalamazoo, Michigan: Metribuzin dissipated with a registrant-calculated half-life of 58 days in the upper 6 inches of silty clay loam soil in a field plot (10 X 10 feet) in Kalamazoo, MI, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 0.20 ppm immediately posttreatment to 0.10 ppm at 58 days and <0.01 ppm at 483 days. In the surface soil at all sampling intervals, DADK and DK were each present at up to 0.26 ppm and DA was ≤0.05 ppm. In the 6- to 12-inch depth, metribuzin was ≤0.10 ppm at all sampling intervals, and DADK, DK, and DA were each ≤0.04 ppm (Table 2). Meteorological data such as air temperature and precipitation were not reported.

Mentha, Michigan: Metribuzin dissipated with a registrant-calculated half-life of 107 days in the upper 6 inches of sandy loam (muck) soil in a field plot (10 X 10 feet) in Mentha, MI, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 1.56 ppm immediately posttreatment to 0.70 ppm at 28 days and 0.04 ppm at 482 days. In the surface soil at all sampling intervals, DADK was present at up to 2.89 ppm, DK was present at up to 0.28 ppm, and DA was ≤0.06 ppm. In the 6- to 12-inch depth, metribuzin was 0.28 ppm (immediately posttreatment), DADK was 0.15 ppm (immediately posttreatment), and DK and DA were each ≤0.02 ppm (Table 3). Meteorological data such as air temperature and precipitation were not reported.

Presque Isle, Maine: Metribuzin dissipated with a registrant-calculated half-life of 93 days in the upper 6 inches of clay loam (muck) soil in a field plot (10 X 10 feet) in Presque Isle, ME, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 0.90 ppm immediately posttreatment, to 0.32 ppm at 30 days, 0.10 ppm at 67 days, and 0.02 ppm at 729 days. In the soil surface layer at all sampling intervals, DADK was ≤0.04 ppm, and DK and DA were each ≤0.01 ppm. In the 6- to 12-inch depth, metribuzin was ≤0.31 ppm (immediately posttreatment), DADK was ≤0.08 ppm, and DK and DA were each ≤0.03 ppm (Table 4). The total rainfall was 6.92 inches at the 30-day sampling and 36.86 inches at the 365-day sampling; total rainfall was 67.46 inches. The average air temperatures at Presque Isle, ME were 10-70 °F.

<u>Presque Isle, Maine</u>: Metribuzin dissipated with a registrant-calculated half-life of 67 days in the upper 6 inches of sandy clay loam (muck) soil in a field plot (10 feet X 10 feet) in Presque Isle, ME, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 1.15 ppm immediately posttreatment to 0.32 ppm at 30 days, 0.11 ppm at 67 days, and 0.02 ppm at 729 days. In the surface soil at all sampling intervals, DADK was 0.05-0.14 ppm, and DK and DA were each ≤0.08 ppm. In the 6- to 12-inch depth, metribuzin was ≤0.21 ppm (immediately posttreatment), DADK was 0.04-0.11 ppm, and DK and DA were each ≤0.03 ppm (Table 5). The total rainfall was 6.92 inches at the 30-day sampling and 35.32 inches at the 365-day sampling; total rainfall was 65.92 inches. The average air temperatures at Presque Isle, ME were 10-70 °F.

<u>Holtville, California</u>: Metribuzin dissipated with a registrant-calculated half-life of 68 days in the upper 6 inches of sandy clay loam soil in a desert field plot in Holtville, CA that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 96 oz ai/A in June 1987. In the 0- to 6-inch soil depth, the concentration of metribuzin ranged from 1.57 to 2.65 ppm during the study period. In the surface soil at all sampling intervals, DK was ≤0.11 ppm, and DADK and DA were each ≤0.02 ppm. In the 6- to 12-inch soil depth, metribuzin was 0.08-0.19 ppm, and DADK, DK, and DA were each <0.01 ppm (Table 6). No rain occurred during the study and the site was not irrigated; air and soil temperatures were not reported.

<u>Benoit, Mississippi</u>: Metribuzin dissipated with a registrant-calculated half-life of 42 days in the upper 6 inches of loamy sand soil in a field plot in Benoit, MS, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 32 oz ai/A in August 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin declined from 0.47 ppm immediately posttreatment to 0.12 ppm at 42 days. In the surface soil at all sampling intervals, DADK and DK were each ≤0.08 ppm, and DA was ≤0.03 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were each <0.01 ppm (Table 7). The total rainfall during the study period was 2.7 inches. The air and soil temperatures were not reported.

<u>Benoit, Mississippi</u>: Metribuzin dissipated with a registrant-calculated half-life of 37 days in the upper 6 inches of sandy loam soil in a field plot in Benoit, MS, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 96 oz ai/A in August 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin ranged from 0.44 to 1.30 ppm during the study. In the surface soil at all sampling intervals, DADK was present at up to 0.31 ppm, DK was 0.14-0.23 ppm, and DA was 0.09-0.19 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were each ≤0.02 ppm (Table 8). The total rainfall during the study period was 2.7 inches. The air and soil temperatures were not reported.

Howe, Indiana: Metribuzin dissipated with a registrant-calculated half-life of 9 days in the upper 6 inches of sandy loam soil in a field plot in Howe, IN, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 32 oz ai/A in July 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin declined from 0.62 ppm immediately posttreatment to 0.05 ppm at 28 days. In the surface soil at all sampling intervals, DADK was present at up to 0.16 ppm, DK was ≤0.01 ppm, and DA was present at up to 0.26 ppm. In the 6- to 12-inch depth, all residues were ≤0.02 (Table 9). Rain plus irrigation totaled 3.51 inches during the study period. The minimum and maximum air temperatures were 43 and 96 F; the minimum and maximum soil temperatures (depth not reported) were 65 and 89 °F.

Adams Gardens, Texas: Metribuzin dissipated with a registrant-calculated half-life of 26 days in the upper 6 inches of sandy loam soil in a field plot (6.6 m x 30 m) in Adams Gardens, TX, that was treated (broadcast-incorporation) with metribuzin (4 lb ai/gal EC or 75% dry flowable) at 32 oz ai/A in June 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin was 0.04-0.30 ppm. In the surface soil at all sampling intervals, DADK was ≤0.09 ppm, DK was ≤0.05 ppm, and DA was ≤0.02 ppm. In the 6- to 12-inch depth, all residues were <0.01 ppm at all sampling intervals (Table 10). The total rainfall during the study period was 3.62 inches. The average soil temperatures (depth not reported) at Adams Gardens, TX were 80-93 °F during study period. The air temperatures were not reported.

Adams Gardens, Texas: Metribuzin dissipated with a registrant-calculated half-life of 64 days in the upper 6 inches of sandy loam soil in a field plot (6.6 m x 30 m) in Adams Gardens, TX, that was treated (broadcast-incorporation) with metribuzin (4 lb ai/gal EC or 75% dry flowable) at 96 oz ai/A in June 1987. In the 0- to 6-inch soil depth the average concentration of metribuzin was 0.30-1.03 ppm. In the surface soil at all sampling intervals, DADK was ≤0.22 ppm, DK was ≤0.13 ppm, and DA was ≤0.07 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were each <0.01 ppm at all sampling intervals (Table 11). The total rainfall during the study period was 3.62 inches. The average soil temperatures (depth not reported) at Adams Gardens, TX were 80-93 °F during study period. The air temperatures were not reported.

Vero Beach, Florida: Metribuzin dissipated with a registrant-calculated half-life of 12 days in the upper 6 inches of sand soil in a field plot in Vero Beach, FL, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 32 oz ai/A in June 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin was 0.80 ppm immediately posttreatment, 0.11 ppm at 30 days, and 0.04 ppm at 61 days. In the surface soil at all sampling intervals, DADK, DK, and DA were each ≤0.02 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were ≤0.01 ppm (Table 12). The total rainfall was 11 inches during the study period. Some temperature data were provided, but the labeling was inadequate to allow interpretation of the data.

COMMENTS:

1. The soil may not have been sampled deeply enough at several sites to accurately define the depth of leaching. The 6- to 12-inch deep layers contained residues at these sites: Michigan (both sites), Maine (sandy clay loam soil and clay loam soil), Mississippi (96 oz ai/A application rate), and California.

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2. The nominal application rates were not confirmed; the metribuzin concentration in the immediate posttreatment soil samples was 20-160% of the expected.

3. The soil was sampled too infrequently to accurately assess the dissipation of metribuzin. Some sites, including Mississippi, Indiana, and Florida, were only sampled 3-4 times during the entire study period. Also, the majority of sites were sampled immediately posttreatment, then not again until approximately 30 days posttreatment, by which time 55-92% of the metribuzin had dissipated. In Michigan (Mentha), metribuzin declined 55% between the first and second samplings; in Florida, metribuzin declined 86%; in Indiana, metribuzin declined 92%; and in Maine, metribuzin in the sandy clay loam soil declined 72% and in the clay loam soil declined 64%.

4. The data were too variable to accurately assess the dissipation of metribuzin. In Mississippi (96 oz ai/A application rate), metribuzin was 1.00 ppm immediately posttreatment, 1.30 ppm at 14 days, and 1.02 ppm at 31 days, and then declined to 0.44 ppm at 42 days. In Michigan (Kalamazoo), metribuzin was 0.20 ppm immediately posttreatment, 0.15 ppm at 29 days, 0.10 ppm at 58 days, 0.28 ppm at 114 days, and ≤0.03 ppm after 257 days. In California, metribuzin was 2.63-2.65 ppm immediately posttreatment and at 28 days, 1.57 ppm at 48 days, 2.40 ppm at 62 days, and 2.11 ppm at 77 days. In Texas (32 oz ai/A), metribuzin was 0.25 ppm immediately posttreatment, 0.30 ppm at 30 days, 0.24 ppm at 44 days, and 0.04-0.05 ppm at 60 and 74 days. In Texas (96 oz ai/A), metribuzin was 0.62 ppm immediately posttreatment, 1.03 ppm at 30 days, 0.54 ppm at 44 days, and 0.30-0.38 ppm at 60 and 74 days, respectively.

5. The metribuzin formulation used in the studies conducted in Texas was unclear. The summary report and data tables (Tables 10 and 11) indicate that a 4 lb ai/gal EC was applied. However, the field report indicated that a 75% dry flowable formulation was used.

6. The sites in Michigan apparently were contaminated with residues prior to the start of the studies as indicated by the presence of detectable residues, up to 0.08 ppm (on a wet weight basis), in the control samples (Table 1).

7. No pretreatment soil samples were collected from the Maine sites. The 6- to 12-inch depth soil samples collected at 122 days posttreatment were used for negative controls.

8. The reporting of the climatological data was inconsistent. The air and/or soil temperatures were not reported for some sites, or the average temperatures for periods outside of the study period were reported. The weather station used in the Michigan studies was ≥90 miles from the study sites.

9. Prior to the initiation of this study, the Mississippi sites had not been cropped in the previous five years. Prior use histories were not reported for the other study sites.

10. The following pesticide applications were reported during the study period: Benoit, MS (both applications rates), paraquat at 5 pt ai/A on July 30, glyphosate at 1 qt/A on August 21; Howe, IN, glyphosate at 1.5 qt/A on August 10; Adams Gardens, TX (both application rates), trifluralin at 1 qt ai/A on June 22; Vero Beach, FL, glyphosate at 75 ml/gal on June 12, July 30, and August 19, 1987.

METRIBUZIN

Page_____ is not included in this copy.

Pages 167 through 178 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 9

CHEM 101101
Metribuzin
§164-1

FORMULATION--14--75 % DRY FLOWABLE

MRID 42236101
Grace, T.J. and T.S. Cain. 1990. Dissipation of Metribuzin in California Soils. Unpublished study performed by Plant Sciences, Inc., Watsonville, CA, Siemer and Associates, Fresno, CA, NET Atlantic, Inc., Bedford, MA and submitted by Mobay Chemical, Kansas City, MO.

DIRECT REVIEW TIME = 2 days

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CONCLUSIONS:

Terrestrial Field Dissipation-(164-1)

1. The 164-1 study is unacceptable at this time but may be upgraded to acceptable. The registrant should clarify the rate of application at the Fresno site (See Comment 1 in COMMENTS section) and verify that the application rate was 2 lbs ai/A.

2. The estimated half-lives of metribuzin in sandy loam soils in California were 128 and 40 days at Watsonville and Fresno, respectively. No leaching of metribuzin or its oxidative degradates were observed below 12 inches of depth at either site except for some detections that were probable contamination or compositing errors at the Fresno site. The degradates deaminated metribuzin (DA) and diketo metribuzin (DK) were not found below 6 inches of depth and not past 7 and 361 days in Watsonville and 60 and 179 days in Fresno, respectively.

METHODOLOGY:

Watsonville (Chualar) Site.

A sandy loam soil in the Salinas Valley near Watsonville, California was fertilized, rototilled, and shaped into beds on 40-inch centers as preparation for planting potatoes. The soil characteristics were 73 % sand, 21 % silt, 5 % clay, 1 % OM, pH 7.6, and CEC of 16.5 meq/100g for the top 2 feet of soil. The soil was sampled to 4 feet of depth, but was not adequately characterized by depth. Metribuzin (Sencor 75 DF) was applied preemergence to the planted beds at a nominal rate of 2 lbs ai/A. Fifteen uncomposited soil samples were taken at day=0 to characterize the uniformity of the application rate. In addition, the soil was sampled at 3, 7, 14, 28, 60, 90, 180, 270, 361, 451, and 614 days after applications and composited (15 cores==>3 cores). Soil cores were "recored" or shaven to eliminate artifacts in data caused by sample contamination.

Fresno Site

A sandy loam soil in the San Joaquin Valley near Fresno, California was fertilized, rototilled, and shaped into beds on 40-inch centers as preparation for planting potatoes. The soil characteristics were 66 % sand, 31 % silt, 2.5 % clay, 0.5 % OM, pH 8.1, and CEC of 9.5 meq/100g for the top 2 feet of soil. The soil was sampled to 4 feet of depth, but was not adequately characterized by depth. Metribuzin was applied preemergence to the planted beds at a nominal rate of 2 lbs ai/A. The plots were divided into 3 sections, and five cores/section were composited into one. Fifteen uncomposited soil samples were taken at day=0 to characterize the uniformity of the application rate. In addition, the soil was sampled at 3, 8, 14, 38, 60, 91, 179, 273, 360 days after applications and composited (15 cores==>3 cores). Soil cores were "recored" or shaved to eliminate artifacts in data.

The composited soil samples were extracted by refluxing with 90:10 acetonitrile:water, followed by filtration and evaporation of the extract to water. The water was partitioned with chloroform in a separatory funnel and the chloroform extract was subjected to silica gel column chromatography to separate parent metribuzin from the metabolites. Florisil column chromatography was used to further separate parent metribuzin from the metabolites. The eluates for the metabolite fractions were then evaporated and reconstituted in toluene for direct GC analysis. Quantitation of each extract was achieved using gas chromatography with an electron capture detector.

Procedural recoveries of metribuzin, DADK, DK, and DA ranged from 75-113 % (mean of 91 %), 73-125 % (mean of 96 %), 67-96 % (mean of 82 %), and 79-102 % (mean of 90%). The method validation recoveries were 73-99 % (mean of 91%), 98-111 % (mean of 105 %), 62-86 % (73 % recovery), and 76-102 % (mean of 90 %), respectively.

DATA SUMMARY:

The calculated half-lives of metribuzin were 128 and 40 days for the Watsonville and Fresno sites. respectively. The difference in half-lives of metribuzin can be readily explained by the cooler soil and air temperatures in Watsonville.

Watsonville site

Metribuzin and its oxidative degradates were not found below 12 inches of depth at the Watsonville site. The degradate DADK was found in the 6-12 inch depth at the detection limit (0.01 ppm) at 180, 270, and 361 day sampling intervals at the Watsonville site, and never leached further.

Fresno site

Metribuzin was detected to 12 inches of depth at the Fresno site at 3 days after application (3.25 inches of precipitation) and to 18-36 inches of depth at 0.02-0.04 ppm at 91 days after treatment (11.5 inches of precipitation). DADK was detected (0.01 ppm) at 24-30 inches of depth at 91 days after treatment. The deep detections at the day=91 sampling interval could have been a result of compositing errors since there were no detections of metribuzin or DADK above trace levels below 12 inches of depth at any other sampling interval. DADK was detected (0.01 ppm; detection limit) at 12-18 inches at 179 days (17.8 inches of precipitation) and at 360 days (23.8 inches of precipitation).

COMMENTS:

1. The rate of application of metribuzin at the Fresno site was not clear from the study. The nominal rate was 2 lbs ai/A in both locations. However, the EFGWB reviewer calculated an application rate of 1.05 lb ai/A at the Fresno location from calibration data on p. 15 of the study. The soil recovery data at day=0 indicated that the nominal rate was applied at both sites. The average soil concentration at Watsonville in the 0-6 inch soil depth was 0.44 ppm (0.12-0.94 ppm, Table 10, p. 52). The average soil concentration at Fresno in the 0-6 inch soil depth was 0.54 ppm (0.12-0.94 ppm, Table 22, p. 64).

2. The location of soil sampling on the plant beds was not stated.

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METRIBUZIN

Page_____ is not included in this copy.

Pages 182 through 213 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.

X 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 8

CHEM 101101 Metribuzin §164-1

FORMULATION--06--WETTABLE POWDER
FORMULATION--12--EMULSIFIABLE CONCENTRATE

STUDY ID 40380901
Delk, J.L. 1987. Dissipation of Sencor and its oxidative metabolites in field soil. Laboratory Project ID SE-8300-87. Mobay Project ID No. Sencor Objective No. 8300. Unpublished study performed by Morse Laboratories Inc. Sacramento, CA, and submitted by Mobay Corporation, Kansas City, MO.

DIRECT REVIEW TIME = 40

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CONCLUSIONS:

Field Dissipation - Terrestrial

1. The terrestrial field dissipation study provides good estimates of persistence under field conditions in Michigan, Maine, and California, but does not satisfy the data requirement since it did not address leaching. The soils were sampled to only 12 inches of depth and did not address the leaching potential of metribuzin at the sites studied in Michigan, Maine, California, Indiana, and Florida. Also, the day=0 recoveries were ≤50 % of the nominal rate in Mississippi and Texas.

2. The half-lives at the Michigan, Maine, and California sites were 58 to 107 days in silty clay loam, muck sandy loam, muck clay loam, and sandy clay loam soils.

METHODOLOGY:

Metribuzin (Sencor 50% WP or Sencor 4 lb ai/gal EC) was incorporated at either 32 or 96 oz ai/A into various soil types in eleven field plots located at nine sites in eight states in 1973 and 1987.

Two methods were used to incorporate metribuzin into the soil. In the mixing method (post hole), the upper 3 inches of soil was excavated from a hole 18 inches in diameter, metribuzin was added to the excavated soil, and the soil was mixed in a cement mixer for approximately 15 minutes. The soil was then returned to the hole and tamped to restore the original surface level. The alternate method was that metribuzin was broadcast on the soil surface and the soil was subsequently tilled to incorporate the metribuzin.

Kalamazoo, Michigan: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of silty clay loam soil (Table 14-a) on July 7, 1973. Soil samples were collected at 0, 29, 58, 114, 257, 380, 483, and 730 days posttreatment.

Mentha, Michigan: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of sandy loam (muck) soil (Table 14-b) on July 11, 1973. Soil samples were collected at 0, 28, 57, 113, 362, 482, and 730 days posttreatment.

Presque Isle, Maine: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of clay loam (muck) soil (Table 14-c) on July 2, 1973. Soil samples were collected at 0, 30, 67, 122, 308, 364, 487, and 729 days posttreatment.

Presque Isle, Maine: Metribuzin (50% WP) was broadcast-incorporated at 32 oz ai/A into a field plot (10 X 10 feet) of sandy clay loam (muck) soil (Table 14-d) on July 2, 1973. Soil samples were collected at 0, 30, 67, 122, 308, 364, 487, and 729 days posttreatment.

Holtville, California: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 96 oz ai/A into sandy clay loam soil (CA, Table 15) in a desert field plot on June 28, 1987. Soil samples were collected at 0, 28, 48, 62, and 77 days posttreatment.

Benoit, Mississippi: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 32 oz ai/A into loamy sand soil (MS-32, Table 15) and at 96 oz ai/A into sandy loam soil (MS-96, Table 15) in a field plot on August 4, 1987. Soil samples were collected from both plots at 0, 14, 31, and 42 days posttreatment.

Howe, Indiana: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 32 oz ai/A into sandy loam soil (IN, Table 15) in a field plot on July 6, 1987. Soil samples were collected at 0, 28, and 45 days posttreatment.

Adams Gardens, Texas: Metribuzin (4 lb ai/gal EC or 75% dry flowable) was broadcast-incorporated at 32 oz ai/A and 96 oz ai/A into unvegetated plots (6.6 m x 30 m) of sandy loam soils (TX-32 and TX-96, respectively; Table 15) on June 22, 1987. Soil samples were collected at 0, 30, 44, 60, and 74 days posttreatment.

Vero Beach, Florida: Metribuzin (4 lb ai/gal EC) was mixed (post hole method) at 32 oz ai/A into sand soil (FL, Table 15) in a field plot on June 28, 1987. Soil samples were collected at 0, 30, 44, and 61 days posttreatment.

The soil was analyzed by the method described in Mobay report 40468. This method involves refluxing of the soil and chromatography of the soil extract on silica gel and Floricil columns followed by GC. The limits of determination were 0.01 ppm for metribuzin, DA, DK, and DADK. Recoveries from soil fortified with 0.01-1.0 ppm were 81-142% for metribuzin, 88-110% for DADK, 70-151% for DK and 70-91% for DA.

The soil samples were stored frozen a maximum of 758 days.

DATA SUMMARY:

Metribuzin dissipated with registrant-calculated half-lives of 9 to 107 days in the upper 6 inches of soil in eleven field plots located at nine sites in eight states treated with metribuzin (50% WP or 4 lb ai/gal EC) at either 32 or 96 oz ai/A (Table 13). The individual experiments were conducted in 1973 and 1987. The dissipation rate of metribuzin appeared to have been affected by both the formulation and the rate of application. The EC formulation of metribuzin applied at 32 oz ai/A dissipated with half-lives of 9 to 42 days; in contrast, the EC formulation applied at 96 oz ai/A dissipated with half-lives of 37 to 68 days. Detection of metribuzin residues from the EC application was generally limited to the 0- to 6-inch soil layer. The WP formulation of metribuzin applied at 32 oz ai/A dissipated with half-lives of 50 to 104 days, and residues in WP-treated soils were detected in the 6- to 12-inch soil layer (the maximum depth of sampling). The metribuzin degradates recovered from the field plots were

6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK),

6-tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)-one (DA), and

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK).

Kalamazoo, Michigan: Metribuzin dissipated with a registrant-calculated half-life of 58 days in the upper 6 inches of silty clay loam soil in a field plot (10 X 10 feet) in Kalamazoo, MI, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 0.20 ppm immediately posttreatment to 0.10 ppm at 58 days and <0.01 ppm at 483 days. In the surface soil at all sampling intervals, DADK and DK were each present at up to 0.26 ppm and DA was ≤0.05 ppm. In the 6- to 12-inch depth, metribuzin was ≤0.10 ppm at all sampling intervals, and DADK, DK, and DA were each ≤0.04 ppm (Table 2). Meteorological data such as air temperature and precipitation were not reported.

Mentha, Michigan: Metribuzin dissipated with a registrant-calculated half-life of 107 days in the upper 6 inches of sandy loam (muck) soil in a field plot (10 X 10 feet) in Mentha, MI, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 1.56 ppm immediately posttreatment to 0.70 ppm at 28 days and 0.04 ppm at 482 days. In the surface soil at all sampling intervals, DADK was present at up to 2.89 ppm, DK was present at up to 0.28 ppm, and DA was ≤0.06 ppm. In the 6- to 12-inch depth, metribuzin was 0.28 ppm (immediately posttreatment), DADK was 0.15 ppm (immediately posttreatment), and DK and DA were each ≤0.02 ppm (Table 3). Meteorological data such as air temperature and precipitation were not reported.

Presque Isle, Maine: Metribuzin dissipated with a registrant-calculated half-life of 93 days in the upper 6 inches of clay loam (muck) soil in a field plot (10 X 10 feet) in Presque Isle, ME, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 0.90 ppm immediately posttreatment, to 0.32 ppm at 30 days, 0.10 ppm at 67 days, and 0.02 ppm at 729 days. In the soil surface layer at all sampling intervals, DADK was ≤0.04 ppm, and DK and DA were each ≤0.01 ppm. In the 6- to 12-inch depth, metribuzin was ≤0.31 ppm (immediately posttreatment), DADK was ≤0.08 ppm, and DK and DA were each ≤0.03 ppm (Table 4). The total rainfall was 6.92 inches at the 30-day sampling and 36.86 inches at the 365-day sampling; total rainfall was 67.46 inches. The average air temperatures at Presque Isle, ME were 10-70 °F.

<u>Presque Isle, Maine</u>: Metribuzin dissipated with a registrant-calculated half-life of 67 days in the upper 6 inches of sandy clay loam (muck) soil in a field plot (10 feet X 10 feet) in Presque Isle, ME, that was treated (broadcast-incorporation) with metribuzin (50% WP) at 32 oz ai/A in July 1973. In the 0- to 6-inch soil depth, metribuzin declined from an average concentration of 1.15 ppm immediately posttreatment to 0.32 ppm at 30 days, 0.11 ppm at 67 days, and 0.02 ppm at 729 days. In the surface soil at all sampling intervals, DADK was 0.05-0.14 ppm, and DK and DA were each ≤0.08 ppm. In the 6- to 12-inch depth, metribuzin was ≤0.21 ppm (immediately posttreatment), DADK was 0.04-0.11 ppm, and DK and DA were each ≤0.03 ppm (Table 5). The total rainfall was 6.92 inches at the 30-day sampling and 35.32 inches at the 365-day sampling; total rainfall was 65.92 inches. The average air temperatures at Presque Isle, ME were 10-70 °F.

<u>Holtville, California</u>: Metribuzin dissipated with a registrant-calculated half-life of 68 days in the upper 6 inches of sandy clay loam soil in a desert field plot in Holtville, CA that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 96 oz ai/A in June 1987. In the 0- to 6-inch soil depth, the concentration of metribuzin ranged from 1.57 to 2.65 ppm during the study period. In the surface soil at all sampling intervals, DK was ≤0.11 ppm, and DADK and DA were each ≤0.02 ppm. In the 6- to 12-inch soil depth, metribuzin was 0.08-0.19 ppm, and DADK, DK, and DA were each <0.01 ppm (Table 6). No rain occurred during the study and the site was not irrigated; air and soil temperatures were not reported.

<u>Benoit, Mississippi</u>: Metribuzin dissipated with a registrant-calculated half-life of 42 days in the upper 6 inches of loamy sand soil in a field plot in Benoit, MS, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 32 oz ai/A in August 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin declined from 0.47 ppm immediately posttreatment to 0.12 ppm at 42 days. In the surface soil at all sampling intervals, DADK and DK were each ≤0.08 ppm, and DA was ≤0.03 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were each <0.01 ppm (Table 7). The total rainfall during the study period was 2.7 inches. The air and soil temperatures were not reported.

<u>Benoit, Mississippi</u>: Metribuzin dissipated with a registrant-calculated half-life of 37 days in the upper 6 inches of sandy loam soil in a field plot in Benoit, MS, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 96 oz ai/A in August 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin ranged from 0.44 to 1.30 ppm during the study. In the surface soil at all sampling intervals, DADK was present at up to 0.31 ppm, DK was 0.14-0.23 ppm, and DA was 0.09-0.19 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were each ≤0.02 ppm (Table 8). The total rainfall during the study period was 2.7 inches. The air and soil temperatures were not reported.

<u>Howe, Indiana</u>: Metribuzin dissipated with a registrant-calculated half-life of 9 days in the upper 6 inches of sandy loam soil in a field plot in Howe, IN, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 32 oz ai/A in July 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin declined from 0.62 ppm immediately posttreatment to 0.05 ppm at 28 days. In the surface soil at all sampling intervals, DADK was present at up to 0.16 ppm, DK was ≤0.01 ppm, and DA was present at up to 0.26 ppm. In the 6- to 12-inch depth, all residues were ≤0.02 (Table 9). Rain plus irrigation totaled 3.51 inches during the study period. The minimum and maximum air temperatures were 43 and 96 F; the minimum and maximum soil temperatures (depth not reported) were 65 and 89 °F.

<u>Adams Gardens, Texas</u>: Metribuzin dissipated with a registrant-calculated half-life of 26 days in the upper 6 inches of sandy loam soil in a field plot (6.6 m x 30 m) in Adams Gardens, TX, that was treated (broadcast-incorporation) with metribuzin (4 lb ai/gal EC or 75% dry flowable) at 32 oz ai/A in June 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin was 0.04-0.30 ppm. In the surface soil at all sampling intervals, DADK was ≤0.09 ppm, DK was ≤0.05 ppm, and DA was ≤0.02 ppm. In the 6- to 12-inch depth, all residues were <0.01 ppm at all sampling intervals (Table 10). The total rainfall during the study period was 3.62 inches. The average soil temperatures (depth not reported) at Adams Gardens, TX were 80-93 °F during study period. The air temperatures were not reported.

<u>Adams Gardens, Texas</u>: Metribuzin dissipated with a registrant-calculated half-life of 64 days in the upper 6 inches of sandy loam soil in a field plot (6.6 m x 30 m) in Adams Gardens, TX, that was treated (broadcast-incorporation) with metribuzin (4 lb ai/gal EC or 75% dry flowable) at 96 oz ai/A in June 1987. In the 0- to 6-inch soil depth the average concentration of metribuzin was 0.30-1.03 ppm. In the surface soil at all sampling intervals, DADK was ≤0.22 ppm, DK was ≤0.13 ppm, and DA was ≤0.07 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were each <0.01 ppm at all sampling intervals (Table 11). The total rainfall during the study period was 3.62 inches. The average soil temperatures (depth not reported) at Adams Gardens, TX were 80-93 °F during study period. The air temperatures were not reported.

<u>Vero Beach, Florida</u>: Metribuzin dissipated with a registrant-calculated half-life of 12 days in the upper 6 inches of sand soil in a field plot in Vero Beach, FL, that was treated (soil mixing) with metribuzin (4 lb ai/gal EC) at 32 oz ai/A in June 1987. In the 0- to 6-inch soil depth, the average concentration of metribuzin was 0.80 ppm immediately posttreatment, 0.11 ppm at 30 days, and 0.04 ppm at 61 days. In the surface soil at all sampling intervals, DADK, DK, and DA were each ≤0.02 ppm. In the 6- to 12-inch depth, metribuzin and its degradates were ≤0.01 ppm (Table 12). The total rainfall was 11 inches during the study period. Some temperature data were provided, but the labeling was inadequate to allow interpretation of the data.

<u>COMMENTS</u>:

1. The soil may not have been sampled deeply enough at several sites to accurately define the depth of leaching. The 6- to 12-inch deep layers contained residues at these sites: Michigan (both sites), Maine (sandy clay loam soil and clay loam soil), Mississippi (96 oz ai/A application rate), and California.

2. The nominal application rates were not confirmed; the metribuzin concentration in the immediate posttreatment soil samples was 20-160% of the expected.

3. The soil was sampled too infrequently to accurately assess the dissipation of metribuzin. Some sites, including Mississippi, Indiana, and Florida, were only sampled 3-4 times during the entire study period. Also, the majority of sites were sampled immediately posttreatment, then not again until approximately 30 days posttreatment, by which time 55-92% of the metribuzin had dissipated. In Michigan (Mentha), metribuzin declined 55% between the first and second samplings; in Florida, metribuzin declined 86%; in Indiana, metribuzin declined 92%; and in Maine, metribuzin in the sandy clay loam soil declined 72% and in the clay loam soil declined 64%.

4. The data were too variable to accurately assess the dissipation of metribuzin. In Mississippi (96 oz ai/A application rate), metribuzin was 1.00 ppm immediately posttreatment, 1.30 ppm at 14 days, and 1.02 ppm at 31 days, and then declined to 0.44 ppm at 42 days. In Michigan (Kalamazoo), metribuzin was 0.20 ppm immediately posttreatment, 0.15 ppm at 29 days, 0.10 ppm at 58 days, 0.28 ppm at 114 days, and ≤0.03 ppm after 257 days. In California, metribuzin was 2.63-2.65 ppm immediately posttreatment and at 28 days, 1.57 ppm at 48 days, 2.40 ppm at 62 days, and 2.11 ppm at 77 days. In Texas (32 oz ai/A), metribuzin was 0.25 ppm immediately posttreatment, 0.30 ppm at 30 days, 0.24 ppm at 44 days, and 0.04-0.05 ppm at 60 and 74 days. In Texas (96 oz ai/A), metribuzin was 0.62 ppm immediately posttreatment, 1.03 ppm at 30 days, 0.54 ppm at 44 days, and 0.30-0.38 ppm at 60 and 74 days, respectively.

5. The metribuzin formulation used in the studies conducted in Texas was unclear. The summary report and data tables (Tables 10 and 11) indicate that a 4 lb ai/gal EC was applied. However, the field report indicated that a 75% dry flowable formulation was used.

6. The sites in Michigan apparently were contaminated with residues prior to the start of the studies as indicated by the presence of detectable residues, up to 0.08 ppm (on a wet weight basis), in the control samples (Table 1).

7. No pretreatment soil samples were collected from the Maine sites. The 6- to 12-inch depth soil samples collected at 122 days posttreatment were used for negative controls.

8. The reporting of the climatological data was inconsistent. The air and/or soil temperatures were not reported for some sites, or the average temperatures for periods outside of the study period were reported. The weather station used in the Michigan studies was ≥90 miles from the study sites.

9. Prior to the initiation of this study, the Mississippi sites had not been cropped in the previous five years. Prior use histories were not reported for the other study sites.

10. The following pesticide applications were reported during the study period: Benoit, MS (both applications rates), paraquat at 5 pt ai/A on July 30, glyphosate at 1 qt/A on August 21; Howe, IN, glyphosate at 1.5 qt/A on August 10; Adams Gardens, TX (both application rates), trifluralin at 1 qt ai/A on June 22; Vero Beach, FL, glyphosate at 75 ml/gal on June 12, July 30, and August 19, 1987.

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METRIBUZIN

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Pages 220 through 231 are not included.

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____ Description of quality control procedures.

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____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

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DATA EVALUATION RECORD

STUDY 9

CHEM 101101 Metribuzin §164-1

FORMULATION--14--75 % DRY FLOWABLE

MRID 42236101
Grace, T.J. and T.S. Cain. 1990. Dissipation of Metribuzin in California Soils. Unpublished study performed by Plant Sciences, Inc., Watsonville, CA, Siemer and Associates, Fresno, CA, NET Atlantic, Inc., Bedford, MA and submitted by Mobay Chemical, Kansas City, MO.

DIRECT REVIEW TIME = 2 days

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CONCLUSIONS:

Terrestrial Field Dissipation-(164-1)

1. The 164-1 study is unacceptable at this time but may be upgraded to acceptable. The registrant should clarify the rate of application at the Fresno site (See Comment 1 in COMMENTS section) and verify that the application rate was 2 lbs ai/A.

2. The estimated half-lives of metribuzin in sandy loam soils in California were 128 and 40 days at Watsonville and Fresno, respectively. No leaching of metribuzin or its oxidative degradates were observed below 12 inches of depth at either site except for some detections that were probable contamination or compositing errors at the Fresno site. The degradates deaminated metribuzin (DA) and diketo metribuzin (DK) were not found below 6 inches of depth and not past 7 and 361 days in Watsonville and 60 and 179 days in Fresno, respectively.

METHODOLOGY:

Watsonville (Chualar) Site.

A sandy loam soil in the Salinas Valley near Watsonville, California was fertilized, rototilled, and shaped into beds on 40-inch centers as preparation for planting potatoes. The soil characteristics were 73 % sand, 21 % silt, 5 % clay, 1 % OM, pH 7.6, and CEC of 16.5 meq/100g for the top 2 feet of soil. The soil was sampled to 4 feet of depth, but was not adequately characterized by depth. Metribuzin (Sencor 75 DF) was applied preemergence to the planted beds at a nominal rate of 2 lbs ai/A. Fifteen uncomposited soil samples were taken at day=0 to characterize the uniformity of the application rate. In addition, the soil was sampled at 3, 7, 14, 28, 60, 90, 180, 270, 361, 451, and 614 days after applications and composited (15 cores==>3 cores). Soil cores were "recored" or shaven to eliminate artifacts in data caused by sample contamination.

Fresno Site

A sandy loam soil in the San Joaquin Valley near Fresno, California was fertilized, rototilled, and shaped into beds on 40-inch centers as preparation for planting potatoes. The soil characteristics were 66 % sand, 31 % silt, 2.5 % clay, 0.5 % OM, pH 8.1, and CEC of 9.5 meq/100g for the top 2 feet of soil. The soil was sampled to 4 feet of depth, but was not adequately characterized by depth. Metribuzin was applied preemergence to the planted beds at a nominal rate of 2 lbs ai/A. The plots were divided into 3 sections, and five cores/section were composited into one. Fifteen uncomposited soil samples were taken at day=0 to characterize the uniformity of the application rate. In addition, the soil was sampled at 3, 8, 14, 38, 60, 91, 179, 273, 360 days after applications and composited (15 cores==>3 cores). Soil cores were "recored" or shaved to eliminate artifacts in data.

The composited soil samples were extracted by refluxing with 90:10 acetonitrile:water, followed by filtration and evaporation of the extract to water. The water was partitioned with chloroform in a separatory funnel and the chloroform extract was subjected to silica gel column chromatography to separate parent metribuzin from the metabolites. Florisil column chromatography was used to further separate parent metribuzin from the metabolites. The eluates for the metabolite fractions were then evaporated and reconstituted in toluene for direct GC analysis. Quantitation of each extract was achieved using gas chromatography with an electron capture detector.

Procedural recoveries of metribuzin, DADK, DK, and DA ranged from 75-113 % (mean of 91 %), 73-125 % (mean of 96 %), 67-96 % (mean of 82 %), and 79-102 % (mean of 90%). The method validation recoveries were 73-99 % (mean of 91%), 98-111 % (mean of 105 %), 62-86 % (73 % recovery), and 76-102 % (mean of 90 %), respectively.

DATA SUMMARY:

The calculated half-lives of metribuzin were 128 and 40 days for the Watsonville and Fresno sites. respectively. The difference in half-lives of metribuzin can be readily explained by the cooler soil and air temperatures in Watsonville.

Watsonville site

Metribuzin and its oxidative degradates were not found below 12 inches of depth at the Watsonville site. The degradate DADK was found in the 6-12 inch depth at the detection limit (0.01 ppm) at 180, 270, and 361 day sampling intervals at the Watsonville site, and never leached further.

Fresno site

Metribuzin was detected to 12 inches of depth at the Fresno site at 3 days after application (3.25 inches of precipitation) and to 18-36 inches of depth at 0.02-0.04 ppm at 91 days after treatment (11.5 inches of precipitation). DADK was detected (0.01 ppm) at 24-30 inches of depth at 91 days after treatment. The deep detections at the day=91 sampling interval could have been a result of compositing errors since there were no detections of metribuzin or DADK above trace levels below 12 inches of depth at any other sampling interval. DADK was detected (0.01 ppm; detection limit) at 12-18 inches at 179 days (17.8 inches of precipitation) and at 360 days (23.8 inches of precipitation).

COMMENTS:

1. The rate of application of metribuzin at the Fresno site was not clear from the study. The nominal rate was 2 lbs ai/A in both locations. However, the EFGWB reviewer calculated an application rate of 1.05 lb ai/A at the Fresno location from calibration data on p. 15 of the study. The soil recovery data at day=0 indicated that the nominal rate was applied at both sites. The average soil concentration at Watsonville in the 0-6 inch soil depth was 0.44 ppm (0.12-0.94 ppm, Table 10, p. 52). The average soil concentration at Fresno in the 0-6 inch soil depth was 0.54 ppm (0.12-0.94 ppm, Table 22, p. 64).

2. The location of soil sampling on the plant beds was not stated.

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15.14 ft^2) immediately after the soil was seeded with soybeans. The soil was contained in an oval, metal tub (8-foot length x 2-foot width x 2-foot depth); a 6-inch layer of sand was placed on the bottom of the tub prior to the addition of the test soil.

The soybean plants were harvested at 32 days postapplication and representative samples were taken. The remainder of the crop was cut into 1-inch sections and and tilled into the upper 6 inches of the soil. At 32, 122, and 270 days postapplication, the treated soil was planted to kale, red beets, and wheat. A 450-watt sodium vapor lamp was used for supplemental light when the test container was maintained indoors under greenhouse conditions; weather permitting, the container was placed outdoors. Rotational crops for each planting interval were harvested at maturity and the plants were divided into distinct parts [wheat heads (defined as grain plus chaff) and straw; beet tops and bulbs; kale leaves]. Immature wheat plants (forage) were also sampled during the 122- and 270-day intervals. Soil cores (1-inch diameter) were collected from the upper 6 inches of the soil immediately postapplication and at each planting and harvest interval (postapplication days 32, 122, 255, 374). All samples were stored frozen (-10 °C) until analysis.

<u>Plant tissue</u>: Plant tissues were diced and homogenized in liquid nitrogen. Triplicate aliquots of the samples were combusted and analyzed for total radioactivity by LSC. The remaining tissues were analyzed according to the analytical scheme shown in Figure 2. Duplicate plant tissue subsamples (kale leaves; wheat forage, heads, and straw; beet tops and bulbs) were homogenized twice in methanol:-water (4:1, v:v) and vacuum-filtered each time. The extracts were combined and analyzed for total radioactivity by LSC. The extracted tissues were further extracted by refluxing in methanol:water (4:1, v:v) for 3 hours at 85 °C. The samples were vacuum-filtered, and the extracts were combined and added to the initial extracts. The combined extract was then concentrated to the aqueous phase by rotary evaporation (<35 C) and partitioned three times with ethyl acetate; aliquots of the organic and aqueous phases were analyzed by LSC. The organic fraction was then concentrated by rotary evaporation and analyzed by one-dimensional TLC on silica gel plates developed in the following systems: hexane:dimethoxyethane:methylene chloride:acetic acid (60:40:10:1, v:v:v:v; C), benzene:ethyl acetate:acetic acid (50:10:1, v:v:v; D), and chloroform:ethyl acetate:acetic acid (100:100:1, v:v:v; E). Additional analysis of the organic fraction was done using reverse phase (C_8 column) HPLC with a linear gradient elution of 10-60% acetonitrile:water (0.4% acetic acid); standards of metribuzin residues were co-chromatographed along with the test solutions (TLC and HPLC). Extracts of the plant tissues were also co-chromatographed with similar plant extracts from other planting intervals.

Aliquots of the aqueous phases of the plant tissue extracts were transferred to glass containers and lyophilized for ≥24 hours. Residues resulting from the process were reconstituted in 0.1 M acetate buffer solution (pH 5.0). Beta-glucosidase was added to the mixture which was incubated in darkness at 37 °C for 24 hours and then partitioned three times with ethyl acetate; aliquots of the aqueous and organic fractions were analyzed by LSC. Control samples consisting of plant tissue extracts in buffer solution without the enzyme were also analyzed. Additional aliquots of the aqueous phases were lyophilized as described above, reconstituted in methanol:water (9:1, v:v), and analyzed using TLC on silica gel plates developed in 1-butanol:acetic acid:water (4:1:1, v:v:v; F).

DATA EVALUATION RECORD

STUDY 10

CHEM 101101 Metribuzin §165-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE

STUDY ID 40838402
Christopher, R.J., J.B. Lane, and G.D. Parker. 1988. Residues of metribuzin (Sencor) in rotational crops and soils. Laboratory Project ID No. SE-052301; Mobay No. 98324. Unpublished study performed by Mobay Corporation, Agricultural Chemicals Division, Stilwell, KS/Kansas City, MO, and submitted by Mobay Corporation, Agricultural Chemicals Division, Stilwell, KS.

DIRECT REVIEW TIME = 42

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CONCLUSIONS:

Confined Accumulation - Rotational Crops

1. The 165-1 study provides only supplemental data and cannot be upgraded because only a half-rate of compound was applied and phytotoxicity problems were observed with kale and red beets at the 32-day sampling interval. Also, no storage stability data for compounds in plant parts were provided, extremely-sensitive rotational crops were used, and no explanation was given for the occurrence of the degradate DADK in kale at up to 5.9 times the soil concentration. DADK was the only compound that significantly accumulated and with higher plant than soil concentrations.

2. Metribuzin residues accumulated in confined rotational crops (kale, red beets, and wheat) planted 32, 122, and 270 days postapplication in sandy loam soil that had been sprayed with ring-labeled ^{14}C-metribuzin at 0.19 lb ai/A. The major degradate identified in the crops was: deaminated diketo metribuzin (DADK). Minor degradates identified were: 4-methyl-DADK, deamianted metribuzin (DA), diketo metribuzin (DK), OH-t-butyl-DADK, and 3-amino-DA.

METHODOLOGY:

Ring-labeled ^{14}C-metribuzin (labeled in the 5 position; radiochemical purity 98.1%, specific activity 20.8 mCi/mMol, Mobay) was reconstituted in a blank flowable (4 lb ai/gal EC) to yield a water-based formulation. The solution was hand-sprayed, at 0.19 lb ai/A, onto the surface of hand-leveled, sandy loam soil (66% sand, 32% silt, 2% clay, 2.4% organic matter, pH 5.1, CEC 17 meq/100 g; surface area

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4-methyl-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (4-methyl-DADK),

6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (DA),

4-amino-6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DK),

6-(OH-tert-butyl)-1,2,4-triazin-3,5(2H,4H)-dione (OH-t-butyl-DADK), and

3-amino-6-tert-butyl-3(methylthio)-1,2,4-triazin-5(4H)-one (3-amino-DA).

In the kale plants harvested from the 32 days posttreatment sampling interval, metribuzin was 14.4% of the recovered radioactivity, 4-methyl DADK was 4.8%, DA was 1.6%, DADK was 35.7%, DK was 2.2%, OH-t-butyl-DADK was 3.0%, 3-amino-DA was 1.8%, Unknown 3 was 1.3%, Unknown A was 1.1%, Unknown B was 1.0%, uncharacterized diffuse residues were 2.7%, uncharacterized watersoluble residues were 17.7%, and residues remaining at the origin were 9.2% (Table VI). In the beet tops harvested from the 32 days posttreatment sampling interval, metribuzin was 10.1% of the recovered radioactivity, 4-methyl DADK was 8.4%, DA was 1.4%, DADK was 26.1%, DK was 4.6%, OH-t-butyl-DADK was 3.5%, 3-amino-DA was 1.6%, Unknown 3 was 0.5%, Unknown A was 0.4%, uncharacterized diffuse residues were 2.2%, uncharacterized watersoluble residues were 25.9%, and residues remaining at the origin were 7.8%. In the beet bulbs harvested from the 32 days posttreatment sampling interval, metribuzin was 1.7% of the recovered radioactivity, 4-methyl DADK was 3.1%, DA was 0.5%, DADK was 8.1%, DK was 1.9%, uncharacterized diffuse residues were 2.3%, uncharacterized watersoluble residues were 14.1%, residues remaining at the origin were 3.7%, and uncharacterized residues from the refluxate of the extracted solids were 64.6%. In the wheat forage harvested from the 32 days posttreatment sampling interval, metribuzin was 12.5% of the recovered radioactivity, 4-methyl DADK was 1.3%, DA was 0.9%, DADK was 20.9%, DK was 6.0%, OH-t-butyl-DADK was 1.5%, 3-amino-DA was 0.8%, Unknown 1 was 0.6%, Unknown 3 was 2.5%, uncharacterized diffuse residues were 6.4%, uncharacterized watersoluble residues were 38.2%, and residues remaining at the origin were 8.4%. In the mature wheat heads harvested from the 32 days posttreatment sampling interval, metribuzin was 3.1% of the recovered radioactivity, 4-methyl DADK was 0.7%, DA was 0.8%, DADK was 37.9%, DK was 2.1%, OH-t-butyl-DADK was 2.1%, 3-amino-DA was 1.5%, Unknown 3 was 0.5%, uncharacterized diffuse residues were 3.8%, uncharacterized watersoluble residues were 34.2%, and residues remaining at the origin were 6.4%. In the wheat straw harvested from the 32 days posttreatment sampling interval, metribuzin was 7.0% of the recovered radioactivity, 4-methyl DADK was 1.0%, DA was 0.8%, DADK was 20.9%, DK was 1.7%, OH-t-butyl-DADK was 1.7%, 3-amino-DA was 2.1%, Unknown 3 was 0.3%, uncharacterized diffuse residues were 2.2%, uncharacterized watersoluble residues were 41.4%, and residues remaining at the origin were 10.9%.

In the kale plants harvested from the 122 days posttreatment sampling interval, metribuzin was 15.6% of the recovered radioactivity, 4-methyl DADK was 10.5%, DA was 2.5%, DADK was 35.8%, DK was 4.5%, OH-t-butyl-DADK was 2.1%, 3-amino-DA was 1.2%, Unknown 3 was 1.1%, Unknown A was 0.9%, Unknown B was 1.0%, uncharacterized diffuse residues were 3.4%, uncharacterized watersoluble residues were 11.7%, and residues remaining at the origin were 6.0% (Table VII). In the beet tops harvested from the 122 days posttreatment sampling interval, metribuzin was 3.6% of the recovered radioactivity, 4-methyl DADK was 5.5%, DA was 0.7%, DADK was 17.7%, DK was 2.4%, OH-t-butyl-

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Extracted solids from selected plants were refluxed in 1 N HCl for 3 hours; the refluxates were cooled to room temperature and filtered. The filtrates were adjusted to pH 5.5 with 3 N sodium hydroxide and partitioned three times with ethyl acetate; aliquots of the ethyl acetate and aqueous fractions were analyzed by LSC. The combined ethyl acetate fractions from each plant were concentrated using rotary evaporation under a nitrogen stream and analyzed by TLC developed in solvent systems A (not defined), C, and D; metribuzin standards were co-chromatographed along with the test solutions. A portion of the remaining solids was analyzed for unextractable radioactivity by LSC following combustion.

Selected plant extracts (in ethyl acetate) were concentrated to dryness under a stream of nitrogen and reconstituted in acetonitrile. A precipitating agent (1.25 g ammonium chloride and 2.5 mL orthophosphoric acid in 1 L water) was added to the extracts, and the samples were washed by stirring at room temperature for 30-45 minutes and vacuum-filtered with a filtering agent (Super Cel); the filter cakes were washed and filtered again. The filtrates were then combined, partitioned with ethyl acetate, and analyzed by LSC.

Soil: Prior to the compositing of soil cores, triplicate subsamples of the individual soil cores were analyzed for total radioactivity by LSC following combustion; cellulose was added to the subsamples to aid in combustion. The analytical scheme is shown in Figure 3. Duplicate subsamples of soil (composited) were extracted by stirring with methanol for 2 hours at room temperature and then vacuum-filtered. Remaining solids were refluxed in methanol:water (7:3, v:v) for 2 hours, then vacuum-filtered. Aliquots of the individual extracts were analyzed by LSC. The extracts were then combined, concentrated to the aqueous fraction by rotary evaporation, and partitioned three times with methylene chloride:acetonitrile (2:1, v:v). The organic fraction was concentrated to dryness by rotary evaporation and reconstituted in ethyl acetate. Aliquots of the aqueous and organic fractions were analyzed for total radioactivity by LSC. The organic fraction was further analyzed by TLC on silica gel plates developed in solvent system E, and by HPLC as described above; metribuzin standards were co-chromatographed along with the test solution (TLC and HPLC). The extracted soils were analyzed for unextractable radioactivity by LSC following combustion.

DATA SUMMARY:

Metribuzin residues accumulated in confined rotational crops (kale, red beets, and wheat) planted 32, 122, and 270 days postapplication in sandy loam soil that had been hand-sprayed with ring-labeled ^{14}C-metribuzin (radiochemical purity 98.1%; EC) at 0.19 lb ai/A. Soybeans were grown in the treated soil between treatment and the planting of the rotational crops. In the crops, ^{14}C-residues (in metribuzin equivalents) were a maximum of 0.19 ppm in mature kale plants; 0.05 and 0.23 ppm in beet bulbs and tops, respectively; and 0.64, 0.50, and 1.82 ppm in wheat forage, heads (grain plus chaff), and straw, respectively (Table IV). The major degradate identified in the crops was:

6-tert-butyl-1,2,4-triazin-3,5(2H,4H)-dione (DADK).

Minor degradates identified were:

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were 2.6%, uncharacterized diffuse residues were 3.8%, uncharacterized watersoluble residues were 28.8%, and residues remaining at the origin were 3.1%. In the wheat straw harvested from the 270 days posttreatment sampling interval, metribuzin was 1.9% of the recovered radioactivity, 4-methyl DADK was 3.8%, DADK was 27.3%, DK was 1.4%, OH-t-butyl-DADK was 1.7%, Unknown 1 was 1.5%, Unknown 4 was 2.1%, Unknown 5 was 1.1%, uncharacterized diffuse residues were 1.6%, uncharacterized watersoluble residues were 38.3%, and residues remaining at the origin were 6.4%.

In soil samples, ^{14}C-residues (in metribuzin equivalents) were detected at 0.59 ppm immediately postapplication; ^{14}C-residues decreased to 0.09-0.13 ppm at the 32-day rotational crop planting interval, 0.06-0.13 ppm at the 122-day interval, and 0.06-0.07 ppm at the final interval (255 days for soil, Table III). In the soil,

metribuzin,

was 35.1% of the recovered radioactivity at the 32-day interval, decreasing to 3.4% by 374 days postapplication (Table V);

DADK,

was 15.8% of the recovered radioactivity at the 122-day interval, decreasing to 7.8% by 374 days postapplication;

4-methyl-DADK,

was 8.4% of the recovered radioactivity at the 32-day interval, decreasing to 3.5% by 374 days postapplication;

DA,

was 5.4% of the recovered radioactivity at the 32-day interval, decreasing to 1.5% by 374 days postapplication;

DK,

was 4.6% of the recovered radioactivity at the 32-day interval, decreasing to 1.8% by 374 days postapplication; and

OH-t-butyl-DADK,

was 1.6% of the recovered radioactivity at the 122-day interval, decreasing to nondetectable concentrations by the 255-day interval.

Unidentified degradates were present in soil at up to 6.8% of the recovered radioactivity; origin material accounted for up to 7.0%. Bound residues in soil were 25.4% of the recovered radioactivity at the 32-day interval, increasing to 69.0% by 374 days postapplication (Table V).

COMMENTS:

1. The study authors stated that the test substance was applied at less than the maximum application rate (i.e., approximately 1/2 the field application rate) as was necessary for "minimizing phytotoxicity problems with less tolerant rotational crops."

2. Although samples of immature wheat were collected from crops for each planting interval and samples of immature kale were collected from

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DADK was 2.6%, 3-amino-DA was 2.0%, Unknown 3 was 0.2%, Unknown A was 0.5%, uncharacterized diffuse residues were 1.5%, uncharacterized watersoluble residues were 42.2%, and residues remaining at the origin were 10.8%. In the beet bulbs harvested from the 122 days posttreatment sampling interval, metribuzin was 2.0% of the recovered radioactivity, 4-methyl DADK was 7.3%, DA was 1.3%, DADK was 15.6%, DK was 3.9%, uncharacterized diffuse residues were 3.5%, uncharacterized watersoluble residues were 14.1%, residues remaining at the origin were 4.0%, and uncharacterized residues from the refluxate of the extracted solids were 45.8%. In the wheat forage harvested from the 122 days posttreatment sampling interval, metribuzin was 16.6% of the recovered radioactivity, 4-methyl DADK was 2.0%, DA was 0.8%, DADK was 25.3%, DK was 2.3%, OH-t-butyl-DADK was 1.4%, 3-amino-DA was 2.0%, Unknown 1 was 1.4%, Unknown 3 was 0.6%, Unknown B 1.0%, uncharacterized diffuse residues were 2.8%, uncharacterized watersoluble residues were 35.5%, and residues remaining at the origin were 7.3%. In the mature wheat heads harvested from the 122 days posttreatment sampling interval, metribuzin was 3.4% of the recovered radioactivity, 4-methyl DADK was 1.0%, DA was 0.4%, DADK was 29.6%, DK was 1.3%, OH-t-butyl-DADK was 2.8%, 3-amino-DA was 1.8%, Unknown 1 was 2.1%, Unknown 3 was 0.3%, Unknown A was 1.0%, uncharacterized diffuse residues were 2.9%, uncharacterized watersoluble residues were 32.2%, and residues remaining at the origin were 9.5%. In the wheat straw harvested from the 122 days posttreatment sampling interval, metribuzin was 4.0% of the recovered radioactivity, 4-methyl DADK was 2.9%, DA was 1.1%, DADK was 20.0%, DK was 1.6%, OH-t-butyl-DADK was 1.9%, 3-amino-DA was 2.6%, Unknown 1 was 1.3%, Unknown 3 was 0.7%, Unknown A was 1.3%, uncharacterized diffuse residues were 1.7%, uncharacterized watersoluble residues were 38.6%, and residues remaining at the origin were 14.5%.

In the kale plants harvested from the 270 days posttreatment sampling interval, metribuzin was 5.0% of the recovered radioactivity, 4-methyl DADK was 7.7%, DADK was 39.3%, DK was 1.7%, OH-t-butyl-DADK was 2.7%, Unknown 1 was 1.3%, Unknown 3 was 0.9%, uncharacterized diffuse residues were 4.2%, uncharacterized watersoluble residues were 14.8%, residues remaining at the origin were 13.5%, and uncharacterized residues from the refluxate of the extracted solids were 8.9% (Table VIII). In the beet tops harvested from the 270 days posttreatment sampling interval, metribuzin was 1.0% of the recovered radioactivity, 4-methyl DADK was 10.1%, DADK was 21.7%, DK was 1.3%, OH-t-butyl-DADK was 2.0%, Unknown 1 was 0.8%, uncharacterized diffuse residues were 2.5%, uncharacterized watersoluble residues were 46.1%, residues remaining at the origin were 4.3%, and uncharacterized residues from the refluxate of the extracted solids were 10.2%. In the beet bulbs harvested from the 270 days posttreatment sampling interval, 4-methyl DADK was 4.5% of the recovered radioactivity, DA was 1.1%, DADK was 6.0%, DK was 1.2%, uncharacterized diffuse residues were 8.4%, uncharacterized watersoluble residues were 19.7%, residues remaining at the origin were 3.7%, and uncharacterized residues from the refluxate of the extracted solids were 55.4%. In the wheat forage harvested from the 270 days posttreatment sampling interval, metribuzin was 7.9% of the recovered radioactivity, 4-methyl DADK was 1.8%, DADK was 15.2%, DK was 1.7%, OH-t-butyl-DADK was 1.6%, Unknown 1 was 1.6%, Unknown 3 was 0.6%, Unknown 4 was 0.2%, uncharacterized diffuse residues were 3.4%, uncharacterized watersoluble residues were 51.2%, and residues remaining at the origin were 7.0%. In the mature wheat heads harvested from the 270 days posttreatment sampling interval, metribuzin was 2.8% of the recovered radioactivity, 4-methyl DADK was 1.8%, DADK was 22.6%, DK was 2.0%, OH-t-butyl-DADK was 1.5%, Unknown 1 was 1.8%, Unknown 4 was 1.1%, and uncharacterized residues from the refluxate of the extracted solids

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____ 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.

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crop harvested from the final two planting intervals, data were not rep ed for these samples. Immature beet plants were not sampled at any lanting interval.

3. The study author stated that soil was sampled at 255 days for the final rotational crop planting interval, rather than when the actual replanting occurred (at 270 days) in order to coincide with the sampling of soils in a concurrently running aerobic soil metabolism study.

4. Unresolved bands of radioactivity ("diffuse") on the TLC plates accounted for up to 8.4% of the recovered radioactivity for plant samples and up to 4.6% for soil samples.

5. Poor germination of the kale and red beet crops early in the study made additional plantings necessary. The study authors stated that because phytotoxicity problems occurred during the 32-day rotation interval for the kale and red beet crops, the test container was kept inside the greenhouse for that stage of the study. The study authors suggested that the germination problems may have been a complication partly due to the maintenance of the containers within the greenhouse rather than out of doors.

6. Several references were made regarding the use of MS to confirm the identities of the degradates. Although explicit information on such was not included in the Methods section, figures of the mass spectra were provided.

METRIBUZIN

Page_____ is not included in this copy.

Pages 278 through 293 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.

X 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.

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
METRIBUZIN
Last Update on September 10, 1992
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer: JAB	Section Head:	Date: NOV 9 1992

Common Name:METRIBUZIN
Smiles Code:S(C)C(=NN=C1C(C)(C)C)N(N)C1=O
PC Code # :101101 CAS #:21087-64-9 Caswell #:

Chem. Name :4-AMINO-6-tert-BUTYL-3-(METHYLTHIO)-as-TRIZIN-5(4H)-ONE

Action Type:Herbicide

Trade Names:BAY 94337; LEXONE; SENCOR
(Formul'tn):WP, FLOWABLE CONC., DRY FLOWABLE CONC.,
Physical State:

Use Patterns (% Usage) :BROADLEAF WEEDS AND GRASSES IN SOYBEANS, POTATOES, BARLEY, :WINTER WHEAT, ASPARAGUS, SUGARCANE, TOMATOES, LENTILS, PEAS, :AND NONCROPLAND
:

Empirical Form: $C_8H_{14}N_4OS$
Molecular Wgt.: 214.29 Vapor Pressure: 1.20E -7 Torr
Melting Point : °C Boiling Point: °C
Log Kow : 1.60 pKa: @ °C
Henry's : 3.50E-11 Atm. M3/Mol (Measured) 3.08E-11 (calc'd)

Solubility in ...				Comments
Water	1.10E 3	ppm	@20.0 °C	
Acetone	E	ppm	@ °C	
Acetonitrile	E	ppm	@ °C	
Benzene	E	ppm	@ °C	
Chloroform	E	ppm	@ °C	
Ethanol	E	ppm	@ °C	
Methanol	E	ppm	@ °C	
Toluene	E	ppm	@ °C	
Xylene	E	ppm	@ °C	
	E	ppm	@ °C	
	E	ppm	@ °C	

Hydrolysis (161-1)
[V] pH 5.0:STABLE AT pH 5
[ ] pH 7.0:STABLE AT pH 7
[ ] pH 9.0:STABLE AT pH 9
[ ] pH :
[ ] pH :
[ ] pH :

METRIBUZIN

Page 295 is not included in this copy.

Pages ____ through ____ are not included.

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