162-1

Shaughnessy No.: 010501
Date Out of EAB: AUG 24

AUG 24, 1989

To: D. Edwards
Product Manager 12
Registration Division (H-705C)

From: Paul Mastradone, Chief
Environmental Chemistry Review Section #1
Environmental Fate and Ground Water Branch/EFED (H-7507C)

Through: Henry Jacoby, Acting Chief
Environmental Fate and Ground Water Branch/EFED (H-7507C)

Attached, please find the EAB review of . . .

Reg./File # : 707-203

Chemical Name : Dicofol 010501

Type Product : Acaricide

Product Name : Kelthane, Hifol, Mitigan

Company Name : Rohm and Haas Company

Purpose : Addendum to a Standard (Review of aerobic soil metabolism studies)

Date Received: 4-6-89 EFGWB # (s): 90492

Action Code : 660

Deferrals to:

_____ Ecological Effects Branch, EFED

_____ Science Integration and Policy Staff, EFED

_____ Non-Dietary Exposure Branch, HED

_____ Dietary Exposure Branch, HED

_____ Toxicology Branch I, HED

_____ Toxicology Branch II, HED

1. CHEMICAL: Common name:

Dicofol.

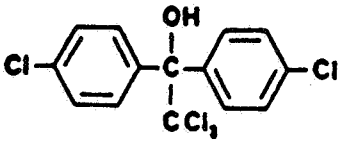
Chemical name:

1,1-bis(4-Chlorophenyl)-2,2,2-trichloroethanol (p,p'-dicofol) and 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2,2-trichloroethanol (o,p'-dicofol).

Trade name(s):

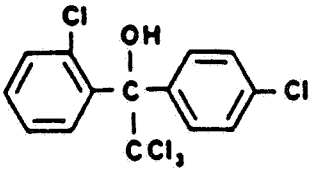
Kelthane, Hifol, Mitigan.

Structures:



1,1-bis(4-chlorophenyl)-2,2,2-trichloroethanol

p,p'-Dicofol



1-(2-chlorophenyl)-1(4'-chlorophenyl)-2,2,2-trichloroethanol

o,p'-Dicofol

Formulations:

1-6% D; 1.5-35% WP; 1-4.5% WP/D; 0.824-4 lb/gallon and 0.44-18.5% EC; 4 lb/gallon FlC; 0.046-12% RTU; 0.075-0.25% PrL; and 1.2% PrD.

Physical/Chemical properties:

Molecular formula: $C_{14}H_9Cl_5O$.
Molecular weight : 370.51.
Physical state : Amber emulsion.
Melting point : 77-78°C (crystals from petroleum ether).
Specific gravity : 1.130 at 20°C.

2. TEST MATERIAL:

Study 1: Uniformly ring-labeled [^{14}C]p,p'-dicofol.
Study 2: Uniformly ring-labeled [^{14}C]o,p'-dicofol.

3. STUDY/ACTION TYPE:

Addendum to a Standard.

4. STUDY IDENTIFICATION:

Daly, D. 1987. Aerobic soil metabolism of ^{14}C-o,p'-dicofol. ABC Laboratory Project ID Final Report #34620. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. (41094201)

Daly, Donna. 1989. Aerobic soil metabolism of ^{14}C-p,p'-dicofol. ABC Final Report #36101. Rohm and Haas Technical Report #34-89-13. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. (41050701)

Tillman, A.M. and D. Daly. 1988. Addendum to the aerobic soil metabolism of ^{14}C-o,p'-dicofol on silt loam soil. Rohm and Haas Technical Report No. 34C-88-23. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. (41094201)

5. REVIEWED BY:

S. Simko
Chemist
EFGWB/EFED/OPP
Review Section #1

Signature: S Simko

Date: 8.14.89

6. APPROVED BY:

Paul Mastradone
Acting Chief
EFGWB/EFED/OPP
Review Section #1

Signature: Paul J Mastradone

Date: AUG 24 1989

7. CONCLUSION:

^{14}C-p,p'-dicofol degraded with an initial half-life of 43 days in aerobic silt loam soil maintained at 25°C in the dark. The major degradation products were 1,1-(p-chlorophenyl)-2,2-dichloroethanol (FW-152); 4,4-dichlorobenzophenone (DCBP); and 3-hydroxy-4,4'-dichlorobenzophenone (3-OH-DCBP). These degradates were very persistent and are very similar to parent dicofol. Minor degradates identified were 4-hydroxy-3,4'-dichlorobenzophenone (4-OH-DCBP) and 4-chlorobenzoic acid/4,4'-dichlorobenzilic acid (CBA/DCBA).

^{14}C-o,p'-dicofol degraded with a half-life of 7.6 days in aerobic silt loam soil maintained at 25°C in the dark. The major degradation products were 1,(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (FW-152); 2,4'-dichlorobenzophenone (DCBP); 2-chlorobenzoic acid (CBA); 3-hydroxy-2,4-dichlorobenzophenone (OH-DCBP); and 2,4'-dichlorobenzhydrol (DCBH). These degradates were very persistent and are very similar to parent dicofol. One minor degradate identified was 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-dichloroethylene (DDE).

8. RECOMMENDATIONS:

These studies fulfill the aerobic metabolism data requirement for dicofol. It should be noted that the degradates are very persistent and are very similar, structurally, to parent dicofol. There is very little information on the toxicology of these degradates.

9. BACKGROUND:

Dicofol is an acaricide registered for use on terrestrial food crop, terrestrial nonfood, greenhouse nonfood, domestic outdoor, and indoor sites. Of the total domestic dicofol usage, approximately 40% is applied to citrus, 26% to cotton, and 10% to ornamentals. Single active ingredient formulations consist of 1-6% D; 1.5-35% WP; 1-4.5% WP/D; 0.824-4 lb/gallon and 0.44-18.5% EC; 4 lb/gallon FlC; 0.046-12% RTU; 0.075-0.25% PrL; and 1.2% PrD. Application rates are 0.3-4.5 lb ai/A (D, WP,EC, FlC); 0.0019-4 lb ai/gallon (WP, EC, FlC); 0.006-0.5 tbsp/gallon (WP, WP/D, EC); 0.1-0.16 ounces/tree (WP/D); and 0.13-1.04 lb ai/50,000 ft^3 (FlC, RTU). Formulations may be tank-mixed with other chemicals, including captan, carbaryl, diazinon, parathion, and sulfur. Foliar applications are made using either ground equipment or aircraft.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: See attached reviews.

11. COMPLETION OF ONE-LINER:

12. CBI APPENDIX:

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

DATA EVALUATION RECORD

STUDY 1

CHEM 010501 Dicofol §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41050701
Daly, Donna. 1989. Aerobic soil metabolism of ^{14}C-p,p'-dicofol. ABC Final Report #36101. Rohm and Haas Technical Report # 34-89-13. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA.

DIRECT REVIEW TIME = 8

REVIEWED BY: E. Hirsh TITLE: Staff Scientist

EDITED BY: K. Patten TITLE: Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

APPROVED BY: S. Simko
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-0237

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

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

2. Dicofol degraded with an initial half-life of 43 days (see discussion) aerobic silt loam soil maintained at 25°C in the dark. The major degradation products were 1,1-(p-chlorophenyl)-2,2-dichloroethanol (FW-152); 4,4-dichlorobenzophenone (DCBP); and 3-hydroxy-4,4'-dichlorobenzophenone (3-OH-DCBP). These degradates were very persistent and are very similar to parent dicofol. Minor degradates identified were 4-hydroxy-3,4'-dichlorobenzophenone (4-OH-DCBP) and 4-chlorobenzoic acid/4,4'-dichlorobenzilic acid (CBA/DCBA).

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the aerobic metabolism of p,p'-dicofol on soil.

4. No additional information on the aerobic metabolism of dicofol is required at this time.

METHODOLOGY:

Thirty 10-g samples of silt loam soil (26% sand, 56% silt, 18% clay, 4.4% organic matter, pH 7.8, CEC 15.2 meq/100 g) were weighed into silanized culture tubes and treated with 11 ppm of uniformly ring-labeled [^{14}C]p,p'-dicofol (radiochemical purity 95.1%, specific activity 9.7 mCi/mmole) dissolved in methanol. The methanol was evaporated, and the treated soils were vortexed, moistened to 75% of field capacity with deionized water, and again vortexed. The treated soils were divided between two metabolism vessels. Humidified air was pumped into the metabolism vessels, then sequentially through tubes containing ethylene glycol, 1 N sulfuric acid and 1 N potassium hydroxide (2 tubes) trapping solutions (Figure 1). The samples were maintained in the dark at 25 ± 1°C, and soil moisture content was adjusted as required. Duplicate soil samples were collected at 0, 1, 3, 7, 14, 31, 60, 90, 121, 182, 274, and 365 days posttreatment. Trapping solutions were changed at the sampling intervals and also at 151, 212, 243, 304, and 335 days posttreatment.

The extraction and analysis procedures for the soil samples are depicted in Figure 2. All soil samples were extracted three times with methanol (vortexing for 10 minutes). Soil samples collected between 14 and 365 days posttreatment were also extracted with acidic methanol (vortexing for 10 minutes), and with 0.5 and 1 M sodium hydroxide (shaking for 6 hours) to determine the distribution of the soil organic fractions. HPLC analysis was the primary method for characterization; one-dimensional TLC analyses were used for confirmational characterizations of [^{14}C]residues in the methanol and acidic methanol extracts. TLC analysis employed three solvent systems (i) hexane:methanol (95:5, v:v), (ii) acetonitrile:water (5:1, v:v), and (iii) chloroform:methanol:acetic acid (85:15:0.1, v:v). Nonradiolabeled standards were cochromatographed with the standards, visualized with UV light, and quantified by LSC following scraping and methanol extraction. Preparative TLC analysis of the 365-day extracts was performed using the hexane:methanol solvent system. Identities of the [^{14}C]compounds isolated by preparative TLC were confirmed using GC/MS. Unextractable [^{14}C]residues remaining in the extracted soil were quantified by LSC following combustion. Radioactivity in the gas trapping solutions was quantified by LSC.

DATA SUMMARY:

[^{14}C]p,p'-Dicofol (radiochemical purity 95.1%), at 11 ppm, degraded with an initial half-life of 43 days in silt loam soil that was incubated in the dark at 25 ± 1°C and 75% of field capacity for 1 year (Table XV, Figures 8 and 10). As determined by HPLC analysis,

[^{14}C]dicofol declined from 88% of the applied at 0 days posttreatment to 56.1% at 1 month, 10.9% at 2 months, and 1.31% at 12 months. The major degradate,

1,1-(p-chlorophenyl)-2,2-dichloroethanol (FW-152),

accounted for a maximum 35.8-44.5% of the applied at 2 to 4 months posttreatment.

4,4-Dichlorobenzophenone (DCBP) and

3-hydroxy-4,4'-dichlorobenzophenone (3-OH-DCBP)

accounted for a maximum 18.1 and 17%, respectively, of the applied radioactivity at 9 months posttreatment.

4-hydroxy-3,4'-dichlorobenzophenone (4-OH-DCBP)

accumulated to a maximum 4.98% of the applied at 3 months posttreatment.

4-chlorobenzoic acid (CBA) and

4,4'-dichlorobenzilic acid (DCBA)

could not be resolved from each other; together they accounted for 0.6-2.88% of the applied during the study. Three [^{14}C]compounds that totaled a maximum 0.16, 1.04, and 4.30% of the applied were isolated but not identified. Volatile [^{14}C]residues (primarily $^{14}CO_2$) totaled 20.9-21.9% of the applied at 12 months, and unextractable residues 10.1-15.1% of the applied at 12 months posttreatment (Tables X and XII). Unextractable residues were evenly distributed between the humic and fulvic acids fractions. The materials balance during the study ranged from 93.7-103.9% of the applied.

COMMENTS:

1. Three degradates, totalling a maximum 0.16, 1.04, and 4.30% of the applied, (0.02, 0.11, and 0.48 ppm) were isolated from the methanol and/or acidic methanol soil extracts but were not identified.

2. The registrant's statistical estimation of the half-life of dicofol, 61 days, was calculated using first-order reaction equations. However, the estimate is inflated (dicofol degrades faster than this figure would indicate); at 60 days posttreatment only 10.9% of the applied radioactivity was identified as dicofol. The registrant's estimate is incorrect because the data are biphasic; initially, dicofol linearly declined at one rate, and then, after 92 days, the dicofol declined at a much slower rate (Figure 10). Therefore, an initial half-life of 43 days was calculated by the Dynamac reviewer

by conducting linear regression analysis on data from 0 through 92 days posttreatment only.

3. Detection limits were not reported.

4. Two duplicate samples were collected on each sampling date. The second sample was used for validation. The first was exaustively extracted and total residues in each fraction were quantified. The second was stored frozen at -22°C for a maximum of 349 days; storage stability was demonstrated. Degradates were characterized in the methanol and acidic methanolic extracts of the second replicate using HPLC.

DATA EVALUATION RECORD

STUDY 2

CHEM 010501 Dicofol §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41094201
Daly, D. 1987. Aerobic soil metabolism of ^{14}C-o,p'-dicofol. ABC Laboratory Project ID Final Report #34620. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA.

STUDY ID 41094201
Tillman, A.M. and D. Daly. 1988. Addendum to the aerobic soil metabolism of ^{14}C-o,p'-dicofol on silt loam soil. Rohm and Haas Technical Report No. 34C-88-23. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA.

DIRECT REVIEW TIME = 16

REVIEWED BY: J. Harlin TITLE: Staff Scientist

EDITED BY: K. Patten TITLE: Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

APPROVED BY: S. Simko
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-0237

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

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

2. Dicofol degraded with a half-life of 7.6 days in aerobic silt loam soil maintained at 25°C in the dark. The major degradation products were 1,(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (FW-152); 2,4'-dichlorobenzophenone (DCBP); 2-chlorobenzoic acid (CBA); 3-hydroxy-2,4-dichlorobenzophenone (OH-DCBP); and 2,4'-di-

chlorobenzhydrol (DCBH). These degradates were very persistent and are very similar to parent dicofol. One minor degradate identified was 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-dichloroethylene (DDE).

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the aerobic metabolism of o,p'-dicofol on soil.

4. No additional information on the aerobic metabolism of dicofol is required at this time.

METHODOLOGY:

Air-dried, sieved (2 mm) silt loam soil (16% sand, 64% silt, 20% clay, 2.4% organic matter content, pH 7.5, CEC 11.2 meq/100 g) was treated with 10 ppm of uniformly ring-labeled [^{14}C]o,p'-dicofol (radiochemical purity 98.2%, specific activity 9.66 x 10^4 dpm/ g, Rohm and Haas) dissolved in methanol. The methanol was evaporated and aliquots (10 g) of the treated soil were weighed into sample tubes, moistened to 75% of field capacity with deionized water, and vortexed. The sample tubes were divided between two metabolism vessels. Humidified air was pumped into the metabolism vessels, then sequentially through tubes containing ethylene glycol, 1 N sulfuric acid, and 1 N potassium hydroxide (2 tubes) trapping solutions (Figure 1). The samples were maintained in the dark at 25 ± 1°C and soil moisture content was adjusted as required. Duplicate soil samples were collected at 0, 1, 3, 7, 14, 30, 60, 90, 120, 180, 220, and 365 days posttreatment. Trapping solutions were changed at each sampling interval.

All soil samples were extracted with methanol by vortexing for 2 minutes, and then centrifuged for 10 minutes; this procedure was repeated two times and the extracts were combined. Triplicate aliquots (1-mL) of the methanol extracts were analyzed for total radioactivity by LSC. The methanol extracts from the Replicate II soil samples were concentrated under a stream of nitrogen and analyzed for dicofol and its degradates using normal phase TLC on silica gel plates developed in hexane:methanol (95:5) and using reverse phase TLC on glass plates developed in acetonitrile:water (5:1). To confirm the identities of degradates in the extracts, the 60 and 90-day extracts were analyzed using preparative one- and/or two-dimensional TLC analyses. The following solvent systems were employed: hexane:methanol (95:5); chloroform:methanol:acetic acid (85:15:0.1); hexane:ethyl acetate:methanol (80:10:10); acetonitrile:water (5:1); hexane:ethyl acetate (5:1); hexane:ethyl acetate (20:1); and, hexane:ethyl acetate:methanol (90:5:5). Identities of the [^{14}C]compounds isolated by preparative TLC were confirmed using GC/MS. Nonradiolabeled standards were cochromatographed with the standards, visualized with UV light, and quantified by scraping and methanol extraction. Unextractable [^{14}C]residues remaining in the extracted

soil were quantified by LCS following combustion. Radioactivity in the gas trapping solutions was quantified by LSC.

Due to high percentages of residues that were not extracted with methanol, selected soil samples from Replicate I (1, 6, 9, and 12 months) were exhaustively extracted as depicted in Figure II. The methanol-extracted soil was extracted with 0.1 N hydrochloric acid/ methanol and centrifuged. The resulting extract was analyzed for total radioactivity by LSC. The soil was extracted with 0.5 N sodium hydroxide and centrifuged, reextracted with 1.0 N sodium hydroxide and centrifuged. The soil was washed with 1 N sodium hydroxide two times, followed by water three times, and was presumably centrifuged. The soil was then analyzed for total radioactivity by LSC following combustion. The aqueous base extracts were combined, acidified to pH 1 using 6 N hydrochloric acid, and partitioned into humic acid and fulvic acid fractions.

DATA SUMMARY:

[^{14}C]o,p'-Dicofol (radiochemical purity 98.2%), at 10 ppm, degraded with a registrant-calculated half-life of 7.6 days in silt loam soil that was incubated in the dark at 25 ± 1°C and 75% of field capacity for 1 year (Table 2). Based on TLC analyses, [^{14}C]dicofol declined from 87.1% of the applied at 0 days posttreatment to 52.4% at 7 days, 27.6% at 14 days, 3.26% at 1 month, and 0.12% at 12 months posttreatment. The major degradate,

1,(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (FW-152),

accounted for a maximum concentration of 31.1% of the applied at 1 month posttreatment (Table 3). Other major degradates were

2,4'-dichlorobenzophenone (DCBP)

which accumulated to a maximum concentration of 18.7% of the applied at 9 months posttreatment,

2-chlorobenzoic acid (CBA) and

3-hydroxy-2,4-dichlorobenzophenone (OH-DCBP)

which comprised up to 14.1 and 11.7% of the applied, respectively, at 3 months posttreatment; and,

2,4'-dichlorobenzhydrol (DCBH)

which reached a maximum concentration of 11.8% of the applied at 12 months posttreatment. One minor degradate,

1-(2-chlorophenyl)-1-(4'-chlorophenyl)-dichloroethylene (DDE)

was <0.70% of the applied during the study. Unidentified degradates comprised a total of 6.6% of the applied throughout the study period. Cumulative [^{14}C]volatiles and unextractable residues were 1.2-3 and 56.7-60.7% of the applied, respectively, by 12 months posttreatment (Tables V, VIII, IX, and XII). Unextractable residues were evenly distributed between humic and fulvic acid fractions (Tables 5-9). The material balance during the study ranged from 84.8 to 115% of the applied.

COMMENTS:

1. Unidentified degradates ("others") reached a maximum concentration of 6.59% of the applied (0.665 ppm) at 1 month posttreatment (Table 3). The study authors did not specify how many degradates were unidentified. According to Subdivision N guidelines, the study authors should have identified all degradates detected at >0.01 ppm.

2. The half-life of dicofol was calculated using only the data for parent compound from methanol soil extracts. The study authors stated that any dicofol present in the soil at early sampling points would extract into methanol, as determined from the data for spiked samples.

3. A temperature deviation (34°C) occurred on two of the test days due to a malfunction of the cooling unit in the environmental chamber. However, extraction and analysis of one extra soil sample indicated that the elevated temperature did not affect the extractability of the test substance from the soil. This did not have a significant effect on the results of the study.

4. Method detection limits were not reported.