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

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

JUL 25 1990

Subject: **DICOFOL** (Acaricide/Miticide)
KELTHANE (Trade name); Terrestrial food crop uses.

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Chief
EPA/OPP/EFED/EFGWB (H7507C)

To: Addressees

Enclosed are the following documents:

1. Environmental-fate assessment for dicofol.
2. Copy of the label of Technical Kelthane.
3. The environmental-fate data-requirements for Dicofol and their status.
4 An appendix with structures of dicofol and its degradates.
5. Copies of the Data Evaluation Records (DER's) on Dicofol.
6. Summary of Literature Information Regarding Dicofol.

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(By Groups; Six in Total)

ENVIRONMENTAL FATE

ASSESSMENT

FOR

DICOFOL

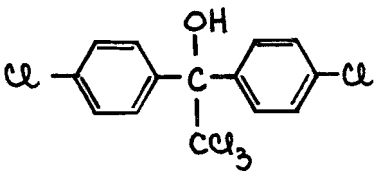
ENVIRONMENTAL FATE ASSESSSMENT FOR DICOFOL:

A complete environmental-fate assessment for dicofol cannot be done at the present time because there are still several data gaps that have to be filled. Based on the available data, EFGWB is concerned about the apparent persistence of dicofol and its major degradates in the environment. No major degradation pathway has been demonstrated. Dicofol, per se, undergoes several rapid biotic or chemical transformations. Under aerobic and anaerobic conditions, dicofol degrades to the following compounds:

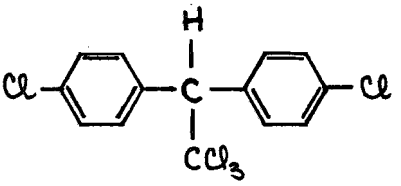
2,4- and 4,4-dichlorobenzophenone (Known as o,p'- and p,p'-DCBP)
1,1-bis(4-chlorophenyl)-2,2-dichloroethanol (p,p'-FW-152)
1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethnol (o,p'-FW-152)
2- and 4-chlorobenzoic acid (o- and p-CBA)
2,4'- and 4,4'-dichlorobenzhydrol (o,p'- and p,p'-DCBH)
3-hydroxy-2,4'-dichlorobenzophenone (3'-OH-o,p'-DCBP)
3-hydroxy-4,4'-dichlorobenzophenone (3-OH-p,p'-DCBP)

These degradates are very persistent and very similar to the parent compound.

p,p'-Dicofol is structuraly closely related to DDT (The p,p'-isomer is the active form of the molecule):



p,p'-dicofol



p,p'-DDT

The EPA document, DDT: A Review of Scientific and Economic Aspects of the Decision to Ban Its Use as a Pesticide, page 106, states:

> "Breakdown of DDT in soil can proceed by several routes depending in part on the redox potential of the soil matrix. Under aerobic conditions, slow conversion to DDE [1,1-dichloro-2,2-bis(p-chlorophenyl ethylene)] will normally occur. Under flooded anaerobic conditions, direct and rapid conversion to DDD (TDE), [1,1-dichloro-2,2-bis(p-chlorophenyl)ethane] can occur which, in turn, can be converted to more polar compounds such as DDA, [bis(p-chlorophenyl)acetic acid]. DDE is quite resistant to microbial

attack and unless lost from the soil it can be stable for extended periods."

Although there are no direct correlations between the degradation of dicofol and DDT, the data do point out a striking similarity between them. This is not surprising given the similarity in their structures.

The following is a summary of the available studies on dicofol:

Dicofol is the common name of the active ingredient in the miticide Kelthane. The manufacturing chemical company is Rohm and Haas Company. Dicofol exists in two isomers, whose chemical names are: 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]. The Chemical Abstracts Registry Number for this chemical is 115-32-2.

Dicofol is a miticide registered for use on terrestrial food crop, terrestrial non-food, greenhouse non-food, 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-.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.

Dicofol has a solubility in water (at 25 °C) of 1.32 ppm, an octanol/water partition coefficient (log Kow) of 6.056, and a vapor pressure of 3.9×10^{-7} torr.

Under hydrolysis conditions, o,p'-dicofol degrades with half-lives of 47 days, 8 hr, and 9 min, at pH's of 5, 7, and 9, respectively. The major degradate in all solutions is DCBP. At pH 7, CBA is also observed. For p,p'-dicofol, degradation half-lives are 85 days, 64 hr, and 26 min, at pH's of 5, 7, and 9, respectively. Major degradates are DCBP and FW-152.

Photodegradation in water studies show that o,p'-dicofol degrades with half-lives of 14.8 days, 1 day, and 32 days in non-sensitized (pH 5), sensitized, and dark solutions, respectively. One major degradate is DCBP. Another unidentified degrate, present at 13.6%, is still under study. For p,p'-dicofol, degradation half-lives are 92.5 days, 4 days, and 149 days in non-sensitized (pH 5), sensitized, and dark solutions, respectively, with major degradate DCBP.

o,p'-Dicofol degrades aerobically at pH 7.5 (silt loam soil) with a half-life of 7.6 days and produces DCBP, FW-152, CBA, 3-OH-DCBP, and DCBH as major products. Degradates are very persistent and very similar to the parent o,p'-dicofol. The other isomer, p,p'-dicofol, degrades aerobically at pH 7.8 (silt loam soil) with a half-life of 43 days and produces DCBP, FW-152, and 3-OH-DCBP as major degradates. Once again, the degradates are very persistent and similar to the parent compound, in this case p,p'-dicofol.

Under anaerobic conditions, although only supplemental information is available, DCBP, DDE, 3-OH-DCBP, and 2-OH-DCBH have been tentatively identified as degradates.

Laboratory leaching and adsorption/desorption studies show that residues are relatively immobile and ground water contamination is not expected. Soil column studies are required in order to verify these results.

Terrestrial field dissipation studies, although not yet acceptable studies, have tentatively identified the following compounds as degradates: DCBP (both isomers), p-CBA, o,p'-DCBH, and p,p'-FW-152. The data developed during these studies were too variable to establish a residue decline curve and accurately assess the dissipation of dicofol. Significant levels of residues were detected in the 0-3 inches of the soil after 181 days.

Dicofol bioaccumulates in bluegill sunfish, with BCF of: 6,600X in fillet, 17,000X in viscera, and 10,000X in whole fish. A depuration half-life of 33 days is observed.

The Ecological Effects Branch (EEB), EFED, has pointed out to EFGWB that there are several avian studies that indicate that dicofol causes problems with egg shell quality similar to those caused by DDE. It is known that DDE (a DDT metabolite) is extremely persistent in the environment, bioconcentrates in fish and wildlife and causes some bird species to produce eggs with poor egg-shell quality.

EFGWB reviewed the Residue Portion of an Avian Reproduction Study deferred by EEB/EFED and found the following results:

1. The feed was contaminated with trace levels of p,p'-DDE.
2. In the carcass:
   a. p,p'-Dicofol comprised 95% of the residue.
   b. The half-life of depuration was 17-20 days.
   c. The remainder of the total residue contained less than 5% DDE.
   d. The half-life of depuration of the total residue (dicofol + p,p'-DDE) was 34-36 days.
3. In the liver, p,p'-DDE comprised 10-40% of the residue and the half-life of depuration was 16 days.
4. In the gastrointestinal tract and contents:
   a. p,p'-FW-152 comprised 43% of the residue.
   b. p,p'-dicofol comprised 41% of the residue.
   c. p,p'-DDE comprised 16% of the residue.
5. The residues in the eggs were 94% p,p'-dicofol.
6. In the hatchlings:
   a. p,p'-dicofol comprised 78% of the residue.
   b. p,p'-FW-152 comprised 15% of the residue.

Therefore, based on dicofol properties and behavior, EFGWB recommends that special attention should be given to dicofol <u>per se</u> and its major metabolites, especially their accumulation and metabolism in different organisms. Dicofol has

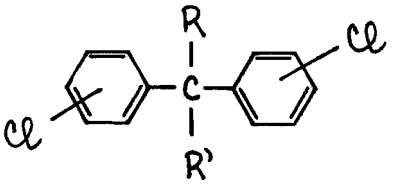
a high octanol/water partition coefficient. Therefore, it could have the following tendencies:

1. A tendency to be very hydrophobic.
2. Accumulate in organic phases such as soil and/or animal tissue.
3. Have large bioconcentration factors (BCF) for aquatic life.
4. Tend not to be biodegradable by microorganisms in soils, and surface water.

This is confirmed by the following results:

1. BCF values on bluegill sunfish show that dicofol accumulates in fish.
2. Terrrestrial field dissipation studies have tentatively shown that the degradates have a longer half-life than the parent compound and that the compounds are not mobile.
3. Laboratory leaching and adsorption/desorption studies show that residues are relatively immobile.
4. In the Residue Portion of an Avian Reproduction Study, p,p'-dicofol comprises most of the residues in almost all the analyses.

Special attention should be given to the fact that dicofol (both isomers) and its degradates have the same chemical structure backbone (shown below)



No ring-opening or substitution has been observed. The main chemical reactions/transformations occur in the carbon atom to which the phenyl-substituted rings are attached. This fact means that they are resistant to breakdown and could share similar physico/chemical properties. The chemical can enter the food web and be bioaccumulated by organisms of higher trophic levels. Physico/chemical properties such as high lipid solubility and low water solubility can lead to retention of chemicals in fatty tissue. The rates of accumulation into organisms vary with the species, with the duration and concentration of exposure, and with environmental conditions. A high retention of chemicals can mean that toxic effects can occur in organisms remote in time as well as geographical area from the point of exposure.

Therefore, EFGWB recommends that:

1. Special attention should be given to dicofol <u>per se</u> and its metabolites and that accumulation and metabolism studies in different organisms should be carried out using dicofol and its metabolites.

2. All the EFGWB data requirements which are still data gaps should be filled. These data requirements are the following:

a. Photodegradation in Water (161-2) for o,p-dicofol.
b. Photodegradation on Soil (161-3) for both isomers of dicofol.
c. Anaerobic Soil Metabolism (162-2) for both isomers of dicofol.
d. Leaching and Adsorption/desorption (163-1) -- Soil column studies.
e. Laboratory Volatility (163-2) for both isomers.
f. Terrestrial Field Dissipation (164-1) for both isomers.
g. Accumulation in Confined Rotational Crops (165-1) for both isomers.
h. Accumulation in Aquatic Non-target Organisms (165-5) for both isomers.

Note:

Some facts about DDT:

1. Highly insoluble in water (Solubility = 1.2 ppb).
2. Vapor pressure = 1.9×10^{-7} mm Hg
3. Octanol/water partition coefficient (log Kow) = 7.48

References:

1. EFGWB reviews.
2. WHO 1989. DDT and its derivatives -- Environmental Aspects. Environmental Health Criteria 83.
3. Lyman, W. J.; Reehl, W. F.; and Rosenblatt, D. H. 1989. Handbook of Chemical Property Estimation Methods -- Environmental Behavior of Organic Compounds. Mc Graw-Hill Book Co., New York.
4. U. S. Environmental Protection Agency. July 1975. DDT: A Review of Scientific and Economic Aspects of the Decision to Ban its Use as a Pesticide. EPA 540/1-75-022.

Attachments

Addressees:

James W. Akerman, EFED/EEB (H7507C)
Dennis Edwards, RD/PM #12 (H7505C)
L. Schnaubelt/Herman Toma, SRRD (Team #74-Sec. II)(H7508C)

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LABEL OF TECHNICAL KELTHANE

For formulation into end-use products intended for use on apples, pears, crabapples, quince, citrus, cotton, dry beans, succulent beans, cotton, mint, grapes, strawberries, walnuts, filberts, pecans, chestnuts, hickory nuts, tomatoes, peppers, hops, melons, cucumbers, squash, cantaloupes, watermelons, pumpkins, lawn and turf grasses, ornamentals, flowers, nursery stock, shade trees, and around buildings.

KELTHANE® TECHNICAL

AGRICULTURAL MITICIDE

7-2692

KEEP OUT OF REACH OF CHILDREN

CAUTION

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

Harmful if swallowed, absorbed through the skin or inhaled. Causes moderate eye, skin, nose or throat irritation. Avoid contact with skin, eyes and clothing. Skin contact with this pesticide may be hazardous; wear chemical-resistant gloves when mixing, loading, or applying this product. Avoid breathing vapors. Wash thoroughly with soap and water after handling and before eating or smoking. Remove contaminated clothing and wash before re-use.

STATEMENT OF PRACTICAL TREATMENT

IF SWALLOWED: Drink 1 to 2 glasses of water and induce vomiting by touching back of throat with finger. Call a physician. Do not induce vomiting or give anything by mouth to an unconscious person.

IF INHALED: Remove the victim to fresh air. Treat the victim symptomatically. Call a physician if problem continues.

IF ON SKIN: Wash exposed area with plenty of soap and water. If irritation persists, call a physician.

IF IN EYES: Flush eyes with plenty of water for at least 15 minutes. If irritation persists, call a physician.

ENVIRONMENTAL HAZARDS

This product is toxic to fish. Do not contaminate water by cleaning of drums or equipment or by disposal of waste.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

NOTE: Consult manufacturer for formulation information and for technical bulletins. Formulators are responsible for obtaining EPA registration for their product.

NOTICE: Before using this product, read the entire Precautionary Statements, Conditions of Sale and Warranty, Directions for Use, and Storage and Disposal Instructions. If the Conditions of Sale and Warranty are not acceptable, return the product unopened within thirty days of purchase to the place of purchase.

CONDITIONS OF SALE AND WARRANTY

Rohm and Haas warrants that the product conforms to its chemical description and is reasonably fit for the purpose stated on the label, only when used in accordance with label directions and under normal conditions of use. ROHM AND HAAS MAKES NO OTHER EXPRESS OR IMPLIED WARRANTIES EITHER OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR USE. Handling, storage and use of the product by Buyer are beyond the control of Rohm and Haas, and Rohm and Haas shall not be liable for, and Buyer assumes responsibility for all personal injury and property damage resulting from the handling, possession, use or resale of the material, whether the same is used alone or in combination with other substances. IN NO EVENT SHALL ROHM AND HAAS BE RESPONSIBLE FOR SPECIAL, INCIDENTAL OR CONSEQUENTIAL DAMAGES, WHETHER BUYER'S CLAIM IS IN CONTRACT, NEGLIGENCE OR OTHERWISE.

STORAGE AND DISPOSAL

Do not contaminate water, food or feed by storage or disposal. Open dumping is prohibited.

PESTICIDE DISPOSAL: Pesticide wastes are toxic. Improper disposal of excess pesticide, spray mixture or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

CONTAINER DISPOSAL: Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by other procedures approved by state and local authorities.

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED:

Scoop or shovel solid material into a suitable container for recovery or disposal. Remove contaminated clothing promptly and wash exposed skin areas with soap and water. Wash clothing before re-use. Keep spill out of all sewers and open bodies of water. Refer to PRECAUTIONARY STATEMENTS.

ROHM HAAS

ACTIVE INGREDIENT

1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol 100%

INERT INGREDIENTS .....

Total .....

ACCEPTED with COMMENTS In EPA Letter Dated: MAR 25 1988

Under the Federal Insecticide, Fungicide, and Rodenticide Act as amended, for the pesticide registered under EPA Reg. No. 707-203

Kelthane is a registered trademark of Rohm and Haas Company

EPA Reg. No. 707-203

EPA Est. No. 707-IT-1

NET CONTENTS

250 KG

(551.2 LBS.)

RQ-KELTHANE

ORM-E

ENVIRONMENTAL-FATE DATA-REQUIREMENTS

FOR

DICOFOL

DICOFOL

Data Requirements Guidelines Reference #	Status	Degradates Formed	Half-life
1. Degradation Studies -- lab			
a. Hydrolysis (161-1) [R]	a. o,p'-dicofol --> fulfilled	a. Major: DCBP (in all sol'ns) At pH 7 CBA was observed	a. pH 5 --> 47 days 7 --> 8 hr 9 --> 9 min
	b. p,p'-dicofol --> fulfilled	b. Major: FW-152; DCBP Minor: DCBA; DCBP; DDE; 3-OH-DCBP; 2-OH-DCBH	b. pH 5 --> 85 days 7 --> 64 hr 9 --> 26 min
b. Photodegradation			
-In Water (161-2) R	a. o,p'-dicofol --> not fulfilled[1]	a. Major: DCBP Others: DCBA;CBA	a. Non-sensitized, pH 5 --> 14.8 days Sensitized --> 1 day Dark --> 32 days
	b. p,p'-dicofol --> fulfilled	a. Non-sensitized: DCBP Others: DCBA, CBA	a. Non-sensitized, pH 5 --> 92.5 days Sensitized --> 4 days Dark --> 149 days
-On Soil (161-3) CR	Both isomers: supplemental[2]	----------	----------
-In Air (161-4) CR	Waived[3]	----------	----------
2. Metabolism Studies -- lab			
a. Aerobic Soil (162-1) [R]	a. o,p'-dicofol --> fulfilled	a. Major: FW-152; DCBP; CBA; OH-DCBP; DCBH Minor: DDE	a. Parent --> 7.6 days Degradates --> Very persistent & very similar to parent dicofol.

2

Cont. DICOFOL

	b. p,p'-dicofol --> fulfilled	b. Major: FW-152; DCBP; 3-OH-DCBP Minor: 4-OH-DCBP; CBA/DCBA	b. Parent --> 43 days Degradates --> Very persistent & very similar to parent dicofol.
b. Anaerobic Soil (162-2) R	Both isomers: supplemental[4]	Tentatively identified: p,p'-FW-152 and both isomers of DCBP; DDE; 3-OH-DCBP; 2-OH-DCBH	Less than 30 days
3. Mobility Studies			
a. Leaching & Adsorption/desorption (163-1) [R]	a. Lab studies --> accepted b. Soil column studies --> not accepted[5]	----------	Residues are relatively immobile & groundwater contamination is not expected
b. Volatility			
-Lab (163-2) CR	----------	----------	----------
-Field (163-3) CR	Waived[3]	----------	----------
4. Dissipation Studies -- field			
a. Soil (164-1) R	One study was terminated ahead of time & time extension is being requested; the second study was unacceptable.	p-CBA; o,p'-DCBP; p,p'-DCBP; o,p'-DCBH; p,p'-FW-152	Parent: 3.7 days Residues: 4.7 days Not mobile
b. Soil, long term (164-5) CR	----------	----------	----------
5. Accumulation Studies			
a. Rotational Crops			
-Confined (165-1) [CR]	Need for study was noted.	----------	----------
-Field (165-2) CR	Study is being carried out.	----------	----------

Cont. DICOFOL

b. In Fish (165-4) [CR]	Acceptable	----------	Dicofol bioaccumulates in bluegill sunfish, with BCF of: 6,600X in fillet; 17,000X in viscera; and 10,000X in whole fish. Depuration $t_{1/2}$ = 33 days.
c. In Aquatic Non-target Organisms (165-5)	----------	----------	----------

1 Degradates obtained >10% should be identified.

2 Demonstration that light energy transferred to natural soil contituents is not transferred to DICOFOL should be provided.

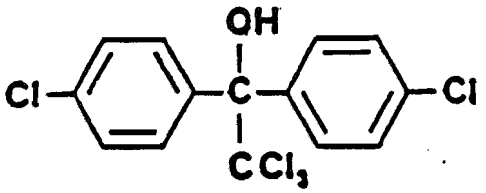
3 Waived as of 12/6/1985. Kelthane (DICOFOL) is a Toxicity Category III and EFGWB has not normally required this test for products in this category.

4 Additional information should be submitted to confirm identity of residues.

5 Unaged soils are required for the study.

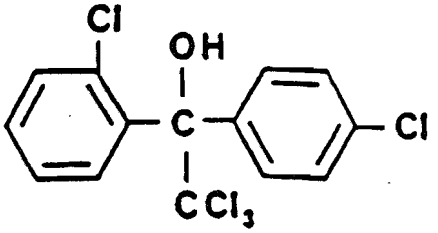
APPENDIX

DICOFOL AND ITS DEGRADATES



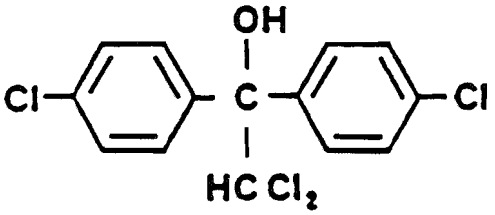
1,1-bis(4-Chlorophenyl)-
2,2,2-trichloroethanol

p,p'-Dicofol



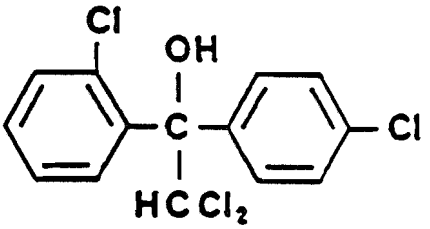
1-(2-Chlorophenyl)-1(4'-chloro-
phenyl)-2,2,2-trichloroethanol

o,p'-Dicofol



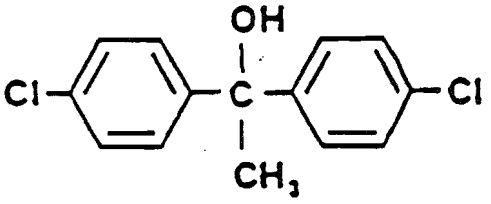
1,1-bis(4-Chlorophenyl)-
2,2-dichloroethanol

p,p'-FW-152



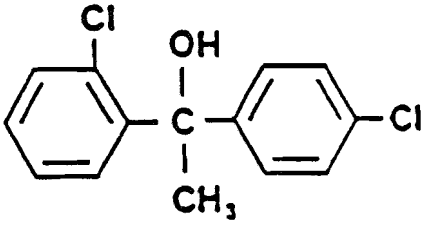
1-(2-Chlorophenyl)-1-(4'-chloro-
phenyl)-2,2-dichloroethanol

o,p'-FW-152



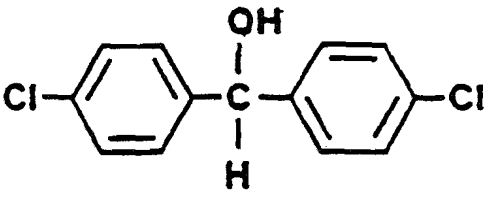
1,1-bis(4-Chlorophenyl)ethanol

p,p'-WW-38A



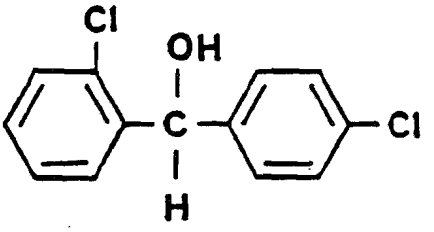
1-(2-Chlorophenyl)-1(4'-
chlorophenyl)-ethanol

o,p-WW-38A



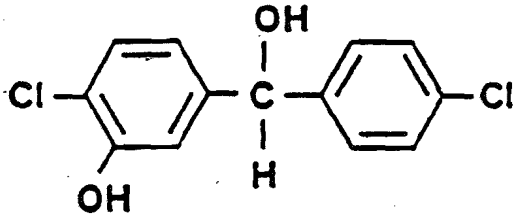
4,4'-Dichlorobenzhydrol

p,p'-DCBH



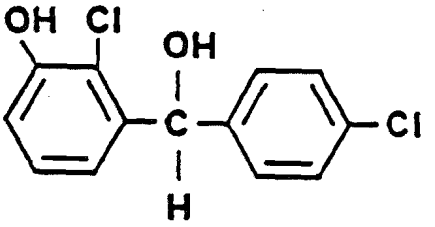
2,4'-Dichlorobenzhydrol

o,p'-DCBH



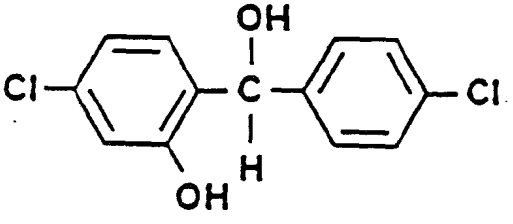
3-Hydroxy-4,4'-dichlorobenzhydrol

3-OH-p,p'-DCBH



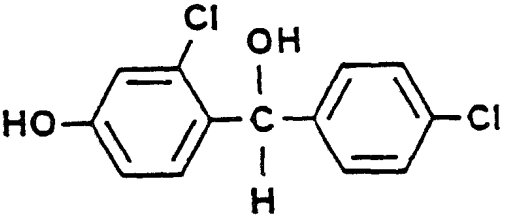
3-Hydroxy-2,4'-dichlorobenz-
hydrol

3-OH-o,p'-DCBH



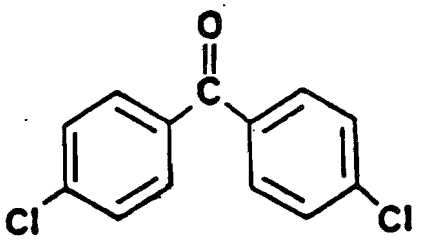
2-Hydroxy-4,4'-dichlorobenzhydrol

2-OH-p,p'-DCBH



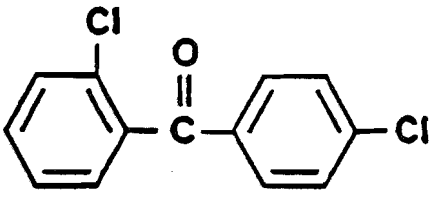
4-Hydroxy-2,4'-dichlorobenz-
hydrol

4-OH-o,p'-DCBH



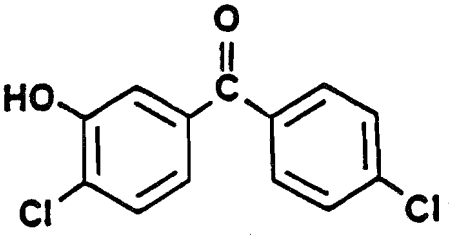
4,4'-Dichlorobenzophenone

p,p'-DCBP



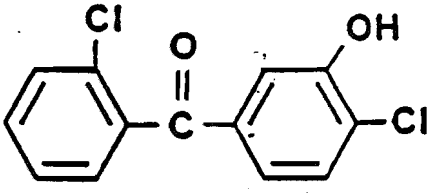
2,4'-Dichlorobenzophenone

o,p'-DCBP



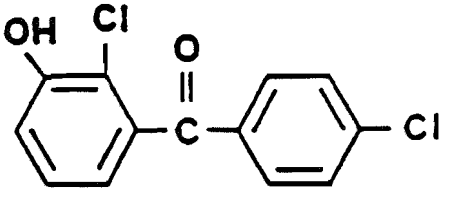
3-Hydroxy-4,4'-dichlorobenzo-
phenone

3-OH-p,p'-DCBP



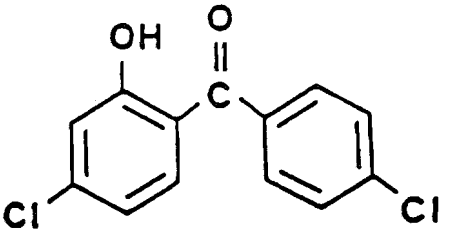
3'-Hydroxy-2,4'-dichlorobenzo-
phenone

3'-OH-o,p'-DCBP



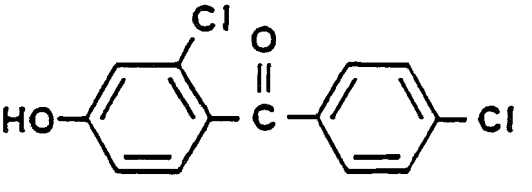
3-Hydroxy-2,4'-dichlorobenzo-
phenone

3-OH-o,p'-DCBP



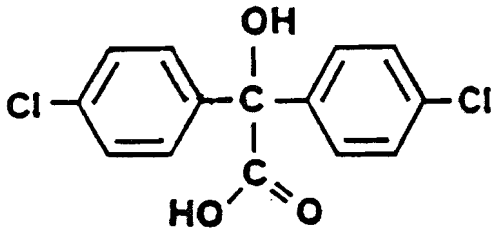
2-Hydroxy-4,4'-dichlorobenzo-
phenone

2-OH-p,p'-DCBP



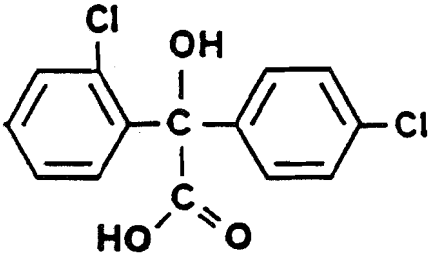
4-Hydroxy-2,4'-dichlorobenzo-
phenone

4-OH-o,p'-DCBP



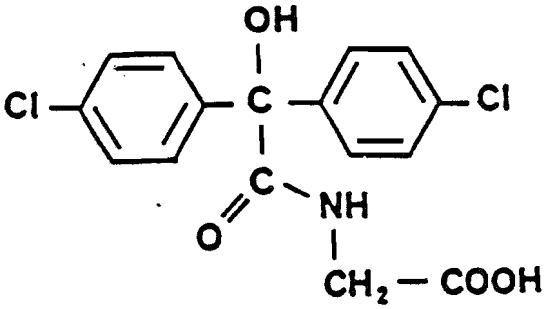
4,4'-Dichlorobenzilic acid

p,p'-DCBA



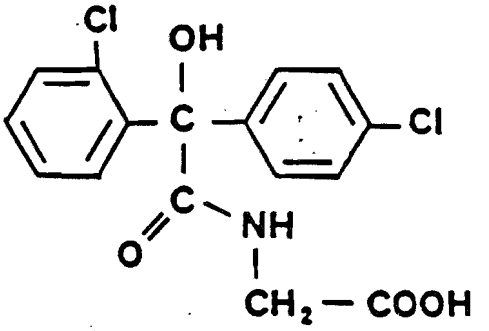
2,4'-Dichlorobenzilic acid

o,p'-DCBA



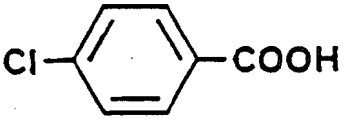
Glycine conjugate of 4,4'-dichoro-benzilic acid

p,p'-DCBA-glycine



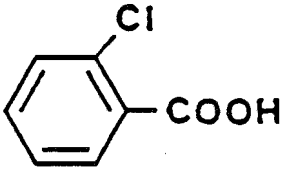
Glycine conjugate of 2,4-Di-chlorobenzilic acid

o,p'-DCBA-glycine



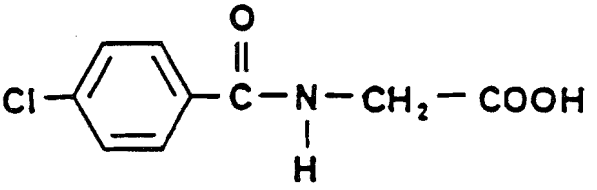
4-Chlorobenzoic acid

4-CBA



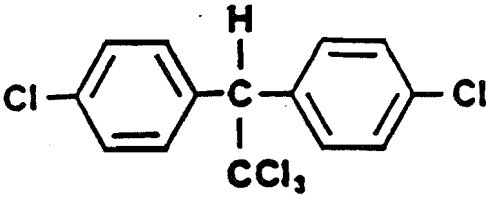
2-Chlorobenzoic acid

2-CBA



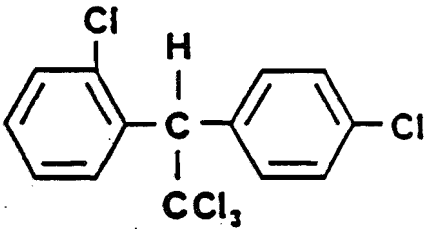
4-Chlorohippuric acid

CHA



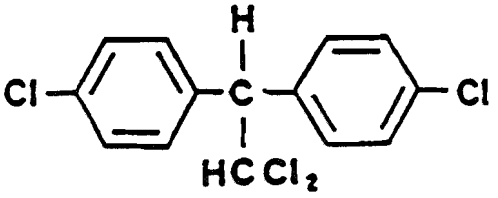
1,1-bis(4-Chlorophenyl)-2,2,2-trichloroethane

p,p'-DDT



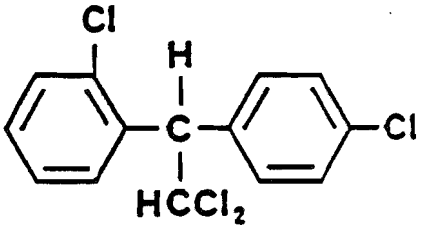
1-(2-Chlorophenyl)-1-(4'-chlorophenyl)-2,2,2-trichloroethane

o,p'-DDT



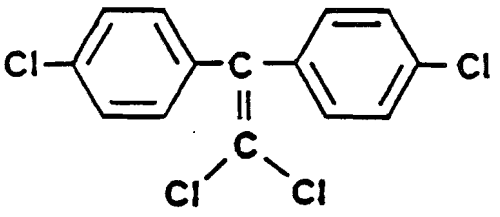
1,1-bis(4-Chlorophenyl)-2,2-dichloroethane

p,p'-DDD



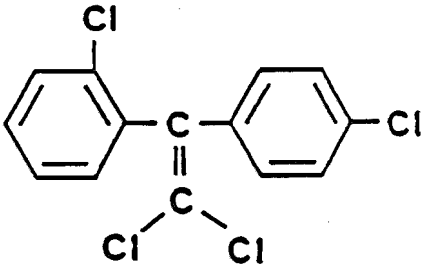
1-(2-Chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethane

o,p'-DDD



1,1-bis(4-Chlorophenyl)-2,2-dichloroethylene

p,p'-DDE



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

o,p'-DDE

DATA EVALUATION RECORDS

ON

DICOFOL

Summary of Data Evaluation Records on Dicofol

Included in the following pages are copies of all the available Data Evaluation Records (DER's) of the studies on dicofol which have been reviewed on the EFGWB/EFED from 1983 to August 1989; that is, after the Registration Standard was issued (copy included). The original reviews were kept in the EFGWB files.

María Isabel Rodríguez

María Isabel Rodríguez
Chemist
Review Section #2
OPP/EFED/EFGWB

July 2, 1990.

Group #1

Dicofol

Table of Contents

Group #1

DATA EVALUATION RECORD

STUDY 1

CHEM 010501 Dicofol §1[illegible]-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.

Table 2

Dicofol Expressed as Total Activity and ppm
Data Used to Generate Half-Life

Sample[1] ID	Total Residues (ppm)	Dicofol as % Total Activity	Dicofol ppm	ln ppm
0-T-S	10.7	87.1	9.32	2.18
1-T-S	10.2	77.3	7.88	2.02
3-T-S	8.84	67.2	5.94	1.84
7-T-S	10.8	52.4	5.66	1.82
14-T-S	10.6	27.6	2.92	0.793
1 mo-T-S	10.1	3.26	3.29	
2 mo-T-S	9.71	1.20	0.116	
3 mo-T-S	9.85	0.95	0.0932	
4 mo-T-S	10.5	0.825	0.0865	
6 mo-T-S	7.16	0.286	0.0204	
9 mo-T-S	9.19	0.646	0.0593	
12 mo-T-S	8.47	0.118	0.00999	

[1]From tlc analysis of methanol extracts, replicate II

Dicofol

Table of Contents

DATA EVALUATION RECORD

STUDY 1

CHEM 010501 Dicofol §161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40849701
Carpenter, M. 1988b. Determination of the photodegradation rate of ^{14}C-p,p'-dicofol in aqueous solution. ABC Laboratory Project ID 36670. Rohm and Haas Technical Report 34C-88-38. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MD, and submitted by Rohm and Haas Company, Spring House, PA.

DIRECT REVIEW TIME = 12

REVIEWED BY:	K. Patten	TITLE:	Staff Scientist
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APPROVED BY:	W. Spangler	TITLE:	Project Manager
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CONCLUSIONS:

Degradation - Photodegradation in Water

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

2. Dicofol photodegraded with a half-life of 92.5 days in a nonsensitized sterile pH 5 aqueous buffer solution at ≈25°C; the half-life decreased to ≈4 days when a sensitizer was added to the solution. In the dark, dicofol hydrolyzed with a half-life of ≥149 days in similar solutions. The major degradate in the nonsensitized solutions was 4,4'-dichlorobenzophenone (DCBP); other degradates identified were 4,4'-dichlorobenzilic acid (DCBA) and 4-chlorobenzoic acid (CBA).

3. This study is acceptable and fulfills EPA Data Requirements for Registering pesticides by providing information on the photodegradation of [^{14}C]p,p'-dicofol in sterile aqueous buffered pH 5 solutions.

4. No additional information on the photodegradation of p,p'-dicofol in water is required at this time.

METHODOLOGY:

Uniformly ring-labeled [^{14}C]p,p'-dicofol (radiochemical purity 94.3%, specific activity 26.39 mCi/g, Amersham Corporation) dissolved in methanol (as a cosolvent) was diluted to a volume of 1000 mL with a sterile aqueous 0.1 M acetate-buffered (pH 5) solution; the final concentration of [^{14}C]dicofol was ≈0.955 ppm and of methanol was 1% (by volume). One-half of the treated solution was sensitized with 1% acetone (by volume). The nonsensitized and sensitized solutions were transferred into silanized glass culture tubes. The tubes were sealed, and half of the tubes were wrapped with aluminum foil to serve as dark controls; the dark controls were apparently incubated separate from the irradiation equipment. The unwrapped tubes were placed on a photolysis apparatus (Figure 7, apparatus not further characterized) and irradiated continually using a xenon arc lamp equipped with dual borosilicate glass filters to eliminate radiation below 290 nm (Tables I-III and Figure 2). The intensity of the irradiation was approximately half that of normal sunlight; 24 hours of artificial light irradiation equaled 12 hours of natural sunlight at 40°N latitude at spring equinox. The study was conducted at 25 ± 1°C; the method of temperature control was not specified. Duplicate tubes containing irradiated or dark control solutions were sampled at 0, 1, 2, 4, 9, 19, and 30 days posttreatment.

Aliquots of each sample were analyzed for total radioactivity using LSC. The remaining samples were extracted 2-3 times with ethyl acetate. The extracts were combined, and the ethyl acetate extracts and the extracted sample solution were analyzed for total radioactivity using LSC. Also, the extracts were analyzed for specific compounds using TLC and HPLC. The extracts were cochromatographed using TLC on silica gel plates developed in either chloroform:methanol (85:15, v:v) or hexane:methanol (95:5, v:v). Some plates were analyzed using a TLC linear scanner; all plates were autoradiographed and viewed under UV. Radioactive zones were scraped from the plate, and the [^{14}C]compounds were desorbed from the silica gel with methanol and quantified using LSC. Recovery efficiencies from the TLC plates ranged from 86.9 to 104.2% of the radioactivity detected by LSC. To confirm the results of the TLC analysis, the extracts from one of the two replicates were analyzed using HPLC with UV (230 nm) detection; individual fractions of the eluate were analyzed by LSC. HPLC recovery efficiencies ranged from 85.2 to 108% of the radioactivity detected by LSC.

In an attempt to characterize unidentified residues, additional analyses were performed. The days 4 and 19 samples from the sensitized irradiated solutions were reanalyzed by TLC as described except with additional

reference standards. Aliquots of the ethyl acetate extract of the day 30 sensitized irradiated solution were extracted with either 1 N potassium hydroxide, 1 N sodium bicarbonate, or 1 N hydrochloric acid; the extracts were neutralized and analyzed by TLC. An aliquot of the ethyl acetate extract of the day 30 sensitized irradiated solution was evaporated to dryness. The residues were redissolved in ethyl acetate, reacted with diazomethane, and analyzed using GC/MS.

In order to determine the volatility of [^{14}C]dicofol from the test solutions, aliquots of the treated solutions were placed in continuous air-flow systems. Humidified, CO_2-free air was passed over the samples, then sequentially through tubes of ethylene glycol, 1 N sulfuric acid, and 1 N potassium hydroxide (two tubes) trapping solutions. Volatility was determined for both the irradiated nonsensitized and sensitized solutions and their dark controls; the treated solutions were apparently incubated with the degradation rate test solutions. The trapping solutions were sampled at 0, 1, 2, 4, 9, 19, and 30 days posttreatment, and analyzed for total radioactivity using LSC. The treated solutions were analyzed using LSC at 0 and 30 days posttreatment to establish a material balance.

DATA SUMMARY:

Uniformly ring-labeled [^{14}C]p,p'-dicofol (radiochemical purity 94.3%), at ≈0.955 ppm, photodegraded with a half-life of 92.5 days in nonsensitized sterile aqueous buffer solutions (0.1 N acetate buffer, pH 5) that were continually irradiated with a borosilicate glass-filtered xenon arc lamp at 25 ± 1°C for 30 days. The intensity of the lamp was reported to be approximately half that of sunlight at spring equinox, 40° N latitude. In contrast, [^{14}C]dicofol degraded with a half-life of 149 days in a similar solution incubated in the dark. The major degradate in both the irradiated and dark control nonsensitized solutions was

4,4'-dichlorobenzophenone (DCBP)

(Tables XIII, XIV, XVIII, and XIX). In the irradiated nonsensitized solutions at 30 days posttreatment, dicofol comprised 75.3% of the recovered, DCBP comprised 7.26%,

4,4'-dichlorobenzilic acid (DCBA)

comprised 0.8%,

4-chlorobenzoic acid (CBA)

comprised 3.0%, and numerous (TLC analysis, Table XVIII) unidentified [^{14}C]compounds were each <6%. The material balances ranged from 93 to 120% of the applied during the study (Tables VI-VII).

Ring-labeled [^{14}C]p,p'-dicofol, at ≈0.955 ppm, photodegraded with a half-life of ≈4 days in irradiated sensitized (1% acetonitrile) sterile

aqueous buffer solutions (0.1 N acetate buffer, pH 5). In contrast, [^{14}C]dicofol degraded with a half-life of 246 days in a similar solution incubated in the dark. In the irradiated sensitized solutions at 30 days posttreatment, CBA was 15% of the applied; the remaining radioactivity was described as a multitude of polar degradates. The material balances ranged from 95 to 117% of the applied during the study, except for an 82% recovery from the irradiated sensitized solution at 30 days (Tables IV-V).

Volatilization from the irradiated nonsensitized and sensitized solutions ranged from 2.6-5.7% of the applied by 30 days posttreatment.

COMMENTS:

1. The half-lives reported in the data summary were obtained from the HPLC data. HPLC data were used because they were considered more accurate in this experiment; half-lives were calculated from both the TLC and HPLC data. The estimated half-lives using TLC and HPLC are in good agreement for the sensitized irradiated solutions (4.01 and 4.07 days, respectively). However, the estimated half-lives are not in agreement for the other treatments (sensitized dark control, and nonsensitized irradiated and dark control), probably because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear. Error due to data extrapolation may also explain why the half-lives of dicofol in the sensitized and nonsensitized dark control solutions do not agree. These two detection methods provide useful information but are too similar to be considered confirmatory.

2. The study author stated that the experiment using sensitized solutions should be considered only as supplemental information to determine degradation rates, and not for identification of photoproducts. It was reported that the degradation of dicofol in the irradiated sensitized solutions produced a multitude of polar degradates (which apparently could not be identified); CBA was the only identifiable compound. No additional degradate information was provided.

3. Air rather than solution temperatures may have been monitored. Some temperature data (thermographs apparently resulting from continuous monitoring of incubation chambers) were included in the 1292-page report, but these data were not labeled and it was uncertain which samples they represented.

4. The photolysis apparatus was illustrated but not otherwise described. For example, the distance the xenon arc lamp was from the treated solutions was not specified and the method of temperature control (to prevent heat buildup from the lamp) was not reported.

5. The material balance for the volatilization portion (a separate

experiment) of the study was poor; only 58-88% of the applied radioactivity was recovered from the treated solutions, possibly because dicofol readily adsorbs to glass. However, sufficient information was provided to demonstrate that volatilization from the aqueous solutions was minimal. The main experiment had an acceptable material balance.

6. The pH of the test solution was measured at the beginning and end of the study and found to have been stable at pH 5.

7. The method detection limits could not be located in the document; they may not have been reported.

8. The light intensity was half that of typical sunlight but the samples were exposed continuously for 24 hours a day. Each day of the experiement was counted as one day of sunlight.

DATA EVALUATION RECORD

STUDY 2

CHEM 010501 Dicofol §161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40849702
Carpenter, M. 1988a. Determination of the photodegradation rate of ^{14}C-o,p'-dicofol in aqueous solution. ABC Laboratory Project ID 36669. Rohm and Haas Technical Report 34C-88-42. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MD, and submitted by Rohm and Haas Company, Spring House, PA.

DIRECT REVIEW TIME = 8

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study cannot be used to fulfill data requirements at this time.

2. Dicofol photodegraded with a half-life of 14.8 days in a nonsensitized sterile pH 5 aqueous buffer solution at ≈25°C; the half-life decreased to ≈1 day when a sensitizer was added to the solution. In the dark, dicofol hydrolyzed with a half-life of ≈32 days in similar solutions. The major degradate in the nonsensitized solutions was 4,4'-dichlorobenzophenone (DCBP); other degradates identified were 4,4'-dichlorobenzilic acid (DCBA), and 2- and 4-chlorobenzoic acid (CBA).

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

   one extractable degradate (R_f 0.61), present in the irradiated nonsensitized solution at up to 12% of the applied radioactivity (13.6% of the recovered), was not identified.

4. In order for this study to fulfill the photodegradation in water (o,p'-dicofol) data requirement, the registrant must identify the degradate at R_f 0.61.

METHODOLOGY:

Uniformly ring-labeled [^{14}C]o,p'-dicofol (radiochemical purity 92.4%, specific activity 43.5 mCi/g, Amersham Corporation) dissolved in methanol (as a cosolvent) was diluted to a volume of 1000 mL with a sterile aqueous 0.1 M acetate-buffered (pH 5) solution; the final concentration of [^{14}C]dicofol was ≈0.965 ppm and of methanol was 1% (by volume). One-half of the treated solution was sensitized with 1% acetone (by volume). The nonsensitized and sensitized solutions were transferred into silanized glass culture tubes. The tubes were sealed, and half of the tubes were wrapped with aluminum foil to serve as dark controls; the dark controls were apparently incubated separate from the irradiation equipment. The unwrapped tubes were placed on a photolysis apparatus (Figure 6, apparatus not further characterized) and irradiated continually using a xenon arc lamp equipped with dual borosilicate glass filters to eliminate radiation below 290 nm (Tables I-III and Figure 2). The intensity of the irradiation was approximately half that of normal sunlight; 24 hours of artificial light irradiation equaled 12 hours of natural sunlight at 40°N latitude at spring equinox. The study was conducted at 25 ± 1°C; the method of temperature control was not specified. Duplicate tubes containing irradiated or dark control solutions were sampled at approximately 0, 1, 2, 7, 14, 21, and 30 days posttreatment.

Aliquots of each sample (plus vial rinse) were analyzed for total radioactivity using LSC. The remaining samples were extracted 2-3 times with ethyl acetate. The extracts were combined, and the ethyl acetate extracts and the extracted sample solution were analyzed for total radioactivity using LSC. Also, the extracts were analyzed for specific compounds using TLC and HPLC. The extracts were cochromatographed using TLC on silica gel plates developed in either chloroform:methanol (85:15, v:v) or hexane:methanol (95:5, v:v). Some plates were analyzed using a TLC linear scanner; all plates were autoradiographed and viewed under UV. Radioactive zones were scraped from the plate, and the [^{14}C]compounds were desorbed from the silica gel with methanol and quantified using LSC. Recovery efficiencies from the TLC plates ranged from 79.5 to 94.8% of the radioactivity detected by LSC. To confirm the results of the TLC analysis, the extracts from one of the two replicates were analyzed using HPLC with UV (230 nm) detection; individual fractions of the eluate were analyzed by LSC. HPLC recovery efficiencies ranged from 88 to 102% of the radioactivity detected by LSC.

In an attempt to characterize unidentified residues, additional analyses were performed. The day 7 samples from the sensitized irradiated solutions and the day 21 samples from the nonsensitized irradiated solutions were reanalyzed by TLC as described except with additional reference standards. Also, the day 30 samples from the sensitized irradiated solutions were separated by HPLC using a greater volume of sample. Fractions 7 through 17 were combined, then analyzed using TLC with the solvent systems previously described and with methanol:acetonitrile:water (35:35:30).

In order to determine the volatility of [^{14}C]dicofol from the test solutions, aliquots of the treated solutions were placed in continuous air-flow systems. Humidified, CO_2-free air was passed over the samples, then sequentially through a C-18 Sep-Pak cartridge and tubes of ethylene glycol, 1 N sulfuric acid, and 1 N potassium hydroxide (two tubes) trapping solutions. Volatility was determined for both the irradiated nonsensitized and sensitized solutions and their dark controls; the treated solutions were apparently incubated with the degradation rate test solutions. The trapping solutions were sampled at the same intervals as the sealed samples, and analyzed for total radioactivity using LSC. The treated solutions were analyzed using LSC at 0 and 30 days posttreatment to establish a material balance.

DATA SUMMARY:

Uniformly ring-labeled [^{14}C]o,p'-dicofol (radiochemical purity 92.4%), at ≈0.965 ppm, photodegraded with a half-life of 14.8 days in nonsensitized sterile aqueous buffer solutions (0.1 N acetate buffer, pH 5) that were continually irradiated with a borosilicate glass-filtered xenon arc lamp at 25 ± 1°C for 30 days. The intensity of the lamp was reported to be approximately half that of sunlight at spring equinox, 40° N latitude. In contrast, [^{14}C]dicofol degraded with a half-life of 31.8 days in a similar solution incubated in the dark. The major degradate in both the irradiated and dark control nonsensitized solutions was

4,4'-dichlorobenzophenone (DCBP)

(Tables XX and XXI). In the irradiated nonsensitized solutions at 30 days posttreatment, dicofol comprised 27.5% of the recovered, DCBP comprised 25.5%,

4,4'-dichlorobenzilic acid (DCBA)

comprised 2.5%,

2-chlorobenzoic acid (2-CBA)

comprised 1.6%,

4-chlorobenzoic acid (4-CBA)

comprised 4.6%, one unidentified [^{14}C]compound (R_f 0.61) was 13.6%, and four unidentified [^{14}C]compounds were each ≤3.1%. In the nonsensitized dark control at 30 days, only dicofol, DCBP, and 4-CBA were identified. The material balances ranged from 88 to 102% of the applied during the study (Tables IV and V).

Ring-labeled [^{14}C]o,p'-dicofol, at ≈0.965 ppm, photodegraded with a half-life of ≈1 day in irradiated sensitized (1% acetonitrile) sterile aqueous buffer solutions (0.1 N acetate buffer, pH 5). In contrast, [^{14}C]dicofol degraded with a half-life of 33.2 days in a similar solution incubated in the dark. In the irradiated sensitized solutions at 30 days posttreatment, CBA was isolated; the remaining radioactivity was described as a multitude of polar degradates. The material balances ranged from 92 to 102% of the applied during the study (Tables VI and VII).

Volatilization from the irradiated nonsensitized and sensitized solutions ranged from 3.8-4.0% of the applied by 30 days posttreatment.

COMMENTS:

1. Subdivision N guidelines for photodegradation in water experiments specify that all degradates present at ≥10% of the applied must be identified. Five degradates isolated from the irradiated nonsensitized solution were not identified; one of those degradates (R_f 0.61) comprised 13.6% of the recovered (12% of the applied) radioactivity.

2. The half-lives reported in the data summary were obtained from the TLC data. TLC data were used because they were considered more accurate; half-lives were calculated from both the TLC and HPLC data. The estimated half-lives using TLC and HPLC are in good agreement for all test solutions. These two detection methods provide useful information but are too similar to be considered confirmatory.

3. The study author stated that the experiment using sensitized solutions should be considered only as supplemental information to determine degradation rates, and not for identification of photoproducts.

4. The photolysis apparatus was illustrated but not otherwise described. For example, the distance the xenon arc lamp was from the treated solutions was not specified and the method of temperature control (to prevent heat buildup from the lamp) was not reported.

5. The pH of the test solution was measured at the beginning and end of the study and found to have been stable at pH 5.

6. The method detection limits could not be located in the document; they may not have been reported.

7. Dicofol adsorbed to the sides of the sample flask although the glassware was silanized prior to use. The flasks were rinsed with ethyl acetate

prior to analysis to remove any adsorbed dicofol.

8. The light intensity was half that of typical sunlight but the samples were exposed continuously for 24 hours a day. Each day of the experiement was counted as one day of sunlight.

DATA EVALUATION RECORD

DICOFOL STUDY 2

CHEM 010501 Dicofol §161-3

BRANCH EAB

FORMULATION--00--ACTIVE INGREDIENT

FICHE/MASTER ID 40460103
Carpenter, M. 1987a. Supplement to photodegradation of ^{14}C-o,p'-dicofol on the surface of soil (MRID No. 40042037). Rohm and Haas Technical Report No. 31C-87-50. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA.

FICHE/MASTER ID 40460101
Carpenter, M. 1987b. Supplement to photodegradation of ^{14}C-p,p'-dicofol on the surface of soil (MRID No. 40042036). Rohm and Haas Technical Report No. 31C-87-49. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA.

SUBST. CLASS = S

DIRECT RVW TIME = 8

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CONCLUSIONS:

Degradation - Photodegradation on Soil

When previously reviewed (06/08/87), both the o,p'- and p,p'-dicofol studies did not fulfill data requirements because the artificial light source (a 275-W General Electric RS-M sunlamp) did not simulate sunlight; the light source did not provide continuous radiation at wavelengths above 290 nm (Figure 1). The

o,p'-dicofol study was also faulted because degradates were incompletely characterized.

The registrant agrees that the irradiation spectra of the artificial light source and sunlight are not similar, but has responded that dicofol does not appreciably absorb light above 290 nm, and that dicofol and its degradate DCBP are unlikely to absorb in the visible light region because of the lack of suitable chromophores. The registrant has also argued that no artificial light source produces a spectrum that is identical to sunlight. The registrant therefore believes that it was unnecessary to irradiate the treated soil with the entire visible light spectrum and the artificial light source used in the study was adequate. Although it is true that only light which is absorbed by a pesticide can directly cause photodegradation, it is possible for light that is outside the absorption spectrum of the compound to indirectly cause degradation via sensitized energy transfer. Various natural soil compounds, especially humic substances, may absorb light energy and transfer it to the pesticide. Since the soil was not irradiated with the entire sunlight spectrum, it is impossible to determine if sensitized energy transfer is a phenomenon observed with dicofol. It is correct that artificial light sources do not produce a spectrum that is identical to sunlight, but there are artificial light sources, such as the xenon arc lamp, whose irradiation spectra closely resemble sunlight; the artificial light source used in these studies irradiated at only a few discrete wavelengths.

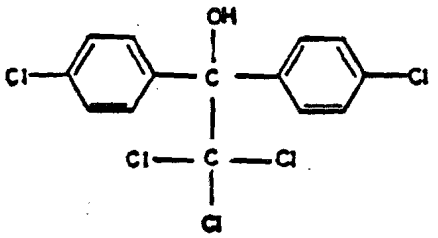
In the o,p'-dicofol study, the registrant has responded that the unidentified degradates, which together comprised up to 34.7% of the applied, were each <10% of the applied. Only degradates >10% of the applied must be identified.

Additional information provided by the registrant is that recovery of dicofol from fortified soil samples ranged from 81.9 to 90.0% for the o,p' form and from 76.3-83.0% for the p,p' form; and the detection limit for both forms was approximately 0.01 ppm.

In conclusion, the photodegradation on soil studies using o,p'-dicofol and p,p'-dicofol are scientifically sound but provide only supplemental information towards the registration of dicofol. If the registrant can demonstrate that light energy absorbed by natural soil constituents is not transferred to dicofol, both studies will be accepted to fulfill data requirements.

DICOFOL

DICOFOL, ACARIN, KELTHANE, MITIGAN, CARBAX



1,1-Bis(p-chlorophenyl)-2, 2,2-trichloroethanol

Table of Contents

Study

MATERIALS AND METHODS:

1,1-Bis(4-chlorophenyl)-1,2,2,2-tetrachloroethane (ER-8) of unspecified purity was dissolved in acetonitrile and added to sterile solutions buffered at pH 5, 7, and 9 (Table 1) to give a final concentration of 1 ppm ER-8 in 1% acetonitrile. The test compound was added both as unlabeled and uniformly ring-labeled [^{14}C]ER-8 (specific activity 0.68 µc/mg, purity unspecified, Rohm and Haas Company). Sets of four bottles (2 labeled, 1 unlabeled, and 1 control without ER-8) were incubated in the dark at 25 C and removed for analysis at 0, 1, 3, 7, 14, and 30 days. Originally 4 ml samples were to be counted directly for LSC analysis and 100 ml portion were to be drawn through a C18 Bond Elut column to isolate ER-8 and any hydrolysis products for TLC analysis. However, the method was later modified to include a methylene chloride solvent extraction of the entire bottle contents followed by radiochemical and GLC analysis of the extracts. After 30 days incubation, methylene chloride extracts were also subjected to TLC analysis to determine the presence of possible hydrolytic products.

REPORTED RESULTS:

No apparent hydrolysis of ER-8 occurred during 30 days of incubation at pH 5, 7, and 9. Decreased recovery of ER-8 at 3 days (Table 2) indicated that either hydrolysis or precipitation of compound was occurring. Shaking of bottles before removal of aliquots for sampling (day 7) resulted in increased recovery of ER-8. The method was therefore, modified to include a methylene chloride extract of the entire bottle contents followed by a methylene chloride rinse of the bottle. Subsequent samplings resulted in high recovery efficiency for ER-8. Analysis of 30-day extracts by TLC indicated that most of the radioactivity from [^{14}C]ER-8 migrated at the same R_f as added standards. No TLC spots were found corresponding to R_f values of suspected degradates.

DISCUSSION:

The experiment was carried out to study hydrolysis of ER-8 rather than dicofol. No information was provided on the hydrolytic behavior of dicofol.

Table 1. Buffer systems employed for hydrolysis study.

Buffer system	Preparation procedure
pH 5.0 (pH 4.95)[a]	12.2 g sodium acetate dissolved in 9 l H_2O and pH adjusted with 0.1 m acetic acid.
pH 7.0 (pH 7.05)	61.2 g KH_2PO_4 and 10.5 g NaOH dissolved in 9 l H_2O.
pH 9.0 (pH 9.1)	85.8 $Na_2B_4O_7.10H_2O$ dissolved in 9 l H_2O and pH adjusted with 0.1 M acetic acid.

[a] Actual pH values of prepared solution.

Table 2. Hydrolysis results for ER-8 at pH 5, 7, and 9.

Time (days)	Buffer	% Recovery LSC	% Recovery GLC
0	pH 5	104	78
1		90	83
3		52[a]	42[a]
7		26(76)[b]	(75)[b]
14		92[c]	90[c]
20		97[c]	86[c]
0	pH 7	100	92
1		94	82
3		85	81
7		79(90)[b]	(90)[b]
14		85[c]	86[c]
20		93[c]	89[c]
0	pH 9	102	83
1		93	73
3		79	82
7		54(88)[b]	(76)[b]
14		72[c]	85[c]
20		93[c]	100[c]

[a] Low recovery probably due to precipitation from solution.

[b] () Indicates value obtained by shaking of bottle prior to sampling.

[c] Procedure modified to include solvent extraction of entire bottle contents and solvent rinse of bottle.

CASE GS0021 DICOFOL STUDY 2 PM

CHEM 010501 Dicofol

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 02

Bennett, R.M., T.L. Whitaker, and M.L. Mathis. 1984. Environmental fate study for ER-8 leaching from aged soil. Unpublished study received Oct. 10, 1984 under 707 Q; submitted by Rohm and Haas Company, Philadelphia, PA. Accession No. 254959.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
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APPROVED BY:
TITLE:
ORG:
TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Aged (33-days) residues of [^{14}C]ER-8 (1,1-bis(4-chlorophenyl)-1,2,2,2-tetrachloroethane (a dicofol residue), were immobile in sandy loam, sand (coarse), sand (fine) and clay loam soil columns; after leaching 12-inch soil columns with 20.0 inches of water, no radioactivity was recovered in the leachate. After 40 days 97.1, 70.4, 75.5, and 88.8%, respectively, of the applied radioactivity remained in the top 1 inch of soil.

MATERIALS AND METHODS:

Sandy loam, sand (coarse), sand (fine) and clay loam soils samples (100 g dry weight equivalents) (Table 1) were fortified with uniformly ring-labeled [^{14}C]-ER-8 (1,1-bis(4-chlorophenyl)-1,2,2,2-tetrachloroethane; 0.68 mCi/g, purity unspecified, Rohm and Haas Company) at 10 ppm and aged for 33 days in an aerobic aging train. The systems were flushed with vapor saturated air and incubated in the dark at room temperature (range unspecified). $^{14}CO_2$ was trapped by bubbling outgoing air through NaOH and radioactivity quantified by LSC.

After the 33-day aging period, metal soil columns (24 inches in length by 3 inches in diameter) were packed to a uniform depth of 12 inches with untreated soil. The soil columns were thoroughly wetted and then treated and aged soils were added to the tops of the columns. Over a period of 40 days, 20.0 inches of water were applied to the soil columns and leachates were assayed daily for radioactivity by LSC.

After the 40-day leaching period the upper portions (6 inches) of the columns were divided into 1-inch segments and the lower portions into 2-inch segments and stored frozen prior to analysis. At analysis each soil segment was combusted in duplicate and the $^{14}CO_2$ evolved was trapped and quantified using LSC.

REPORTED RESULTS:

No $^{14}CO_2$ was detected during the 33-day aging period indicating that extensive degradation of ER-8 did not occur. Essentially all radioactivity recovered from the columns, after the 40-day leaching period, was found in the top 1-inch segment (Table 2). Only trace amounts were found in the 2 or 3 inch depths in some columns. No radioactivity was found in the leachate water. The results indicated strong adsorption of aged ER-8 residues to soil and a low tendency to leach from the soil.

DISCUSSION:

1. Data were provided only for the residue ER-8; not for dicofol.

2. The purity of the test substance was not reported.

3. Radioactive residues were not characterized.

4. Values of soil/water relationships (K_d) were not reported.

5. Soil moisture content during the aging period was not reported.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
	%					
Sandy loam	65.20	22.80	12.00	1.2	5.9	4.20
Sand (Coarse particle size)[a]	91.20	2.80	6.00	0.5	6.0	1.30
Sand (Fine particle size)[a]	92.80	1.20	6.00	0.2	5.2	0.50
Clay loam	36.80	27.20	36.00	1.0	5.1	9.90

[a] Particle sizes not provided.

Table 2. Distribution of radioactivity (% of applied) in soil columns treated with [^{14}C]ER-8 and leached with 20.0 inches of water.

Soil	Depth (inches)	% of applied activity
Sandy loam	1	97.1
Blackstone, VA	2	<1.0
	3	<1.0
	4	<1.0
	5	<1.0
	6	<1.0
	7-8	<1.0
	9-10	<1.0
	11-12	<1.0
Sand (coarse particle)	1	70.4
Blackstone, VA	2	<1.0
	3	<1.0
	4	<1.0
	5	<1.0
	6	<1.0
	7-8	<1.0
	9-10	<1.0
	11-12	<1.0
Agricultural sand	1	75.5
(fine particle)	2	<1.0
Winston - Salem, NC	3	<1.0
	4	<1.0
	5	<1.0
	6	<1.0
	7-8	<1.0
	9-10	<1.0
	11-12	<1.0
Clay loam	1	88.8
Walkertown, NC	2	<1.0
	3	<1.0
	4	<1.0
	5	<1.0
	6	<1.0
	7-8	<1.0
	9-10	<1.0
	11-12	<1.0

DICOFOL

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DYNAMAC
CORPORATION

DICOFOL ADDENDUM

Task 1: Review and Evaluation of Individual Studies

June 24, 1988

Final Report

Contract No. 68-02-4250

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

DICOFOL

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DATA EVALUATION RECORD

DICOFOL STUDY 1

CHEM 010501 Dicofol §161-1

BRANCH EAB

FORMULATION--00--ACTIVE INGREDIENT

FICHE/MASTER ID 40460105
Warren, J. 1987. Supplement to hydrolysis of ^{14}C-p,p'-dicofol (MRID No. 40042032). Rohm and Haas Technical Report No. 31C-87-52. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA.

SUBST. CLASS = S

DIRECT RVW TIME = 3

REVIEWED BY: K. Patten TITLE: Staff Scientist

EDITED BY: W. Higgins TITLE: Staff Scientist

APPROVED BY: W. Spangler TITLE: Project Manager

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

APPROVED BY: L. Lewis
TITLE: Environmental Scientist
ORG: EAB/HED/OPP
TEL: 557-7442

Laurie C. Lewis JUN 30

SIGNATURE:

CONCLUSIONS:

Degradation - Hydrolysis

When previously reviewed (06/08/87), this study did not fulfill data requirements for the pH 5 solution because the material balance was incomplete (30% of the reported application of 1 ppm was not accounted for). However, data for the pH 7 and 9 solutions were accepted. The registrant has responded that the low concentration of [^{14}C]residues in the pH 5 solution was the result of a low application rate. The concentration of total residues in solution throughout the study ranged from 0.658 to 0.720 ppm, with the lowest concentration at initiation and the highest at day 22. This explanation is reasonable and the study will be accepted for pH 5, 7, and 9 solutions using the p,p'-label.

It was also noted in the Discussion section of the original review that the TLC method may have been inadequate because up to 43% of the applied radioactivity either remained at the origin or was not associated with a discrete zone on the TLC plates; recovery from fortified samples and the detection limits were not reported; and attempts had been made to identify origin material, but the attempts had been unsuccessful.

The registrant believes that the TLC method (two-dimensional TLC at the final sampling intervals, one-dimensional at all other intervals) was adequate because the majority of the [^{14}C]residues chromatographed as dicofol or p,p'-dichlorobenzophenone, and because the one- and two-dimensional TLC results were in agreement.. However, EAB currently recommends that if TLC methods are used to separate and quantify [^{14}C]compounds, the test solutions be developed in at least three solvent systems of different polarity to provide maximum confidence in the separation.

The registrant reports that recovery from fortified samples was >100% and that the detection limit was about 0.01 ppm.

The origin material contained a polar compound that has been tentatively identified, using TLC of the samples in a polar solvent system, as 4,4'-dichlorobenzylate. More definitive identification was not made using GC/MS because insufficient quantities of the material were isolated.

In conclusion, the hydrolysis study using p,p'-dicofol is acceptable and partially fulfills data requirements. The previously submitted hydrolysis study using o,p'-dicofol (MRID 40042033) was accepted in fulfillment of the data requirement for that isomer. Taken together, these two studies completely fulfill the hydrolysis data requirement for dicofol.

CASE GS -- DICOFOL STUDY 1 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Warren, J. 1986. Hydrolysis of ^{14}C-p,p'-dicofol (Kelthane). Project Number ABC 33351. Rohm and Haas T.R. No. 310-86-59. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-32.

SUBST. CLASS = S.

DIRECT RVW TIME = 24 (MH) START-DATE END DATE

REVIEWED BY: B. Price
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APPROVED BY: A. Evans
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-1981

SIGNATURE: Alan N. Evans DATE: May 29, 1987

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. After 30 days at 1 ppm, 75% of p,p'-[^{14}C]dicofol (radiochemical purity >93%) remained undegraded in a sterile aqueous buffered (pH 5) solution incubated in the dark at 25 1°C. The half-lives were calculated to be 85 days at pH 5, 64 hours at pH 7, and 26 minutes or 0.43 hours at pH 9. The predominant degradate in all solutions, 4,4'- dichlorobenzophenone, accumulated with time and appeared to resist further degradation. At least three additional degradates, each <9.6%, were isolated but not identified in the pH 5 and 9 test solutions. Attempts to identify the polar degradates (TLC Origin) were unsuccessful.

3. This study contributes toward the fulfillment of EPA Data Requirements for Registering Pesticides. EAB accepts the hydrolysis study for pH 7 and 9 as satisfying requirements, but the study at pH 5 will have to be repeated because the material balance was poor and special emphasis should be placed on complete identification of the degradates with use of analytical methods in addition to TLC, such as HPLC and GC.

MATERIALS AND METHODS:

p,p'-[^{14}C]Dicofol (radiochemical purity >93%, specific activity 26.4 mCi/ Rohm and Haas Company) was added at 1 ppm to boiled, filter-sterilized (0.22 μ) aqueous solutions buffered at pH 5 (0.2 M acetic acid plus 0.2 M sodium acetate), pH 7 (0.2 M sodium phosphate plus 0.2 M disodium phosphate, designated 7.1; and 0.1 M potassium phosphate plus 0.1 M sodium hydroxide, designated 7.2), and pH 9 (0.2 M boric acid and 0.2 sodium borate). The treated solutions were stored in sterile amber bottles in the dark at 25 ± 1°C. The pH 5 solution was sampled at intervals from 0 to 30 days posttreatment, the pH 7 solution from 0 to 7 days posttreatment, and the pH 9 solution from 0 to 1 day posttreatment.

Three aliquots of each solution were analyzed for total radioactivity by LSC. Additional duplicate aliquots were saturated with sodium chloride, acidified with concentrated hydrochloric acid, and stored at 4°C. After all samples had been collected, the acidified samples were extracted three times with ethyl acetate. The organic and aqueous phases were separated and analyzed for total radioactivity using LSC. Aliquots of the organic extracts of the pH 5 and 9 solutions were cochromatographed with the [^{14}C]dicofol stock solution on silica gel TLC plates developed in hexane:methanol (80:20, v:v). Aliquots of the organic extract of the pH 7 solutions were analyzed by TLC on silica gel plates developed in hexane:ethyl acetate:methanol (80:10:10, v:v:v). Radioactive areas were located by autoradiography, scraped from the plates, and quantified by LSC. [^{14}C]Compounds were identified by comparison to the R_f values of standards.

In an attempt to identify hydrolysis products present at the origin, additional TLC analyses were conducted on the solutions from the final sampling intervals. One-dimensional normal-phase TLC plates were developed in hexane:ethyl acetate:methanol (80:10:10:, v:v:v), air-dried, and visualized by using color reagents (purpald, bromcresol purple, bromcresol green, and phosphomolybdic acid) sprayed onto the plates. Also, aliquots of the solutions from the final sampling intervals were analyzed by two-dimensional TLC on silica gel plates developed in benzene:acetonitrite (94:6, v:v) and hexane:ethyl acetate:methanol (80:10:10, v:v:v). Radioactive areas were located by autoradiography and identified by comparison to standards.

REPORTED RESULTS:

After 30 days at 1 ppm, 75% of the p,p'-[^{14}C]dicofol in the pH 5 solution remained undegraded. The half-lives were calculated to be 85 days at pH 5, 64 hours at pH 7, and 26 minutes or 0.43 hours at pH 9 in aqueous buffered solutions incubated in the dark at 25 ± 1°C (Table 1). 4,4'-Dichlorobenzophenone and at least three unidentified degradates (each <9.6%) were formed in the pH 5 and 9 test solutions. 4,4'-Dichlorobenzophenone was the only degradate observed in the pH 7 test solution. Data were similar for the two-dimensional TLC analyses (Table 2).

A positive reaction for carboxylic acid and dicarbecylic acid was observed at the origin in all buffered solutions, and aldehydes were identified at the origin in the pH 5 solutions.

DISCUSSION:

1. The TLC method may have been inadequate; up to ~43% of the applied radioactivity either remained at the origin or was described as "remainder" (not associated with a discrete site).

2. The material balance for pH 5 was low and 30% of material was unaccounted for. EAB recommends the hydrolysis study for pH 5 be repeated.

3. Recovery of dicofol from fortified samples and detection limits were not reported.

4. Two additional procedures (reverse-phase TLC and adjusting the pH of the samples with triethyl amine prior to normal-phase TLC) were attempted in order to identify material at the origin. Both were unsuccessful and therefore are not reviewed in this report.

CASE GS -- DICOFOL STUDY 2 PM --

CHEM 010501 Dicofol

BRANCH FAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Warren, J. 1986. Hydrolysis of ^{14}C-o,p'-dicofol (Kelthane). Project Number ABC 34618. Rohm and Haas T.R. No. 310-86-58. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-33.

SUBST. CLASS = S.

DIRECT RVW TIME = 24 (MH) START-DATE END DATE

REVIEWED BY: B. Price
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APPROVED BY: A. Evans
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-1981

SIGNATURE: DATE: MAY 29 1987

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. After 31 days at 1 ppm, 66% of o,p'-[^{14}C]dicofol remained undegraded in a sterile aqueous buffered (pH 5) solution incubated in the dark at 25 1°C. The calculated half-lives are 47 days at pH 5, 8 hours at pH 7, and 0.15 hour or 9 minutes at pH 9. The major degradate (0.972 ppm) in all solutions was 2,4'-dichlorobenzophenone. 2,4' -Dichlorobenzophenone accumulated with time to become the predominant degradate and appeared to resist further degradation. Chlorobenzoic acid was observed in the pH 7 test solution. Attempts to identify the polar degradates (TLC Origin) were unsuccessful.

3. This study fulfills EPA Data Requirements for Registering Pesticides for o, p' -dicofol.

MATERIALS AND METHODS:

o,p'-[^{14}C]Dicofol (radiochemical purity >91%, specific activity 43.5 mCi/g Rohm and Haas Company) was added at 1 ppm to boiled, filter-sterilized (0.22) aqueous solutions buffered at pH 5 (0.2 M acetic acid plus

0.2 M sodium acetate), pH 7 (0.1 M potassium phosphate plus 0.1 M sodium hydroxide; designated 7.1; and 0.2 M tris [hydroxymethyl] aminomethane plus 0.2 M hydrochloric acid, designated 7.2), and pH 9 (0.2 M boric acid and 0.2 sodium borate). The treated solutions were stored in sterile amber bottles in the dark at 25 1°C. The pH 5 solution was sampled at intervals from 0 to 31 days posttreatment, the pH 7 solution from 0 to 7 days posttreatment and the pH 9 solution from 0 to 1 hour posttreatment.

Two aliquots of each solution were analyzed for total radioactivity by LSC. Additional duplicate aliquots were saturated with sodium chloride, acidified with concentrated hydrochloric acid, and stored at 4°C. After all samples had been collected, the acidified samples were extracted three times with ethyl acetate. The organic and aqueous phases were separated and analyzed for total radioactivity using LSC. Aliquots of the organic extracts of the pH 5 and 9 solutions were co-chromatographed with the [^{14}C]dicofol stock solution on silica gel TLC plates developed in hexane:methanol:ethyl acetate (80:10:10, v:v:v). Aliquots of the organic extracts of the pH 7 and 9 solutions were analyzed by TLC on silica gel plates developed in hexane:ethyl acetate: methanol (80:10:10, v:v:v). Radioactive areas were located by autoradiography, scraped from the plates, and quantified by LSC. [^{14}C]Compounds were identified by comparison to the R_f values of standards.

In an attempt to identify hydrolysis products present at the origin, additional TLC analyses were conducted on the solutions from the final sampling intervals. One-dimensional normal-phase TLC plates were developed in hexane:ethyl acetate:methanol (80:10:10, v:v:v), air-dried, and visualized using color reagents (purpald, bromcresol purple, bromcresol green and phosphomolybdic acid) sprayed onto the plates. Also, aliquots of the solutions from the final sampling intervals were analyzed by two-dimensional TLC on silica gel plates developed in benzene: acetonitrite (94:6, v:v) and hexane:ethyl acetate:methanol (80:10:10, v:v:v).

REPORTED RESULTS:

o,p'-[^{14}C]Dicofol, at 1 ppm, degraded with half-lives of 47 days at pH 5, 8 hours at pH 7, and 0.15 hour or 9 minutes at pH 9 in aqueous buffered solutions incubated in the dark at 25 1°C (Table 1). 2,4'-Dichlorobenzophenone was the only degradate isolated in all solutions. 2,4'-Dichlorobenzophenone and chlorobenzoic acid were formed in the pH 7.1 test soluion. Data were similar for the two-dimension TLC analyses (Table 2).

A positive reaction for carboxylic acid and dicarboxylic acid was observed at the origin in all buffered solutions, and aldehydes were observed at the origin in the pH 7.2 solutions.

DISCUSSION:

1. The TLC method may have been inadequate; up to 27% of the applied radioactivity either remained at the origin or was described as "remainder" (not associated with a discrete site).

2. Recovery of dicofol from fortified samples and detection limits were not reported.

3. Two additional procedures (reverse-phase TLC and adjusting the pH of the samples with triethyl amine prior to normal-phase TLC) were attempted in order to identify material at the origin. These were inconclusive and therefore are not reviewed in this report.

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CASE GS -- DICOFOL STUDY 3 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Carpenter, M. 1986. Aqueous photolysis of ^{14}C-p,p'-dicofol (Kelthane). ABC Final Report No. 34277. Rohm and Haas Technical Report No. 310-86-64. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-34.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: W. Higgins
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TEL: 557-1981

SIGNATURE: DATE: MAY 29 1987

CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is scientifically valid.

2. p,p'-[^{14}C]Dicofol (purity 97.6%), at 0.8-0.9 ppm, degraded with an calculated half-life of 37.5 days in sterile aqueous buffered (pH 5) solutions containing 1% methanol (cosolvent) that were irradiated with artificial light at 28°C. In the dark controls, dicofol degraded with a calculated half-life of 174 days. In sterile aqueous buffered (pH 5) solutions containing 1% acetone (photosensitizer), dicofol degraded with a calculated half-life of 8.2 hours when irradiated and 18.3 days in the dark. 4,4'-Dichlorobenzophenone was the only degradate isolated (0.07 ppm) in the irradiated nonsensitized solution; 4,4'-dichlorobenzophenone (0.05 ppm) and 3-hydroxy-4,4'-dichlorobenzophenone (0.11 ppm) were isolated in the irradiated sensitized solution.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the light source did not simulate sunlight and degradates were not adequately characterized.

MATERIALS AND METHODS:

p,p'-[^{14}C]Dicofol (purity 97.6%, specific activity 5.86 x 10^4 dpm/μg, Rohm and Haas Company) dissoved in methanol was added at 0.818 ppm to a sterile, aqueous, pH 5 buffered (acetic acid:sodium acetate) solution that contained 1% methanol as a cosolvent. Also, p,p'-[^{14}C]dicofol was added at 0.942 ppm to additional pH 5 buffered solution that had been sensitized with 1% acetone (v:v). The treated solutions were transferred to silanized culture tubes, which were filled as completely as possible to minimize interactions with air. Half of the samples were wrapped in aluminum foil to serve as dark controls. All of the tubes were placed in a photolysis apparatus which used a 275-W General Electric RS-M sunlamp (Figure 1) as the source of irradiation, and were incubated at 28°C. Samples were taken at intervals up to 30 days posttreatment and stored at 4°C until analysis.

The samples were extracted three times with ethyl acetate. The ethyl acetate extract and the extracted buffered solution were analyzed for total radioactivity by LSC and for specific compounds by TLC with reference compounds on silica gel plates developed in hexane:methanol (95:5, v:v). The plates were visualized using shortwave UV light and autoradiography. Radioactive areas were identified by comparison to the reference standards, scraped from the plates, and quantified by LSC.

In order to quantify volatilization during aqueous photodegradation, aliquots of the treated nonsensitized (50-mL) and sensitized (95-mL) solutions were placed in gas washing bottles and the bottles were attached to a positive pressure air flow system (Figure 2). Moistened CO_2-free air was passed through the head space of the bottle containing the treated solution, then through tubes of ethylene glycol, 1 N sulfuric acid, 1 N potassium hydroxide, and 1 N potassium hydroxide trapping solutions. The samples were irradiated using the sunlamp described previously; duplicate solutions were incubated in the dark as controls. The trapping solutions were sampled at intervals up to 30 days posttreatment and were analyzed for total radioactivity by LSC after all the samples had been collected.

REPORTED RESULTS:

p,p'-[^{14}C]Dicofol degraded with a calculated half-life of 37.5 days, in irradiated nonsensitized pH 5 buffer solutions (Table 1). In the nonsensitized dark control, dicofol degraded with a calculated half-life of 174 days. In the sensitized solutions, p,p'-[^{14}C]dicofol degraded with a calculated half-life of 8.2 hours when irradiated, compared to 18.3 days in the dark (Table 2). p,p'-[^{14}C]Dicofol degraded to 4,4'-dichlorobenzophenone in both the nonsensitized and sensitized solutions (maximum of 0.07 and 0.05 ppm, respectively), and to 3-hydroxy-4,4'-dichlorobenzophenone in the irradiated sensitized solution (maximum of 0.106 ppm at day 24).

A total of 0.040 and 0.016 ppm of [^{14}C]residues were volatilized during 30 days of incubation from the irradiated nonsensitized buffered solution and its dark control, respectively (Table 3). A total of 0.009

and 0.002 ppm of [^{14}C]residues were volatilized during 24 hours of incubation from the irradiated sensitized buffered solution and its dark control, respectively. The material balance for the volatile analysis study ranged from 57.5 to 85.6% of the applied.

DISCUSSION:

General

1. The light source did not provide continuous radiation at wavelengths above 290 nm to simulate sunlight and the absorption spectra of the chemical was not reported.

2. The registrant claimed that the recording thermometer consistently measured the test solution temperature 3-4°C higher than the true solution temperature, as determined by a mercury thermometer. The reviewer reported the recording thermometer measurements.

3. The ^{14}C-label position for p,p'-[^{14}C]dicofol was not specified.

4. Detection limits were not specified.

Solution Analysis

1. Degradates were not adequately characterized. Up to 49.6% of the recovered radioactivity was classified as remainder. In addition, up to 49.8% of the recovered radioactivity remained at the origin. The TLC procedure employed was inadequate to separate the test solution into its compoments.

2. Although two different TLC procedures were described in the methodology, data from only one procedure were presented.

Volatile Analysis

Between 14.4 and 42.5% of the applied radioactivity was not accounted for by the conclusion of the study. The lack of accountability was attributed by the registrant to adsorption of the material to the test container walls.

CASE GS -- DICOFOL STUDY 4 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Carpenter, M. 1986. Aqueous photolysis of ^{14}C-o,p'-dicofol. ABC Final Report No. 34466. Rohm and Haas Technical Report No. 310-86-65. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-35.

SUBST. CLASS = S.

DIRECT RVW TIME = 16 (MH) START-DATE END DATE

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APPROVED BY: A. Evans
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-1981

SIGNATURE: A. Evans DATE: MAY 29 1987

CONCLUSIONS:

Degradation - Photodegradation in Water

This study could not be validated because of anomalies in the data. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the light source did not simulate sunlight and degradates were not adequately characterized.

MATERIALS AND METHODS:

o,p'-[^{14}C]Dicofol (purity 98.2%, specific activity 5.84 x 10^6 dpm/mL, Rohm and Haas Company) dissolved in methanol was added at 0.842 ppm to a sterile, aqueous, pH 5 buffered (acetic acid:sodium acetate) solution that contained 1% methanol as a cosolvent. In addition, o,p'-[^{14}C]dicofol was added at 0.791 ppm to additional pH 5 buffered solution sensitized with 1% acetone (v:v). The treated solutions were transferred to silanized culture tubes, which were filled as completely as possible to minimize interactions with air. Twelve tubes of both the nonsensitized and sensitized solutions were covered with aluminum foil to serve as dark controls. An additional twelve tubes of each solution were

placed in a photolysis apparatus which used a 275-W General Electric RS-M sunlamp (Figure 1) as the source of irradiation, and were incubated at 29 ± 1.2°C. Samples were taken at intervals from 0 to 30 days posttreatment and stored at 4°C until analysis.

The samples were extracted three times with ethyl acetate. The ethyl acetate extract and the extracted buffered solution were analyzed for total radioactivity by LSC and for specific compounds by TLC with reference compounds using silica gel plates developed in hexane:methanol (95:5, v:v). The plates were visualized using shortwave UV light and autoradiography. Radioactive areas were scraped from the plates and quantified by LSC. Identification was accomplished by comparison to standards.

In order to quantify volatilization during aqueous photodegradation, aliquots of the treated nonsensitized and sensitized solutions were placed in gas washing bottles and the bottles were attached to a positive pressure air flow system (Figure 2). Moistened CO_2-free air was passed through the head space of the bottle containing the treated solution, then through ethylene glycol, 1 N sulfuric acid, 1 N potassium hydroxide, and 1 N potassium hydroxide trapping solutions. The samples were irradiated using the sunlamp described previously; duplicate solutions were incubated in the dark as controls. The trapping solutions were sampled at intervals up to 30 days posttreatment and were analyzed for total radioactivity by LSC after all the samples had been collected.

REPORTED RESULTS:

o,p'-[^{14}C]Dicofol degraded with half-lives of 2-7 days in the irradiated, nonsensitized buffered solution and <7 days in irradiated, sensitized buffered solution (Tables 1 and 2). In the dark controls, o,p'-[^{14}C]-dicofol degraded with half-lives of 7-14 days in both the nonsensitized and sensitized buffered solutions. o,p'-[^{14}C]Dicofol degraded to 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (0.06 ppm at day 14) in the irradiated nonsensitized buffered solution, and to 2,4'-dichlorobenzophenone (maximum of 0.23 ppm) in both the nonsensitized and sensitized buffered solutions.

A total of 0.018 and 0.002 ppm of [^{14}C]residues were volatilized during 30 days of incubation from the irradiated nonsensitized buffered solution and its dark control, respectively (Table 3). A total of 0.015 and 0.004 ppm of [^{14}C]residues were volatilized from irradiated sensitized buffered solution and its dark control, respectively. The material balance for the volatile analysis study ranged from 42.9 to 71.7% of the applied.

DISCUSSION:

General

1. The light source did not provide continuous radiation at wavelengths above 290 nm to simulate sunlight and the absorption spectrum of the chemical was not reported.

2. Several anomolies existed in the data. No discussion was made of the sudden drop in concentration of o,p'-[^{14}C]dicofol between days 7 and 14 and days 21 and 30 in the nonsensitized, dark control solution (Table 1). Also, the concentration of o,p'-[^{14}C]dicofol in the irradiated sensitized solution was variable, with unexpected low values on days 1 and 2 (Table 2). The registrant attributes this to contamination of those samples. In addition, >50% of the applied radioactivity was not accounted for in the volatility study. The lack of accountability was attributed to adsorption of the material to the test container walls, but the registrant did not explain why this was a problem in the volatile study but not in the solution analysis.

3. The registrant claimed that the recording thermometer consistently measured the test solution temperature 3-4°C higher than the true solution temperature, as determined by a mercury thermometer. The reviewer reported the recording thermometer measurements.

4. Detection limits were not specified.

5. The ^{14}C-label position for o,p'-[^{14}C]dicofol was not specified.

Solution Analysis

1. Degradates were not adequately characterized. The TLC system employed was inadequate; up to 93.4% of the recovered radioactivity remained at the origin.

2. Although three different TLC procedures were described in the methodology, data from only one procedure were presented.

Volatile Analysis

1. Trapping solutions were not analyzed until all samples were collected, and samples were stored at room temperature.

2. The material balance was incomplete; >50% of the applied radioactivity could not be accounted for.

CASE GS -- DICOFOL STUDY 5 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Carpenter, M. 1986. Photodegradation of ^{14}C-p,p'-dicofol on the surface of soil. ABC Report No. 34278. Rohm and Haas Report No. 310-86-50. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-36.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: B. Price
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APPROVED BY: A. Evans
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-1981

SIGNATURE: DATE: MAY 29 1987

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is scientifically valid.

2. p,p'-[^{14}C]Dicofol (radiochemical purity 93.2%), at 11.2 ppm, degraded with a half-life of 21-30 days on silt loam soil irradiated with artificial light at 21 1°C. Dicofol appeared to be stable during the 30 days of incubation in the dark control. 4,4'-Dichlorobenzophenone (25.1% of the recovered) and 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (6.6% of the recovered) were the only identified degradates in both the irradiated and dark control samples; one unknown, at 3.6% of the recovered, was isolated in the dark control samples. After 30 days of incubation, unextractable [^{14}C]residues accounted for 2.68 and 0.640 ppm in the irradiated and dark control samples, respectively; volatiles totaled 0.27 ppm in both treatments.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because light source did not simulate sunlight and degradates were not adequately characterized.

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MATERIALS AND METHODS:

Ring-labeled p,p'-[^{14}C]dicofol (radiochemical purity 93.2%, specific activity 26.4 mCi/g, Rohm and Haas Co.) was applied at 11.2 ppm to thirty-two glass vials containing silt loam soil (1-g weight, 1-mm depth; 16% sand, 64% silt, 20% clay, 2.4% organic matter, pH 7.5, CEC 11.2 meq/ 100 g). Sixteen of the vials were placed uncovered in a stainless steel photolysis chamber and irradiated with a 275-W General Electric Type RS sunlamp (Figure 1) located 10 inches above the chamber. A Pyrex borosilicate plate glass (1/8-inch thickness) was located between the light source and the samples. A constant flow of air (100 mL/minute) through the chamber led to four gas traps filled with ethylene glycol, 1 N sulfuric acid, 1 N potassium hydroxide, and 1 N potassium hydroxide. The temperature within the chamber was maintained at 21 1°C by the constant flow of water through the chamber water jacket. The remaining sixteen samples were covered, wrapped in foil, placed in a dark chamber identical to the one previously described, and incubated at 25 1°C. Irradiated and dark control soils and gas trapping solutions were removed at intervals up to 30 days posttreatment.

The soil samples were extracted three times with methanol, the extracts were combined, and aliquots of the extracts were analyzed using LSC. Additional aliquots, as well as radiolabeled reference standards, were analyzed by TLC on silica gel plates developed in chloroform:methanol (95:5). Radioactive zones on the plates were visualized with autoradiography, identified by comparison to the reference standards, scraped, and quantified by LSC. The extracted soil was analyzed for unextractable radioactivity using LSC following combustion. The trapping solutions were analyzed for total volatile radioactivity by LSC.

To confirm the results of the one-dimensional TLC analysis, irradiated and dark samples from day 30 were spotted onto TLC plates, overspotted with unlabeled dichlorobenzophenone (DCBP), and developed upwards in benzene:acetonitrile (94:6) and sideways in hexane:ethyl acetate:methanol (80:10:10). Radioactive and unlabeled compounds were visualized and identified.

REPORTED RESULTS:

p,p'-[^{14}C]Dicofol degraded with a half-life of 21-30 days on silt loam soil irradiated with artificial light at (Table 1). Dicofol appeared to be stable during the 30 days of incubation in the dark control. 4,4'-Dichlorobenzophenone (25.1% of the recovered) and 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (6.6% of the recovered) were the only identified degradates in both the irradiated and dark control samples; one unknown, at 3.6% of the recovered, was isolated in the dark control samples (Table 2). After 30 days of incubation, unextractable [^{14}C]residues accounted for 2.68 and 0.640 ppm in the irradiated and dark control samples, respectively; volatiles totaled 0.27 ppm in both treatments.

DISCUSSION:

1. The light source does not provide continuous radiation at wavelengths above 290 nm to simulate sunlight and the absorption spectra of the chemical was not reported.

2. Recovery of dicofol from fortified samples and detection limits were not reported.

3. Recoveries from the individual TLC plates (% of applied to TLC plate) were not reported, but appeared to be quite variable.

4. Temperatures in the photolysis chamber were cooler (21°C) than the temperatures in the dark control (25°C).

5. Data from the TLC plates were reported as "percent recovered from the TLC plate" rather than "percent of applied," so the concentration of degradates could not be converted to "ppm".

CASE GS -- DICOFOL STUDY 6 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Carpenter, M. 1986. Photodegradation of ^{14}C-o,p'-dicofol on the surface of soil. ABC Report No. 34465. Rohm and Haas Report No. 310-86-49. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-37.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is scientifically valid.

2. o,p'-[^{14}C]Dicofol (radiochemical purity 98.2%), at 10.4 ppm, degraded with a calculated half-life of 30.3 days on silt loam soil irradiated with artificial light at 21 ± 1°C. Dicofol degraded with a calculated half-life of 65.4 days in the dark control. 2,4'-Dichlorobenzophenone (<29% of the recovered) was the only degradate identified in both the irradiated and dark control samples; two [^{14}C]compounds in the irradiated soil and one in the dark control were isolated (each <2.2% of the recovered) but not identified. After 30 days of incubation, unextractable [^{14}C]residues accounted for 2.04 and 1.06 ppm in the irradiated and dark control samples, respectively; volatiles totaled <0.25 ppm in both treatments.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the light source did not simulate sunlight and the degradates were incompletely characterized.

MATERIALS AND METHODS:

Ring-labeled o,p'-[^{14}C]dicofol (radiochemical purity 98.2%, specific activity 43.5 mCi/g, Rohm and Haas Co.) was applied at 10.4 ppm to twenty-eight glass vials containing silt loam soil (1-g weight, 1-mm depth; 16% sand, 64% silt, 20% clay, 2.4% organic matter, pH 7.5, CEC 11.2 meq/100 g). Fourteen of the vials were placed uncovered in a stainless steel photolysis chamber and irradiated with a 275-W General Electric Type RS sunlamp (Figure 1) located 10 inches above the chamber. A Pyrex borosilicate plate glass (1/8-inch thickness) was located between the light source and the samples. A constant flow of air (100 mL/minute) through the chamber led to four gas traps filled with ethylene glycol, 1 N sulfuric acid, 1 N potassium hydroxide and 1 N potassium hydroxide. The temperature within the chamber was maintained at 21 ± 1°C by the constant flow of water through the chamber water jacket. The remaining fourteen samples were covered, wrapped in foil, placed in a dark chamber identical to the one previously described, and incubated at 24°C. Irradiated and dark control soils and gas trapping solutions were removed at intervals up to 30 days posttreatment.

The soil samples were extracted three times with methanol, the extracts were combined, and aliquots of the extracts were analyzed using LSC. Additional aliquots, as well as radiolabeled reference standards, were analyzed by TLC on silica gel plates developed in chloroform:methanol (95:5). Radioactive zones on the plates were visualized with autoradiography, identified by comparison to the reference standards, scraped, and quantified by LSC. The extracted soil was analyzed for unextractable radioactivity using LSC following combustion. The trapping solutions were analyzed for total volatile radioactivity by LSC.

REPORTED RESULTS:

o,p'-[^{14}C]Dicofol degraded with a calculated half-life of 30.3 days on silt loam soil irradiated with artificial light (Table 1). Dicofol degraded with a calculated half-life of 65.4 days in the dark control. 2,4'-Dichlorobenzophenone (≤29% of the recovered) was the only degradate identified in both the irradiated and dark control samples; two [^{14}C]compounds in the irradiated soil and one in the dark control were isolated (each ≤2.2% of the recovered) but not identified (Table 2). After 30 days of incubation, unextractable [^{14}C]residues accounted for 2.04 and 1.06 ppm in the irradiated and dark control samples, respectively; volatiles totaled ≤0.25 ppm in both treatments.

DISCUSSION:

1. The light source does not provide continous radiation at wavelengths above 290 nm to simulate sunlight and the absorption spectra of the chemical was not reported.

2. The degradates were incompletely characterized; at least two degradates were isolated but not identified.

3. Recovery of dicofol from fortified samples and detection limits were not reported.

4. Data from the TLC plates were reported as "percent recovered from the TLC plate" rather than "percent of applied".

5. Temperatures in the photolysis chamber were cooler (21 ± 1°C) than the temperatures in the dark control (24°C).

6. The registrant indicated that the two-dimensional TLC analysis described in Study 5 (p,p'-dicofol) was not used to identify photodegradation products for the o,p'-dicofol study due to inconsistencies with the standards.

CASE GS -- DICOFOL STUDY 7 PM --

CHEM 010501 Dicofol

BRANCH FAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Daly, D. and A.M. Tillman. 1986. Four-month interim report on the aerobic metabolism of ^{14}C-o,p'-dicofol on silt loam soil. ABC interim Report No. 34620. Rohm and Haas Technical Report No. 310-86-47. Prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. Acc. No. 400420-38.

SUBST. CLASS = S.

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

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SIGNATURE: Alan Evans DATE: MAY 29 1987

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This four month interim study is scientifically valid.

2. o,p'-[^{14}C]Dicofol (radiochemical purity 98.2%), at 10 ppm, degraded with a calculated half-life of for parent of 10.2 days in silt loam soil moistened to 75% of field capacity and incubated in the dark at 21-34°C. The degradates tentatively identified by TLC were 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (FW-152; maximum concentration 2.48 ppm), 2,4'-dichlorobenzophenone (maximum concentration 1.31 ppm), hydroxy-2,4'dichlorobenzophenone (maximum concentration 1.50 ppm), 2-chlorobenzoic acid (maximum concentration 1.18 ppm), and 2,4'--dichlorobenzhydrol (maximum concentration 0.73 ppm). At 120 days (end of this interim period) major soil residues were tentatively identified as hydroxy -DCBP, 2 -Chlorobenzoic acid and o,p' -dichlorobenzhydrol (DCBH). Volatile compounds totaled 0.09 ppm after 120 days. Unextractable residues comprised up to 4.61 ppm.

3. This interim study does not fulfill EPA Data Requirements for Registering Pesticides because identities of major soil degradates were not confirmed through use of adequate methodology. TLC is inadequate to confirm chemical structures.

MATERIALS AND METHODS:

o,p'-[^{14}C]Dicofol (uniformly ring-labeled, radiochemical purity 98.2%, specific activity 43.5 mCi/g, Rohm and Haas Company) was applied at 10 ppm to test tubes containing sieved (2-mm) silt loam soil (16% sand, 64% silt, 20% clay, 2.4% organic matter, pH 7.5, CEC 11.2 meq/100 g). The soil moisture was adjusted to 75% of field capacity, and the tubes were transferred to a glass vessel (3000 mL) attached sequentially to tubes containing ethylene glycol, sulfuric acid, and potassium hydroxide volatile trapping solutions (Figure 1). The system was maintained under positive pressure in the dark at 25°C. Soil and trapping solutions were sampled at intervals up to 120 days posttreatment.

Soil samples were extracted (vortex shaking for 2 minutes) three times with methanol, and the extracts were combined. Aliquots of the extracts were analyzed for total extractable radioactivity by LSC, and the remainder was frozen (-15°C) until further analysis. Then, aliquots of the thawed extracts were analyzed by LSC. Additional aliquots were reduced and then cochromatographed by TLC with nonradiolabeled standards on silica gel plates developed with hexane:methanol (95:5). Nonlabeled standards were located using UV light. Radioactivity was located by autoradiography, and identified by comparison to nonlabeled standards. Radioactive compounds were quantified by scraping radioactive zones from the TLC plates and analyzing the scrapings by LSC. The identities of 2-chlorobenzoic acid and 2,4'-dichlorobenzhydrol were confirmed using two-dimensional TLC. Silica gel plates were developed first in hexane:ethyl acetate:methanol (80:10:10) and then in hexane:methanol (95:5). The plates were then analyzed as described above. Extracted soils were analyzed for unextractable radioactivity by LSC following combustion. Trapping solutions were analyzed by LSC.

REPORTED RESULTS:

o,p'-[^{14}C]Dicofol (10 ppm) degraded with a calculated half-life of 10.2 days for parent (Table 1). The degradates 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (FW-152; maximum concentration 2.48 ppm), 2,4'-dichlorobenzophenone (maximum concentration 1.31 ppm), hydroxy-2,4'-dichlorobenzophenon e (maximum concentration 1.50 ppm), 2-chlorobenzoic acid (maximum concentration 1.18 ppm), and 2,4' -dichlorobenzhydrol (maximum concentration 0.73 ppm) were isolated. Volatile compounds totaled 0.09 ppm after 120 days. Unextractable residues comprised up to 4.85 ppm.

o,p' -Dichlorobenzophenone (o,p' -DCBP) was present in extracts in increasing amounts from day 0 (4.7%) through day 90 (21.7%), and then declined to 14.4% of the extracted ^{14}C in four month samples. Similarly, o,p' -FW-152 was observed in increasing quantities in extracts from day 0 through 30 (0.4-42.0%) after which the amounts of FW-152 declined to 7.6% of the four month extracted ^{14}C. Amounts of o,p' -dichlorobenzhydrol o,p' -DCBH), hydroxy-DCBP and 2-chlorobenzoic acid increased continually during the first four months of the study to 14.9%, 32.2% and 25.3%

of the total ^{14}C, extracted respectively. The presence of 2-chlorobenzoic acid and DCBH (but not hydroxy -DCBP) were confirmed by two dimensional TLC.

DDE increased over time and reached 1.1% of extracted ^{14}C by day 120. Mean ^{14}C -residue mass balance was 102%, based on initial concentration.

DISCUSSION:

1. The identities of soil degradates were not adequately confirmed.

2. Unidentified degradates were isolated at up to 0.58 ppm (Table 1).

3. Reverse-phase TLC data were provided by the registrant. Although the procedure was apparently carried out to confirm the identities of degradates from standard TLC plates, separation of degradates on reverse phase plates was unsatisfactory. Therefore, the reverse phase TLC data are not reported in this review.

4. Although the average temperature throughout the study was 25°C, the incubation temperatures ranged from 21-34°C.

CASE GS -- DICOFOL STUDY 8 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Daly, D. and A.M. Tillman. 1986. Anaerobic metabolism of ^{14}C-p,p'-dicofol on silt loam soil. ABC Final Report No. 33350. Rohm and Haas Technical Report No. 310-86-41. Prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted Rohm and Haas Company, Spring House, PA. Acc. No. 400420-39.

SUBST. CLASS = S.

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

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SIGNATURE: DATE: MAY 29 1987

CONCLUSIONS:

Metabolism - Anaerobic Soil

1. This portion of the study is scientifically valid.

2. p,p'-[^{14}C]Dicofol (radiochemical purity >93%) was incubated in silt loam soil moistened to 60% of field capacity and incubated in the dark at 25± 2°C under aerobic conditions for 30 days. The soil was then converted to anaerobic conditions. p,p'-[^{14}C]Dicofol declined with a half-life of <30 days from 7.08 ppm to 0.51 ppm during 60 days of incubation under anaerobic conditions. The major degradate was 1,1-bis-(4-chlorophenyl)-2,2-dichloroethanol (maximum concentration 3.9 ppm). 4,4'-Dichlorobenzhydrol and 4,4' -dichlorobenzophenone were also present at about 0.5-1 ppm when the study was terminated. 1,1-Bis (4-chlorophenyl)-2,2-dichloroethylene (DDE), 3-hydroxy-4,4'-dichlorobenzophenone, and 2-hydroxy-4,4'-dichlorobenhydrol were isolated at≤ 0.48 ppm. [^{14}C]Residues (uncharacterized) were isolated in water samples at up to 0.39 ppm (relative to water). Volatile compounds totaled 0.026 ppm by 90 days posttreatment. Unextractable residues were 3.05 ppm at study completion.

3. This portion of the study can fulfill EPA anaerobic Data Requirments for Registering Pesticides provided that structures of significant residues are adequately confirmed.

MATERIALS AND METHODS:

p,p'-[^{14}C]Dicofol (label position not specified, radiochemical purity >93%, specific activity 26.4 mCi/g, Rohm and Haas Company) was applied at 10 ppm to sieved (2-mm) silt loam soil (26% sand, 56% silt, 18% clay, 2.4% organic matter, pH 7.8, CEC 15.2 meq/100 g). Soil moisture was adjusted to 60% of field capacity. The treated soil was incubated in a glass vessel (3000 mL) attached sequentially to tubes containing ethylene glycol, sulfuric acid, and potassium hydroxide volatile trapping solutions (Figure 1). The system was maintained under positive pressure in the dark at 25 2°C. Soil and trapping solutions were sampled at intervals up to 30 days posttreatment.

Soil samples were extracted (vortex shaking for 2 minutes) three times with methanol and the extracts were combined. Aliquots of the extracts were analyzed for total extractable radioactivity by LSC, and the remainder was frozen (-15°C) until further analysis. Aliquots of the thawed extracts were analyzed by LSC. Additional aliquots were reduced and then cochromatographed with nonradiolabeled standards on normal-phase and reverse-phase TLC plates. Normal-phase silica gel TLC plates were developed with hexane:methanol (95:5), and reverse-phase TLC plates were developed with acetonitrite:water (5:1). Nonlabeled standards were located using UV light. Radioactive compounds were located by autoradiography, and identified by comparison to nonlabeled standards. Radioactivity was quantified by scraping radioactive zones from TLC plates and analyzing the scrapings by LSC. Extracted soils were analyzed for unextractable radioactivity by LSC following combustion. Trapping soluions were analyzed by LSC.

After 30 days of incubation under aerobic conditions, the treated soil was flooded with deionized water and incubated anaerobically for 60 days. Soil, water, and trapping solutions were sampled immediately before establishing anaerobic conditions (30 days posttreatment) and at 60 and 90 days posttreatment (30 and 60 days after anaerobic conditions were established). Water samples and volatile trapping solutions were analyzed for total radioactivity by LSC. Soil samples were analyzed as described above.

REPORTED RESULTS:

p,p'-[^{14}C]Dicofol declined from 7.08 ppm to 0.51 ppm during 60 days of anaerobic incubation, with a half-life of <30 days (Tables 1 and 2). The major degradates were 1,1-bis(4-chlorophenyl)-2,2-dichloroethanol (maximum concentration 3.92 ppm) and 4,4'-dichlorobenzhydrol (maximum concentration 1.31 ppm). 4,4'-Dichlorobenzophenone, 1,1-bis(4-chlorophenyl)-2,2-dichloroethylene, 3-hydroxy-4,4'-dichlorobenzophenone, and

2-hydroxy-4,4'-dichlorobenzhydrol were also isolated. Residues (uncharacterized) were isolated in water samples at up to 0.39 ppm (relative to water). Volatile compounds totaled 0.026 ppm. Unextractable residues were 3.05 ppm at study termination.

DISCUSSION:

1. Under 30 days aerobic soil laboratory conditions, p'p -dicofol did not undergo significant degradation. However, when anaerobic conditions were established after 30 days, degradation proceed faster than under aerobic conditions to form 1,1 -bis(4-chlorophenyl -2,2 -dichlorethanol as a major degradate. The 4,4' -dichlorobenzophenone and the 4,4' -dichlorobenzhydrol were also formed under aerobic conditions but he the 1,1 -bis(4-chlorophenyl -2,2 -dichloroethanol was only formed in small amounts under aerobic conditions.

CASE GS -- DICOFOL STUDY 9 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC)

FICHE/MASTER ID No MRID CONTENT CAT 01

Hoffman, CK. 1985. A field dissipation study of Kelthane miticide in Fresno, CA. Report No. 310-86-72. Unpublished study prepared by Enviro-Bio-Tech, Bernville, PA and Rohm and Haas Co., Philadelphia, PA, and submitted by Rohm and Haas Co., Philadelphia, PA. Acc. No. 400420-40.

SUBST. CLASS = S.

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Terrestrial

This study is scientifically invalid because the data are too variable to accurately assess the dissipation of dicofol in soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the soils were not sampled deep enough to define the extent of leaching and the soils were not analyzed for all probable degradates. Also, the maximum application rate was not used.

MATERIALS AND METHODS:

Field plots (5 x 10 feet) of sandy loam soil (60.5% sand, 32% silt, 8% clay, 0.44% organic matter, pH 5.6, CEC 6.9 meq/100 g) within an apple orchard located in Fresno, California, were sprayed with dicofol (kelthane MF, 43.5% EC; 4-5:1 ratio of the p,p':o,p' isomers) at either 1.5 or 3.0 lb ai/A on October 1, 1985, and seeded with barley. There were four treated plots and one untreated control. Soil samples (0- to 3-, 3- to 6-, and 6- to 12-inch depths) were taken immediately after treatment and at various intervals up to 181 days posttreatment. All

All soil samples were frozen within two hours after sampling and stored frozen until analysis.

Soil samples (10 g) were extracted with iso-propanol:toluene (1:1) by shaking for 15 minutes. The extracts were filtered, then analyzed by GC with electron capture detection. The detection limit was 0.01 ppm. Recoveries from soil fortified at 0.01-5.0 ppm ranged from 70 to 112% for o,p'-dicofol and from 70 to 110 % for p,p'-dicofol. Recoveries for 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (o,p'-FW-152) and 1,1'-bis(4-chlorophenyl)-2,2-dichloroethanol (p,p'-FW-152) averaged 91 and 93%, respectively (no additional data provided).

REPORTED RESULTS:

During the 181-day field study, air temperatures ranged from 29 to 102°C, and precipitation plus irrigation totaled 15.54 inches (Table 1).

In the control soil, o,p'- and p,p'-dicofol were not detected (<0.01 ppm) at any sampling interval.

In the 1.5 lb ai/A treatment, p,p'-dicofol varied from <0.01 ppm to 0.87 ppm with no discernible pattern in the 0- to 3-inch depth, was 0.17 ppm in the 3- to 6-inch depth, and was 0.12 ppm in the 6- to 12-inch depth (Table 1). o,p'-Dicofol was 0.08 ppm in the 0- to 3-inch depth and <0.01 ppm (not detected) in the 3- to 6- and 6- to 12-inch depths at all sampling intervals. 1-(2-Chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (o,p'-FW-152) was 0.03 ppm and 1,1-bis-(4-chlorophenyl)-2,2-dichloroethanol (p,p-FW-152) was <0.01 ppm in all depths at all sampling intervals.

In the 3.0 lb ai/A treatment, p,p'-dicofol varied from <2.7 ppm to 0.02 ppm, following a generally downward trend, in the 0- to 3-inch depth, was 0.33 ppm in the 3- to 6-inch depth, and was 0.33 ppm in the 6- to 12-inch depth (Table 1). o,p'-Dicofol was 0.22 ppm in the 0- to 3-inch depth and <0.01 ppm (not detected) in the 3- to 6- and 6- to 12-inch depths at all sampling intervals. 1-(2-Chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (o,p'-FW-152) was 0.06 ppm and 1,1'-bis(4-chlorophenyl)-2,2-dichloroethanol (p,p-FW-152) was <0.01 ppm in all depths at all sampling intervals.

DISCUSSION:

1. The soils were not sampled deep enough to define the extent of leaching; as much as 0.33 ppm of p,p'-dicofol were detected in the 6- to 12-inch depth.

2. The data were too variable to establish a residue decline cure and accurately assess the dissipation of dicofol and its degradates FW-152, and its o,p' isomer and the pattern of formation and decline of degradates in soil.

3. It could not be determined if the samples were analyzed for degradates other than o,p'-FW-152 and p,p'-FW-152. DCBP (2,4'- and 4,4'-dichlorobenzophenone), hydroxy -DCBP CBA (2-chlorobenzoic acid), and DCBH (2,4'- and 4,4'dichlorobenzhydrol) were identified as major degradates in the laboratory aerobic soil metabolism studies (Study 7 and 8).

CASE GS -- DICOFOL STUDY 10 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Hoffman, CK. 1985. A field dissipation study of Kelthane miticide in Cleveland, MS. Rohm and Haas Technical Report No. 310-86-71. Unpublished study prepared by Enviro-Bio-Tech, Bernville, PA, and Rohm and Haas Co., Philadelphia, PA. and submitted by Rohm and Haas Co., Philadelphia, PA. Acc. No. 400420-41.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

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SIGNATURE: DATE: May 3 1987

CONCLUSIONS:

Field Dissipation - Terrestrial

This study is scientifically invalid because the data are too variable to accurately assess the dissipation of dicofol in soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the soils were not sampled deep enough to define the extent of leaching and the soils were not analyzed for all probable degradates. Also, the maximum recommended application rate was not used.

MATERIALS AND METHODS:

Field plots (5 x 10 feet) of silt loam soil (29.2% sand, 47.5% silt, 23.2% clay, 0.70% organic matter, pH 5.9, CEC 16.3 meq/100 g) located in Cleveland, MS, were sprayed with dicofol (Kelthane MF, 43.5 EC; 4-5:1 ratio of the p,p':o'p' isomers) at either 1.5 or 3.0 lb ai/A on July 16, 1986 and and planted with sorghum. There were two treated plots and one untreated control. Soil samples (0- to 3-, 3- to 6-, and

6- to 12-inch depths) were taken immediately after treatment and at various intervals up to 68 days posttreatment. All soil samples were frozen within two hours after sampling and stored frozen until analysis.

Soil samples (10 g) were extracted with iso-propanol:toluene (1:1) by shaking for 15 minutes. The extracts were filtered, then analyzed by GC with electron capture detection. The detection limit was 0.01 ppm. Recoveries from soil fortified at 0.01 - 5.0 ppm ranged from 70 to 92% for o,p'-dicofol and from 75 to 102% for p,p'-dicofol. Recoveries for 1-(2-chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (o,p'-FW-152) and 1,1'-bis(4-chlorophenyl)-2,2-dichloroethanol (p,p'-FW-152) averaged 80 and 76%, respectively (no additional data provided).

REPORTED RESULTS:

During the 68-day field study, air temperatures ranged from 56 to 108°C, and precipitation plus irrigation totaled 5.23 inches (Table 1).

In the control soil, o,p'- and p,p'-dicofol were not detected (<0.01 ppm) at any sampling interval.

In the 1.5 lb ai/A treatment, p,p'-dicofol varied from <0.05 ppm to 1.40 ppm with no discernible pattern in the 0- to 3-inch depth, was 0.40 ppm in the 3- to 6-inch depth, and was 3.10 ppm in the 6- to 12-inch depth (Table 1). o,p'-Dicofol was 0.31 ppm in the 0- to 3-inch depth, 0.08 ppm in the 3- to 6-inch depth, and 0.71 ppm in the 6- to 12-inch depth. 1-(2-Chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (o,p'-FW-152) was 0.02 ppm and 1,1'-bis(4-chlorophenyl)-2,2-dichloroethanol (p,p-FW-152) was <0.01 ppm in all depths at all sampling intervals.

In the 3.0 lb ai/A treatment, p,p'-dicofol varied from 0.08 ppm to 2.20 ppm, following a generally downward trend, in the 0- to 3-inch depth, was 0.26 ppm in the 3- to 6-inch depth, and was 0.76 ppm in the 6- to 12-inch depth (Table 1). o,p'-Dicofol was 0.61 ppm in the 0- to 3-inch depth and 0.06 ppm in the 3- to 6- and 6- to 12-inch depths at all sampling intervals. 1-(2-Chlorophenyl)-1-(4'-chlorophenyl)-2,2-dichloroethanol (o,p'-FW-152) was 0.06 ppm and 1,1'-bis(4-chlorophenyl)-2,2-dichloroethanol (p,p-FW-152) was <0.01 ppm in all depths at all sampling intervals.

DISCUSSION:

1. The soils were not sampled deep enough to define the extent of leaching; as much as 3.10 ppm of p,p'-dicofol were detected in the 6- to 12-inch depth.

2. The data were too variable to establish a residue decline curve and accurately assess the dissipation of dicofol and its degradates FW-152, and its o,p' isomer and the pattern of formation and decline of degradates in soil.

3. It could not be determined if the samples were analyzed for degradates other than o,p'-FW-152 and p,p'-FW-152. DCBP (2,4'- and 4,4'-dichlorobenzophenone), hydroxy -DCBP CBA (2-chlorobenzoic acid), and DCBH (2,4'- and 4,4'dichlorobenzhydrol) were identified as major degradates in the laboratory aerobic soil metabolism studies (Study 7 and 8).

CASE GS -- DICOFOL STUDY 11 PM --

CHEM 010501 Dicofol

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Tillman, A.M. 1986. The bioconcentration, elimination and metabolism of ^{14}C-dicofol by bluegill sunfish (Lepomis macrochirus). Report No. 310-86-17. Prepared and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. No. 265330.

SUBST. CLASS = S.

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study is scientifically valid.

2. Although steady state was not attained, total p,p'-[^{14}C]dicofol residues accumulated in bluegill sunfish with bioconcentration factors of 6,600, 17,000, and 10,000x in fillet (body, muscle, skin, skeleton), viscera (fins, head, internal organs), and whole fish, respectively, during 28 days of exposure to phenyl-labeled [^{14}C]dicofol (radiochemical purity 98%) at a nominal concentration of 0.006 ppm in a flow-through system. Maximum levels of [^{14}C]residues were 23 ppm in fillet, 65 ppm in viscera, and 43 ppm in whole fish. Parent dicofol comprised >94% of the radioactivity in extracts from fillet and viscera. Using a computer modeling program (BIO FAC), the registrant estimated a whole fish BCF of 25,000 at 90% steady-state conditions. After 56 days of depuration, [^{14}C]residues in fillet, viscera, and the whole fish were 5.2, 19 and 11 ppm, respectively.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the bioaccumulation of p,p'-dicofol in bluegill sunfish.

MATERIALS AND METHODS:

Bluegill sunfish (Lepomis macrochirus; average length and weight of 61 mm and 7.9 g, respectively) were held in culture tanks on a 16-hour daylight photoperiod for 14 days prior to the initiation of the study. Flow-through aquatic exposure systems were prepared using two 70-L aquaria. Aerated well water (Table 1) was provided to each aquarium at a rate of 7 turnovers per day. The aquaria were immersed in a water bath and maintained at 22 2°C.

Bluegill sunfish (130) were placed in each aquarium, and one aquarium was continuously treated with phenyl-labeled p,p'-[^{14}C]dicofol (radiochemical purity 98%, specific activity 26.4 mCi/g, ICI) in ethanol at 0.006 ppm. The second aquarium was treated with ethanol alone at 0.05 mL/L and served as a control. Following a 28-day exposure period, the [^{14}C]dicofol-treated water was replaced with untreated water for a 56-day depuration period. The treated water was sampled prior to introducing the fish, and then water samples and fish (6, 15, or 25) were taken from the treated and control aquaria after 4 hours and 1, 3, 7, 14, 21, and 28 days of exposure. During the depuration period, water samples and [^{14}C]dicofoltreated and untreated fish were taken on days 1, 3, 7, 10, 14, 35, and 56.

Radioactivity in the water samples was quantified using LSC. Aliquots of the water samples were adjusted to pH 2 with concentrated hydrochloric acid and extracted three times with ethyl acetate. The extracts were combined, rinsed with brine, dried over anhydrous sodium sulfate, and concentrated by evaporation. The extract was analyzed by radio-HPLC and TLC. TLC was performed with silica gel plates developed in hexane: methanol (95:5) and reverse-phase plates developed in acetonitrite:water (5:1). Unlabeled reference standards were cochromatographed with the extracts, and detected under UV light. Radioactive areas were detected by autoradiography and quantified by scraping the area from the plate and counting with LSC.

Pooled samples (3 fish) of whole fish, fillet (body, muscle, skin, skeleton), and viscera (fins, head, internal organs) were homogenized with dry ice and analyzed for total radioactivity using combustion and LSC. Homogenized fillet and viscera samples were extracted two times with ethyl ether, then two times with ethyl acetate, and finally twice with methanol. The ethyl ether and ethyl acetate extracts were combined, concentrated by evaporation, and analyzed by radio-HPLC and TLC, as previously described. The extracted tissues were analyzed for unextractable radioactivity by combustion and LSC.

REPORTED RESULTS:

Total p,p'-[^{14}C]dicofol residues in water ranged from 0.0024 to 0.0061 ppm during the exposure period (Table 2). Dicofol comprised 67% of the recovered radioactivity in the 28-day exposure period water sample (Table 3). Throughout the study, the temperature, pH, and dissolved oxygen content of the treated water ranged from 21 to 22°C, 8.0 to 8.2, and 6.8 to 8.9 mg/L, respectively, and was comparable to the control aquarium.

No mortality of the fish in the treated or untreated aquaria was observed during the study. After 28 days of exposure, bioconcentration factors were 6600x in fillet, 17000x in viscera, and 10000x in whole fish (Table 2). Maximum levels of [^{14}C]dicofol residues occurred after 28 days of exposure in fillet (23 ppm), after 1 day of depuration in whole fish (43 ppm), and after 3 days of depuration in viscera (65 ppm). Parent dicofol comprised >94% of the radioactivity in extracts from fillet and viscera (Table 3). Degradates detected included 1,1-bis(4-chlorophenyl)-2,2-dichloroethanol (FW-152), 4,4'-dichlorobenzophenone, 4,4'-dichlorobenzhydrol, and 3-hydroxy-4,4'-dichlorobenzhydrol.

After 56 days of depuration, [^{14}C]dicofol residues in fillet, viscera, and whole fish were 5.2, 19 and 11 ppm, respectively. The half-life of elimination was estimated to be 33± 2 days.

DISCUSSION:

1. A steady-state equilibrium of dicofol in the fish was not achieved during the test period. The registrant calculated that it would take 122 days to achieve 90% steady-state. In addition, during the 14-day depuration period, there was little or no decrease in the concentration of the accumulated material. Dicofol does accumulate and is shown to persist during the initial 14 days of depuration.

2. The registrant provided no explanation for the low level (67% of the recovered radioactivity) of parent dicofol in the extract from the 28-day exposure water sample. However, studies were performed which determined that dicofol was stable in ethanol (dissolving solvent for stock solution) and in the test water.

3. After the introduction of the fish into the [^{14}C]dicofol treated water, [^{14}C]dicofol residue levels were significantly lower than the proposed nominal concentration of 0.006 ppm. The registrant proposed that the test substance was absorbed by the fish faster than it could be added to the system.

4. A preliminary study was conducted to determine the LC_{50} valve of dicofol for bluegill sunfish. The 7-day LC_{50} valve was determined to be >1.5 ppm (highest concentration tested) and the 7-day no-observed-effect level (NOEL) was 0.34 ppm. In view of these results, the registrant chose an exposure level of 0.006 ppm (1/50th of the 7-day NOEL) for the bioaccumulation study.

Table 1. Chemical characteristics of the aerated well water.

Parameters	Concentration
Temperature	15-20°C[b]
Dissolved oxygen[a]	9.2-10.1 ppm[b]
pH	7.8-8.3[b]
Hardness ($CaCO_3$)	225-275 ppm[b]
Alkalinity ($CaCO_3$)	325-375 ppm[b]
Conductivity	700 µmhos/cm
NO_3-N	0.74 ppm
NO_3- and NO_2-N	0.74 ppm
PO_4-P	<0.10 ppm
Aluminum	<20 ppb
Arsenic	<0.2 ppb
Cadmium	<2 ppb
Chromium	<3 ppb
Cobalt	<4 ppb
Copper	<3 ppb
Iron	12 ppb
Lead	<5 ppb
Mercury	<0.5 ppb
Nickel	<15 ppb
Silver	<5 ppb
Zinc	11 ppb
Measured organophosphorus pesticides	--c
Measured organochlorine pesticides plus PCB's	--c

[a] After aeration.

[b] Represents seasonal variation, with the monthly range not exceeding 10%.

[c] Less than minimum detectable limits for organophosphorus and organochlorine which were <0.10 and <0.50 ppb, respectively.

Table 2. Total [^{14}C]dicofol residues (ppm) and fish tissues during a 28-day exposure period and a 56-day depuration period.

Sampling interval (days)		Water	Fillet[a]		Viscera[b]		Whole fish	
			ppm	BCF[c]	ppm	BCF	ppm	BCF
Exposure	0[d]	0.0061	--	--	--	--	--	--
	4 hours	0.0028	0.31	70	0.62	140	0.41	93
	1	0.0024	1.2	320	2.9	760	1.9	500
	3	0.0029	3.1	860	6.2	1700	6.0	1700
	7	0.0035	5.9	1700	17	4900	12	3400
	14	0.0031	13	3700	32	9100	20	5700
	21	0.0036	15	4300	44	13000	32	9100
	28	0.0039	23	6600	60	17000	35	10000
Depuration	1	0.00039	20	--	60	--	43	--
	3	0.00029	20	--	65	--	37	--
	7	0.00017	18	--	55	--	33	--
	10	0.00016	17	--	50	--	33	--
	14	0.00018	16	--	55	--	31	--
	35	ND[e]	11	--	31	--	21	--
	56	ND	5.2	--	19	--	11	--

[a] Body, muscle, skin, and skeleton.

[b] Fins, head, and internal organs.

[c] Daily bioconcentration factor (BCF) obtained by dividing the tissue concentration by the mean measured water concentration up to and including the respective sampling day.

[d] Samples taken immediately prior to addition of fish.

[e] Not detected, detection limits were: water (0.00011 ppm); whole fish (0.0054 ppm); fillet (0.0056 ppm); and viscera (0.0060 ppm). Reported recoveries from whole fish, fillet, and viscera fortified with 3348 dpm of [^{14}C]dicofol ranged from 94 to 103%.

Table 3. Distribution of radioactivity (% of recovered from extracts) in fish tissues and water during a 28-day exposure period and a 56-day depuration period.[a]

Sampling interval (days)		Dicofol	FW-152[b]	DCBP[c]	DCBH[d]	3-OH-DCBH[e]	Unknown	Baseline[f]
				Viscera				
Exposure	28	94.2	4.45	0.1	0.4	1.6	0.2	0.2
Depuration	14	96.8	2.35	0.1	0.3	0.4	0.15	0.15
	35	96.5	2.05	ND	0.8	2.0	0.15	0.15
				Fillet				
Exposure	28	97.7	0.9	ND	0.8	--	0.2	0.1
Depuration	14	97.0	2.1	0.1	0.2	0.4	0.15	0.15
	35	97.4	1.45	0.1	0.2	0.2	0.15	0.25
				Water				
Exposure	28	67	2.9	ND	0.4	4.7	--	18.9
Depuration	14	89.2	4.7	0.1	0.2	1.7	--	1.8

[a] Approximately 88-100% of the sample radioactivity was extractable from the fish tissues. Recoveries of radioactivity from TLC plates ranged from 87 to 119% of the applied.

[b] 1,1-bis(4-chlorophenyl)-2,2-dichloroethanol.

[c] 4,4'-Dichlorobenzophenone.

[d] 4,4'-Dichlorobenzhydrol.

[e] 3-Hydroxy-4,4'-dichlorobenzhydrol.

[f] The registrant did not define what this term actually refers to.

EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed in this report but do not fulfill data requirements unless noted in the Recommendations section of this report. Identifications of residues was tentatively based only on TLC.

After 30 days at 1 ppm, 75% of p,p'-[^{14}C]dicofol (radiochemical purity >93%) remained undegraded in a sterile aqueous buffered (pH 5) solution incubated in the dark at 25°C. The half-lives were calculated to be 85 days at pH 5, 64 hours at pH 7, and 26 minutes or 0.43 hours at pH 9. The predominant degradate in all solutions was 4,4'-dichlorobenzophenone. At least three additional degradates, each <9.6%, were isolated but not identified in the pH 5 and 9 test solutions.

After 31 days at 1 ppm, 66% of o,p'-[^{14}C]dicofol remained undegraded in a sterile aqueous buffered (pH 5) solution incubated in the dark at 25°C. The calculated half-lives are 47 days at pH 5, 8 hours at pH 7, and 0.15 hour or 9 minutes at pH 9. The predominantr degradate in all solutions was 2,4'-dichlorobenzophenone. Chlorobenzoic acid was observed in the pH 7 test solution.

p,p'-[^{14}C]Dicofol (radiochemical purity >93%) was incubated in silt loam soil moistened to 60% of field capacity and incubated in the dark at 25 ± 2°C under aerobic conditions for 30 days. The soil was then converted to anaerobic conditions. While under anaerobic conditions p,p'-[^{14}C]Dicofol declined from 7.08 ppm to 2.48 after 30 days and to 0.51 ppm after 60 days. The predominant degradate was 1,1-bis (4-chlorophenyl)-2,2-dichloroethanol (maximum concentration 3.9 ppm). Other degradates were 4,4'-dichlorobenzhydrol and 4,4'-Dichlorobenzophenone at about 0.5 ppm. 1,1,-bis (4-chlorophenyl)-2,2-dichloroethylene, 3-hydroxy-4,4'-dichlorobenzophenone, and 2-hydroxy-4,4'-dichlorobenhydrol were isolated at ≤0.48 ppm. [^{14}C]Residues (uncharacterized) were isolated in water samples at up to 0.39 ppm (relative to water). Volatile compounds totaled 0.026 ppm by 90 days posttreatment. Unextractable residues were 3.05 ppm at study

Although steady state was not attained, total p,p'-[^{14}C]dicofol residues accumulated in bluegill sunfish with bioconcentration factors of 6600, 17000, and 10000x in fillet (body, muscle, skin, skeleton), viscera (fins, head, internal organs), and whole fish, respectively, during 28 days of exposure to phenyllabeled [^{14}C]dicofol (radiochemical purity 98%) at a nominal concentration of 0.006 ppm in a flow-through system. Levels of [^{14}C]residues reached 23 ppm in fillet, 65 ppm in viscera, and 43 ppm in whole fish. Parent dicofol comprised >94% of the radioactivity in extracts from fillet and viscera. After 56 days of depuration, [^{14}C]residues in fillet, viscera, and the whole fish were 5.2, 19 and 11 ppm, respectively. Whole fish BCF at 90% steady state was estimated to be 25,000 using a computer modeling program (BIOFAC).

RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate of and the exposure to humans and nontarget organisms to dicofol. The submission of data relevant to registration requirements for terrestrial food crop, terrestrial nonfood, greenhouse nonfood, domestic outdoor, and indoor use sites is summarized below:

Hydrolysis studies: Two studies (Warren, 1986a and Warren, 1986b) were reviewed and are scientifically valid. One study (Warren, 1986b) fulfills data requirements for o,p'-dicofol. The second study (Warren, 1986a) contributes towards the fulfillment of data requirements by providing information on hydrolysis of p,p'-dicofol in sterile aqueous buffered solutions at pH 7 and 9. Additional study on the hydrolysis of p,p'-dicofol at pH 5 is required.

Photodegradation studies in water: Two studies were reviewed. The first study (Carpenter, 1986b) could not be validated because of anomalies in the data. In addition, this study would not fulfill data requirements because the light source did not simulate sunlight. The second study (Carpenter, 1986a) is scientifically valid, but does not fulfill data requirements because the light source did not simulate sunlight. All data are required.

Photodegradation studies on soil: Two studies were reviewed and are scientifically valid. The first study (Carpenter, 1986d) does not fulfill data requirements because the light source did not simulate sunlight and the degradates were incompletely characterized. The second study (Carpenter, 1986c) does not fulfill data requirements because the light source did not simulate sunlight. All data are required.

Aerobic soil metabolism studies: One interim report was reviewed and is scientifically valid but does not fulfill data requirements because identification of degradates was not confirmed. This information should be submitted with the final report.

Anaerobic soil metabolism studies: One study (Daly and Tillman, 1986b) was reviewed and is scientifically valid and can fulfill EAB's data requirements provided the identity of the major residues is confirmed.

Anaerobic aquatic metabolism studies: No data were reviewed; however, no data are required because dicofol has no aquatic or aquatic impact uses.

Aerobic aquatic metabolism studies: No data were reviewed; however, no data are required because dicofol has no aquatic or aquatic impact uses.

Leaching and adsorption/desorption studies: No data were reviewed, but data are required as specified in section 8 of the attached EAB report.

Laboratory volatility studies: Data for greenhouse use were reviewed and found acceptable. No data are required.

Field volatility studies: No data were reviewed. The data requirement was waived in the EAB review of 12/6/85.

Terrestrial field dissipation studies: Two studies (Hoffman, 1985a and Hoffman, 1985b) were reviewed and are scientifically invalid because the data are too variable to accurately assess the dissipation of dicofol in soil. In addition, both studies would not fulfill data requirements because the soils were not sampled deep enough to define the extent of leaching and the soils were not analyzed for all probable degradates. All data are required.

Aquatic field dissipation studies: No data were reviewed; however, no data are required because dicofol has no aquatic or aquatic impact uses.

Forestry dissipation studies: No data were reviewed; however, no data are required because dicofol has no forestry uses.

Dissipation studies for combination products and tank mix uses: No data were reviewed; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed. The data requirement is deferred pending the receipt of acceptable field dissipation data.

Confined accumulation studies on rotational crops: No data were reviewed, but all data are required.

Field accumulation studies on rotational crops: No data were reviewed. The data requirement is deferred pending the receipt of acceptable confined accumulation data.

Accumulation studies on irrigated crops: No data were reviewed; however, no data are required because dicofol has no aquatic food crop or aquatic nonfood uses.

Laboratory studies of pesticide accumulation in fish: One study (Tillman, 1986) was reviewed and is scientifically valid. This study fulfills data requirements by providing information on the bioaccumulation of p;p'-dicofol in bluegill sunfish.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed. A waiver request was denied in the EAB memorandum of 1/21/86.

Reentry studies: No data were reviewed with this submission, but data may be required pending further toxicological evaluation.

REFERENCES

The following studies were reviewed as new submittals:

Carpenter, M. 1986a. Aqueous photolysis of ^{14}C-p,p'-dicofol (Kelthane). ABC Final Report No. 34277. Rohm and Haas Technical Report No. 310-86-64. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-34.

Carpenter, M. 1986b. Aqueous photolysis of ^{14}C-o,p'-dicofol. ABC Final Report No. 34466. Rohm and Haas Technical Report No. 310-86-65. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-35.

Carpenter, M. 1986c. Photodegradation of ^{14}C-p,p'-dicofol on the surface of soil. ABC Report No. 34278. Rohm and Haas Report No. 310-86-50. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-36.

Carpenter, M. 1986d. Photodegradation of ^{14}C-o,p'-dicofol on the surface of soil. ABC Report No. 34465. Rohm and Haas Report No. 310-86-49. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-37.

Daly, D. and A.M. Tillman. 1986a. Four-month interim report on the aerobic metabolism of ^{14}C-o,p'-dicofol on silt loam soil. ABC interim Report No. 34620. Rohm and Haas Technical Report No. 310-86-47. Prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. Acc. No. 400420-38.

Daly, D. and A.M. Tillman. 1986b. Anaerobic metabolism of ^{14}C-p,p'-dicofol on silt loam soil. ABC Final Report No. 33350. Rohm and Haas Technical Report No. 310-86-41. Prepared by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted Rohm and Haas Company, Spring House, PA. Acc. No. 400420-39.

Hoffman, CK. 1985a. A field dissipation study of Kelthane miticide in Fresno, CA. Report No. 310-86-72. Unpublished study prepared by Enviro-Bio-Tech, Bernville, PA and Rohm and Haas Co., Philadelphia, PA, and submitted by Rohm and Haas Co., Philadelphia, PA. Acc. No. 400420-40.

Hoffman, CK. 1985b. A field dissipation study of Kelthane miticide in Cleveland, MS. Rohm and Haas Technical Report No. 310-86-71. Unpublished study prepared by Enviro-Bio-Tech, Bernville, PA, and Rohm and Haas Co., Philadelphia, PA. and submitted by Rohm and Haas Co., Philadelphia, PA. Acc. No. 400420-41.

Tillman, A.M. 1986. The bioconcentration, elimination and metabolism of ^{14}C-dicofol by bluegill sunfish (Lepomis macrochirus). Report No. 310-86-17. Prepared and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. No. 265330.

Warren, J. 1986a. Hydrolysis of ^{14}C-p,p'-dicofol (Kelthane). Project Number ABC 33351. Rohm and Haas T.R. No. 310-86-59. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-32.

Warren, J. 1986b. Hydrolysis of ^{14}C-o,p'-dicofol (Kelthane). Project Number ABC 34618. Rohm and Haas T.R. No. 310-86-58. Prepared by Analytical Bio-Chemistry Laboratories, Columbia, MO, and submitted by Rohm and Haas Company, Philadelphia, PA. Acc. No. 400420-33.