

US EPA ARCHIVE DOCUMENT

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To: Dennis Edwards
Product Manager 12
Registration Division (TS-767C)

From: Paul Mastradone, Chief *PM*
Environmental Chemistry Review Section #1
Environmental Fate and Ground Water Branch/EFED (TS-769C)

Through: Henry Jacoby, Acting Chief *Henry Jacoby*
Environmental Fate and Ground Water Branch/EFED (TS-769C)

Attached, please find the EAB review of . . .

Reg./File # : 707-202

Chemical Name : Dicofol 010501

Type Product : Acaricide

Product Name : Kelthane, Hifol, Mitigan

Company Name : Rohm and Haas Company

Purpose : Addendum to a Standard (Review of photodegradation in water studies)

Date Received: 12-29-88

Action Code: 660

Date Completed: _____

EFGWB # (s): 90246

Monitoring Study Requested: _____

Total Reviewing time: days

Monitoring Study Volunteered: _____

- Deferrals to:
- Ecological Effects Branch, EFED
 - Science Integration and Policy Staff, EFED
 - Non-Dietary Exposure Branch, HED
 - Dietary Exposure Branch, HED
 - Toxicology Branch, HED

1. CHEMICAL: Common name:

Dicofol.

Chemical name:

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

Trade name(s):

Kelthane, Hifol, Mitigan.

Structures:

Formulations:

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

Physical/Chemical properties:

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

2. TEST MATERIAL:

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

3. STUDY/ACTION TYPE:

Addendum to a Standard.

4. STUDY IDENTIFICATION:

Carpenter, M. 1988a. Determination of the photodegradation rate of ¹⁴C-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 Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. (40849702)

Carpenter, M. 1988b. Determination of the photodegradation rate of ¹⁴C-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 Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by Rohm and Haas Company, Spring House, PA. (40849701)

5. REVIEWED BY:

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Signature: S Simko
Date: P-11-P9

6. APPROVED BY:

Paul Mastradone
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Signature: Paul Mastradone
Date: AUG 24 1989

7. CONCLUSION:

Dicofol (p,p') 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).

Dicofol (o,p') 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).

8. RECOMMENDATIONS:

These studies fulfill the photodegradation in water data requirement for dicofol.

9. BACKGROUND:

Dicofol is an acaricide registered for use on terrestrial food crop, terrestrial nonfood, greenhouse nonfood, domestic outdoor, and indoor sites. Of the total domestic dicofol usage, approximately 40% is applied to citrus, 26% to cotton, and 10% to ornamentals. Single active ingredient formulations consist of 1-6% D; 1.5-35% WP; 1-4.5% WP/D; 0.824-4 lb/gallon and 0.44-18.5% EC; 4 lb/gallon FlC; 0.046-12% RIU; 0.075-0.25% PrL; and 1.2% PrD. Application rates are 0.3-4.5 lb ai/A (D, WP, EC, FlC); 0.0019-4 lb ai/gallon (WP, EC, FlC); 0.006-0.5 tbsp/gallon (WP, WP/D, EC); 0.1-0.16 ounces/tree (WP/D); and 0.13-1.04 lb ai/50,000 ft³ (FlC, RIU). Formulations may be tank-mixed with other chemicals, including captan, carbaryl, diazinon, parathion, and sulfur. Foliar applications are made using either ground equipment or aircraft.

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

11. COMPLETION OF ONE-LINER:

12. CBI APPENDIX:

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

Dicofol

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INTRODUCTION

Dicofol is an acaricide registered for use on terrestrial food crop, terrestrial nonfood, greenhouse nonfood, domestic outdoor, and indoor sites. Of the total domestic dicofol usage, approximately 40% is applied to citrus, 26% to cotton, and 10% to ornamentals. Single active ingredient formulations consist of 1-6% D; 1.5-35% WP; 1-4.5% WP/D; 0.824-4 lb/gallon and 0.44-18.5% EC; 4 lb/gallon FlC; 0.046-12% RTU; 0.075-0.25% PrL; and 1.2% PrD. Application rates are 0.3-4.5 lb ai/A (D, WP, EC, FlC); 0.0019-4 lb ai/gallon (WP, EC, FlC); 0.006-0.5 tbsp/gallon (WP, WP/D, EC); 0.1-0.16 ounces/tree (WP/D); and 0.13-1.04 lb ai/50,000 ft³ (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.

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 ¹⁴C-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, MO, and submitted by Rohm and Haas Company, Spring House, PA.

DIRECT REVIEW TIME = 12

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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 [¹⁴C]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 [¹⁴C]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 [¹⁴C]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 [¹⁴C]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 [¹⁴C]dicofol from the test solutions, aliquots of the treated solutions were placed in continuous air-flow systems. Humidified, CO₂-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 ISC. The treated solutions were analyzed using ISC at 0 and 30 days posttreatment to establish a material balance.

DATA SUMMARY:

Uniformly ring-labeled [¹⁴C]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, [¹⁴C]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 [¹⁴C]compounds were each <6%. The material balances ranged from 93 to 120% of the applied during the study (Tables VI-VII).

Ring-labeled [¹⁴C]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, [¹⁴C]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.

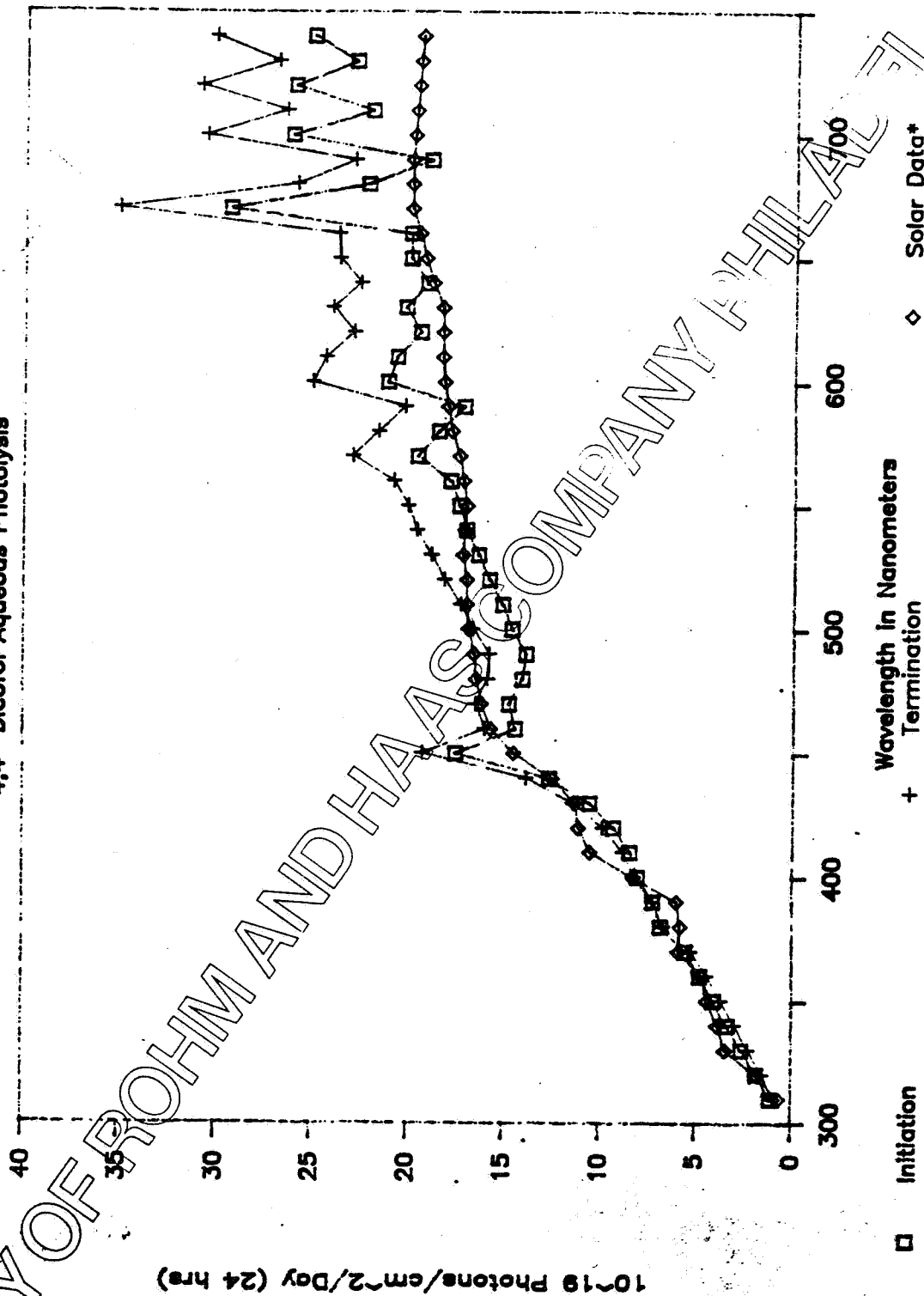
COMMENTS:

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 experiment was counted as one day of sunlight.

Spectral Irradiance Comparison
4,4'-Dicofof Aqueous Photolysis



U.S. Environmental Protection Agency, TSCA Test Guidelines, Federal Register, Vol. 50, No. 188, Sept. 27, 1985, pp. 39316ff.

ABC LABS #36670-52 of 1292

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 $25 \pm 1^\circ\text{C}$; 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 ISC. 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 ISC. 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 ISC. Recovery efficiencies from the TLC plates ranged from 79.5 to 94.8% of the radioactivity detected by ISC. 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 ISC. HPLC recovery efficiencies ranged from 88 to 102% of the radioactivity detected by ISC.

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 [¹⁴C]dicofol from the test solutions, aliquots of the treated solutions were placed in continuous air-flow systems. Humidified, CO₂-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 ISC. The treated solutions were analyzed using ISC at 0 and 30 days posttreatment to establish a material balance.

DATA SUMMARY:

Uniformly ring-labeled [¹⁴C]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, [¹⁴C]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 [¹⁴C] compound (R_f 0.61) was 13.6%, and four unidentified [¹⁴C] 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 [¹⁴C]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, [¹⁴C]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 experiment was counted as one day of sunlight.