6-6-85

Shaughnessy #: 081901

Date out of EAB: _____

Signature: _____

hydrolysis - stable
photo - water, soil
air -

To: H. Jacoby
Product Manager # 21
Registration Division (TS-767)

From: John Jordan, Ph.D., Acting Chief
Registration Standards, Section #2
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

leaching
volatility

Attached please find the EAB review of:

Reg./File No.: 50534-7

Chemical: Chlorothalonil

Type Product: Fungicide

Product Name: _____

Company Name: SDS Biotech

Submission Purpose: Response to RS

Action Code: 615

Date In: 4/24/85

EAB # 5555

Date Completed: 6/6/85

TAIS (level II)	Days
40	2

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

Conclusions

Degredation Study - Photodegredation in Water

1) This study cannot be validated as the data in Table 1 appear to indicate contradictory results or indicate laboratory procedural problems such as extractability. Please see discussion section for details.

2) The study does not fullfill EPA Data Requirement Guidelines for Registration of Pesticides (as noted in the original reviews) because no half lives were reported and were unestimatable for some of the data; recovery values for techniques used were unreported; pH levels and temperature used in studies were insufficient and insufficient precautions were taken to prevent volitilization or adsorption of the test product. Please see discussion section for details.

MATERIALS AND METHODS

Aliquots of ring-labeled [^{14}C]-chlorothalonil (Daconil, 99.3% radiochemical purity, specific activity 3630 dpm/ug, Diamond Shamrock Corp.) dissolved in benzene were placed in three beakers and the benezene allowed to evaporate. Two milliliters of pH 5 and 7 buffers were added to beakers 1 and 2, respectively, along with 300 ml deionized distilled water; the resulting chlorothalonil concentration was 0.5 ppm. Into the third beaker, 300 ml of 0.1 N HCl was added resulting in a concentration of 0.2 ppm chlorothalonil. All solutions were mixed continuously at 8 C and placed 12 inches below a GE sunlamp (Type RS, 175 W).

At various intervals, including immediately posttreatment (prior to irradiation), 0.5 ml subsamples were assayed for radioactivity by LSC. Additional subsamples (5.0 ml) were acidified using 10 drops of sulfuric acid (1:1; presumably diluted with water), extracted with 10 ml of isopropyl ether, and both the ether and aqueous phases were assayed (0.5 ml aliquots) by using LSC. In addition, a 5.0 ml aliquot of the ether phase was concentrated and analyzed by using silica gel TLC. TLC plates were developed in hexane:acetone (1:1) and visualized by fluorescence. The radioactive spots were assayed by using radiochromatogram scanning and LSC.

REPORTED RESULTS

No significant loss of radioactivity occurred throughout the duration of the experiment as determined by LSC. Increases in radioacitivity over time (Table 1) were postulated to be due to evaporation of the solvent or to [^{14}C]-chlorothalonil not going into solution completely at the initial sampling. In the 0.1 N HCl solution, ^{14}C remained in the ether phase of the extracts;

no degradation of chlorothalonil had occurred after 90 hours, as determined by TLC. After 90 hours of exposure, 93-100% of the chlorothalonil in the solution buffered at pH 5 and 7, had degraded into an unidentified water soluble compound more polar than the parent compound or the degradates, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) and 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221) (Table 1). Evaporation of the aqueous phase resulted in the formation of crystals; it is postulated that chlorothalonil was converted to a salt compound.

Discussion

1) Explaination for increased levels of chlorothalanil in water appears to show poor design, extractability and/or laboratory technique problems.

   a) If evaporation accurred the decrease in the volume of the water should have been readily noticable. If the initial detectable concentration in the water was .35 (ether aqueous) ppm and increased to a total (ether + aqueous) of .46 ppm the volume of water would have had to decrase by 25%. In a beaker containing 300 ml of water a 25% decease in water volume (approx. 75 ml) should have been noted and the sample rejected or appropriate correction factors applied.

   b) The solubility of the compound in water should be well known to the registrant. The level of addition of chlorothalonil to water for this experiment should have been determined with this in mind prior to compound addition. If the compound was not thoroughly solubilized prior to the beginning of the experiment a fundemental assumption (e.g. photodegradation of chlorothalonil in water) has been violated and the experiment unacceptable.

   c) If the chlorothalonil adhered to the glass surfaces as proposed the experiment is invalid as stated above. Also if degredation products are formed in the levels suggested (>10% of initial conc.) they must, by EPA guidelines for the Registration of Pesticides 1983, be identified and are not.

2. The study does not fulfill, EPA Data Requirements for Registering Pesticides (1983) because:

   a) no half-lives reported and data were insufficient to estimate photolytic half-life for chlorothalonil in the pH 7 buffered solution.

   b) The experiment was conducted at 8°C. Tests should have conductors at 25° $\pm$ 1°C.

c) Recovery values are not reported for techniques used.

d) Photodegradation studies need not be conducted in 0.1N HCl (pH 1) and are not within the range found in the aquatic environment associated with use pattern of chlorothalonil.

e) No photodegredation in water study done with basic solution (pH 9) and is required.

f) Precautions taken to minimize volatilization of test substance (using 8°C water bath) were insufficient.

CASE GS0097 CHLOROTHALONIL STUDY 6 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 05052005 GUIDELINE 40 CFR 163.62-7c

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00040543 CONTENT CAT 01

Szalkowski, M.B. 19??. Photodegradation and mobility of Daconil and its major metabolite on soil thin films. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:096466-F.

SUBST. CLASS = T; CHEM R29053 IS TRANSF. PRODUCT OF CHEM 081901

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

REVIEWED BY: C. Rodgers and S. Simko
TITLE: Staff Scientists
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SIGNATURE: C.S. Rodgers S. Simko DATE: June 15, 1983

APPROVED BY:
TITLE:
ORG:
TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This portion of the study is scientifically valid.

2. [^{14}C]Chlorothalonil and its major degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) were stable to photolysis on two silt loam and three silty clay loam soils; after UV irradiation for the equivalent of 168 12-hour days of sunlight, ~97 and 84% of the extractable radioactivity was identified as chlorothalonil and DAC-3701, respectively.

3. This portion of the study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because insufficient information was provided regarding the light source.

Mobility - Leaching and Adsorption/Desorption

1. This portion of the study is scientifically valid.

2. [^{14}C]Chlorothalonil was not mobile (R_f 0.0) and the degradate, [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) was found to have low to intermediate mobility (R_f 0.25-0.43) in two silt loam and three silty clay loam soils, as evaluated using soil TLC.

3. This portion of the study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the rapid (unaged) leaching of chlorothalonil and DAC-3701 in silt loam and silty clay loam soils.

MATERIALS AND METHODS:

Degradation - Photodegradation on Soil

Two silt loam and three silty clay loam soils (Table 1) were passed through a 65-mesh sieve (<0.25 mm) to remove all medium and coarse sand, and applied as a slurry to glass TLC plates at an average thickness of 461 µm. The soil TLC plates were allowed to air dry for 24 hours. Ring-labeled [^{14}C]-chlorothalonil (specific activity 3630 dpm/µg, radiochemical purity 99.3%, Diamond Shamrock Corp.) and ring-labeled [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, specific activity 4114 dpm/µg, radiochemical purity 98.2%, Diamond Shamrock Corp.) in benzene, were applied 3 cm from the bottom of each TLC plate at 5-6 µg/plate. The solvent was evaporated and the soil TLC plates were placed 12 inches from a GE sunlamp (Type RS, 175 W) for the equivalent of 168 12-hour days of sunlight. The UV radiation peaked at 297 nm; light intensity at the soil surface was 165 µE/m^2/sec.

Mobility - Leaching and Adsorption/Desorption

After the soil TLC plates described above were irradiated, additional 5-6 µg aliquots of [^{14}C]chlorothalonil and [^{14}C]DAC-3701 were applied to the soil TLC plates as nonexposed standards. To determine the mobility of the compounds, the soil TLC plates were developed in distilled water to a distance of 13 cm, air dried for 2 days, and the radioactive spots located by using autoradiography.

Acetone, ether, and aqueous extracts were prepared from these soil TLC plates by an undescribed method. The aqueous extract was extracted three times with isopropyl ether, the ether phases were combined, and the total radioactivity of the aqueous and ether phases was determined using LSC. Aliquots of the ether phase were concentrated to volumes <0.5 ml and applied, along with standards, to silica-gel TLC plates as 2-cm bands. The chlorothalonil TLC plates were developed with hexane:acetone (1:1) to a distance of 15 cm from the origin. DAC-3701 TLC plates were developed by ascending chromatography first with benzene:acetone (8:2) to a distance of 16 cm from the origin, air dried, and then with benzene:methanol (2:1) in a second direction to a distance of 9 cm. The standards were visualized under UV light and the R_f regions were marked. Radioactive spots were removed from the plates and quantified by using LSC.

REPORTED RESULTS:

Degradation - Photodegradation on Soil

After an exposure period equivalent to 168 12-hour days of sunlight, >91.1% of the extractable radioactivity was found in the organic phase for both chlorothalonil and DAC-3701 (>90.4% of the applied radioactivity was extractable). In the ether extracts from irradiated soil samples, ~97% of the residues were identified as parent compound in the chlorothalonil study, and ~84% of the residues were identified as parent compound in the DAC-3701 study (Tables 2 and 3). The ether extract of the nonirradiated (standard) chlorothalonil samples contained 92.5% parent compound.

Mobility - Leaching and Adsorption/Desorption

Chlorothalonil was immobile (R_f 0.0) in all five test soils as determined by soil TLC analysis. The mobility of the degradate, DAC-3701, ranged from low to intermediate (R_f 0.25-0.43) (Table 1). Irradiation of the samples had no effect on the mobility of either test substance.

DISCUSSION:

Degradation - Photodegradation on Soil

1. Immediate posttreatment samples were not collected; therefore, application rates could not be confirmed. Recoveries of the test substances at the end of the experiment ranged from 90.4 to 121.2% of the original (theoretical) application.

2. The data submitted to describe the characteristics of the GE Sunlamp used in this study need further clarification (Reg. file no. 50534-8. Light source in photodegradation study on chlorothalonil.) No explanatory information was provided with the data; therefore, the data can not be fully evaluated. The data are presented in three different forms that do not appear to describe the same light source. The light intensity data are representative of the sunlamp at a distance of 76.2 cm from the irradiated surface. Data are needed for the distance at which this study was conducted. It was not specified whether wavelengths below 280 nm were excluded. Data should be provided relating the intensity of the radiation used to that of natural sunlight.

3. Although degradation products were not identified, they were not produced in amounts >10% yield.

Mobility - Leaching and Adsorption/Desorption

1. The mobility of the irradiated samples reportedly did not differ significantly from that of the nonirradiated standards. This is to be expected since the organic phase of the extracted irradiated samples, contained ~90% parent compound.

2. It was not stated whether air-dried or oven-dried soils were used. The use of oven-dried soils would be expected to alter the mobility of chlorothalonil.

Table 1. Soil characteristics and the mobility of chlorothalonil and DAC-3701[a] on irradiated and nonirradiated soil TLC plates (expressed as Rf values).

Location	Soil type	Organic carbon	Sand	Clay	Silt	pH	Chlorothalonil (R_f)		DAC-3701 (R_f)	
			%				Non-irradiated	Irradiated	Non-irradiated	Irradiated
York, NE	Silt loam	1.91	1.4	27.1	71.5	5.6	0.0	0.0	0.30	0.25
Blackburn, MO	Silt loam	1.93	1.2	24.7	74.1	6.0	0.0	0.0	0.43	0.41
Macombe, IL	Silty clay loam	2.31	0.6	25.8	73.6	5.1	0.0	0.0	0.33	0.34
Ellsworth, IL	Silty clay loam	2.57	2.4	25.3	72.3	5.3	0.0	0.0	0.32	0.34
Rosemont, MN	Silty clay loam	3.40	13.7	22.6	63.7	5.6	0.0	0.0	0.39	0.35

[a] 4-Hydroxy-2,5,6-trichloroisophthalonitrile.

Table 2. Distribution of radioactivity of chlorothalonil ether extracts on silica-gel TLC plates.

Not exposed to light[a]		Exposed to light[b]	
R_f	Distribution (%)[c]	R_f	Distribution (%)[c]
0.07	1.2	0.03	--
0.23[d]	0.7	0.10	0.4
0.37	1.5	0.23[d]	0.4
0.53	2.5	0.37	0.5
0.70	0.9	0.53	0.3
0.83[e]	92.5	0.80	1.2
1.00	0.7	0.95[e]	97.0
--	--	1.00	0.3

[a] [^{14}C]DAC-3701 applied to soil TLC plates as nonexposed standard and developed immediately after treatment.

[b] [^{14}C]DAC-3701 treated soil TLC plates exposed to the equivalent of 168 12-hour days of sunlight.

[c] Related to radioactivity remaining on TLC plates.

[d] R_f region of authentic DAC-3701 standard.

[e] R_f region of authentic chlorothalonil standard.

Table 3. Distribution of radioactivity of a DAC-3701 ether extract on a silica-gel TLC plate.

Exposed to sunlight for 168 days	
R_f	Distribution (%)
0.03	2.3
0.22	2.3
0.37[a]	84.0
0.53	3.8
0.66	1.5
0.75	2.6
0.84	0.0
0.97[b]	3.4
1.00	0.0

[a] R_f region of authentic DAC-3701 standard.

[b] R_f region of authentic chlorothalonil standard.

CASE GS0097 CHLOROTHALONIL STUDY 2 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 05101505 GUIDELINE 40 CFR 163.62-7b/c

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00040540 CONTENT CAT 01

Szalkowski, M.B. 1976. Photodegradation of Daconil in aqueous systems. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:096466-C.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

REVIEWED BY: C. Rodgers and S. Simko
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SIGNATURE: C. S. Rodgers S. Simko DATE: June 7, 1983

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is scientifically valid.

2. Ring-labeled [^{14}C]chlorothalonil was not photodegraded in acid solution (0.1 N HCl-pH 1) after 90 hours of irradiation by artificial sunlight; however, in buffered solution (pH 5 and 7) >90% of the applied chlorothalonil was converted to polar water soluble compounds that could not be partitioned into organic solvents. The water soluble polar compounds were not identified.

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3. This study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because the data presented for the irradiated aqueous buffered solution at pH 7 are inadequate to estimate a half-life, photodegradation was not studied at 25 ± 1 C, photoproducts were not identified and the wavelength and intensity of the artificial light source and its relationship to natural sunlight were not provided in a clear manner for either the irradiated buffered solutions (pH 5 and 7) or the aqueous 0.1 N HCl solution.

MATERIALS AND METHODS:

Aliquots of ring-labeled [^{14}C]chlorothalonil (Daconil, 99.3% radiochemical purity, specific activity 3630 dpm/µg, Diamond Shamrock Corp.) dissolved in benzene were placed in three beakers and the benzene was allowed to evaporate. Two milliliters of pH 5 and 7 buffers were added to beakers 1 and 2, respectively, along with 300 ml deionized distilled water; the resulting chlorothalonil concentration was ~0.5 ppm. Into the third beaker, 300 ml of 0.1 N HCl was added resulting in a concentration of 0.2 ppm chlorothalonil. All solutions were mixed continuously at 8 C and placed 12 inches below a GE sunlamp (Type RS, 175 W).

At various intervals, including immediately posttreatment (prior to irradiation), 0.5 ml subsamples were assayed for radioactivity by using LSC. Additional subsamples (5.0 ml) were acidified using 10 drops of sulfuric acid (1:1; presumably diluted with water), extracted with 10 ml of isopropyl ether, and both the ether and aqueous phases were assayed (0.5 ml aliquots) by using LSC. In addition, a 5.0 ml aliquot of the ether phase was concentrated and analyzed by using silica gel TLC. TLC plates were developed in hexane:acetone (1:1) and visualized by fluorescence. The radioactive spots were assayed by using radiochromatogram scanning and LSC.

REPORTED RESULTS:

No significant loss of radioactivity occurred throughout the duration of the experiment as determined by LSC. Slight increases in radioactivity over time (Table 1) were postulated to be due to evaporation of the solvent or to [^{14}C]chlorothalonil not going into solution completely at the initial sampling. In the 0.1 N HCl solution, ^{14}C remained in the ether phase of the extracts; no degradation of chlorothalonil had occurred after 90 hours, as determined by TLC. After 90 hours of exposure, ~93-100% of the chlorothalonil in the solution buffered at pH 5 and 7, had degraded into an unidentified water soluble compound more polar than the parent compound or the degradates, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) and 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221) (Table 1). Evaporation of the aqueous phase resulted in the formation of crystals; it is postulated that chlorothalonil was converted to a salt compound.

DISCUSSION

1. In a letter from EPA to Diamond Shamrock Corporation regarding PP# 6F1749 dated August 3, 1976, an explanation was requested for the reactivity of chlorothalonil in the buffered solution (pH 5 and 7) indicated by this study, and the stability of chlorothalonil in the identical buffers in the hydrolysis study [refer to review of Study 1 (00040539)]. In a subsequently submitted response by Diamond Shamrock Corporation, it was postulated that the unidentified degradate obtained upon exposure of chlorothalonil in phosphate buffered solutions to artificial sunlight was a phosphate salt of chlorothalonil. However, no data were submitted in support of the postulation.

2. Dark controls were not included in the experiment. However, Study 1 (00040539) demonstrated chlorothalonil (in the dark) to be stable to hydrolysis at pH 5 and 7. Therefore, the data obtained from the dark control of Study 1 can be used as the dark control in this study.

3. The data presented were insufficient to estimate a photolytic half-life for chlorothalonil in the pH 7 buffered solution.

4. The experiment was conducted at 8 C. Test procedures require that photodegradation studies in water should be conducted at 25 ± 1 C.

5. The data submitted to describe the characteristics of the GE Sunlamp used in this study need further clarification (Reg. file no. 50534-8. Light source in photodegradation study on chlorothalonil.) No explanatory information was provided with the data; therefore, the data can not be fully evaluated. The data are presented in three different forms that do not appear to describe the same light source. The light intensity data are representative of the sunlamp at a distance of 76.2 cm from the irradiated surface. Data are needed for the distance at which this study was conducted. It was not specified whether wavelengths below 280 nm were excluded. Data should be provided relating the intensity of the radiation used to that of natural sunlight.

6. Recovery values and the sensitivity for the method were not reported.

7. Photodegradation studies conducted in 0.1 N HCl (pH 1) are not within the pH range of the aquatic environment associated with the use patterns for chlorothalonil.

Table 1. Partitioning of radioactivity, expressed as ppm [^{14}C]chlorothalonil, into isopropyl ether from three irradiated solutions.

Exposure time (hrs)	pH 5		pH 7		0.1 N HCl	
	Ether phase	Aqueous phase	Ether phase	Aqueous phase	Ether phase	Aqueous phase
0	0.35	0.00	0.34	0.00	0.13	0.00
1	0.48	0.01	0.39	0.01	--[a]	--
2	0.45	0.01	0.39	0.01	--	--
17	0.20	0.15	--	--	0.17	0.00
24	--	--	--	--	0.16	0.00
90	0.05	0.41	0.02	0.34	0.18	0.01

[a]No data reported.

CASE GS0097 CHLOROTHALONIL STUDY 4 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 05052005 GUIDELINE 40 CFR 163.62-7c

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00040542 CONTENT CAT 01

Szalkowski, M.B. 1975. Photodegradation of Daconil and 4-hydroxy-2,5,6-trichloroisophthalonitrile on silica gel plates. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL: 096466-E.

SUBST. CLASS = T; CHEM R29053 IS TRANSF. PRODUCT OF CHEM 081901

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

REVIEWED BY: S. Simko
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SIGNATURE: S. Simko DATE: June 15, 1983

APPROVED BY:
TITLE:
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CONCLUSION:

Degradation - Photodegradation on Soil

This study is scientifically invalid because dark controls were not used. In addition, this study would not satisfy EPA Data Requirements for Registering Pesticides (1983) because photodegradation was studied on silica-gel plates and not on soil, and the light source was not fully characterized.

MATERIALS AND METHODS:

Ring-labeled [^{14}C]chlorothalonil (Daconil, Diamond Shamrock Corp., specific activity 3630 dpm/µg, radiochemical purity 99.3%) was applied to silica-gel plates at 5.6 µg in 55 µl of benzene. Of six samples, three were overlayered wth 12 µl of a saturated solution of the photosensitizer, anthraquinone, in benzene. This procedure was repeated using the degradate 4 hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, Diamond Shamrock Corp., specific activity 4114 dpm/µg, radiochemical purity 98.2%) at 6.7 µg in 4 µl of benzene. The plates were placed 16 inches from a GE sunlamp (Type RS, 175 W) with a radiation peak at 297 nm and an intensity of 165 µE/m^2/sec. After the equivalent of 1.3 12-hour days of sunlight, samples 1 and 2 were covered to prevent further exposure. After the equivalent of 32 12-hour days of sunlight, samples 3 and 4 were covered. All plates were removed after the equivalent exposure of 168 12-hour days of sunlight.

The plates were developed in benzene:acetone (8:2), dried and redeveloped in benzene:methanol (2:1). The TLC plates had a fluorescent indicator which was viewed under UV light. The radioactive spots were located by autoradiography and quantified by using LSC.

For identification of the degradates, a benzene solution containing 5 g of nonradioactive chlorothalonil was evenly spread across the surface of five 20 x 20 cm silica-gel TLC plates and irradiated as previously described for the equivalent exposure of 224 12-hour days. The silica gel was then transferred to a chromatographic column containing 6.5 cm of fresh silica gel and topped with 2 cm of anhydrous sodium sulfate. The column was eluted with 240 ml benzene:methanol (2:1) followed by 200 ml of methanol. The eluted fractions were analyzed by using TLC and the resulting portions containing parent compounds were discarded. The material(s) remaining at the origin of the TLC plates was combined and applied again to TLC plates and developed to separate any remaining chlorothalonil and DAC-3701. The materials at the origin of the plates were removed and combined, and then extracted with methanol. The methanolic extract was concentrated to a small volume for characterization by mass, infrared, and emission spectroscopy. This procedure was repeated using nonradiolabeled DAC-3701.

To confirm the identification of degradates, radiolabeled [^{14}C]chlorothalonil and DAC-3701 were separately applied in 15 cm bands to the bottom of TLC plates and irradiated for the equivalent of 224 12-hour days. The plates were then developed and the material remaining at the origin was removed and extracted with methanol:1% formic acid acetone (1:9). The extracts were concentrated, dissolved in water, and combined with sulfuric acid to break any salts. The samples were then extracted twice with n-butanol. These extracts and the remaining aqueous phases were radioassayed by using LSC. The butanol extracts were repeatedly washed with distilled water, concentrated and analyz by using TLC. Both acidic and nonacidic solvent systems were used in the TLC analysis.

REPORTED RESULTS:

After the equivalent of 168 12-hour days exposure, 46 and 54% of the radioactivity applied as chlorothalonil and DAC-3701, respectively, remained as parent compound. Respective values for the studies with the photosensitizers were 55.6 and 53.6% (Table 1). Of the residues that remained in the chlorothalonil studies after the exposure period, 30.0% was parent compound, 15.6% was DAC-3701, and 27.4% was polar material that did not move from the TLC origin. The same general trend was observed in studies with the photosensitizer. Of the residues remaining in the DAC-3701 study after the exposure period, 53.9% was parent compound and 33.0% was polar origin material (Table 1). Mass and IR spectrometry indicated the presence of the sodium salt of DAC-3701 in the polar material. Acidification followed by extraction and TLC analysis of this material demonstrated that the majority was converted to DAC-3701.

DISCUSSION:

1. Photodegradation was not studied on soil and dark controls were not employed.

2. After the exposure period, up to 54% of the ^{14}C activity was unaccounted for. These losses were assumed to be due to volatility; however, no attempt was made to trap or identify volatile components. Therefore, a materials balance was not conducted.

3. Recovery values and sensitivity for the method were not reported.

4. The data submitted to describe the characteristics of the GE Sunlamp used in this study need further clarification (Reg. file no. 50534-8. Light source in photodegradation study on chlorothalonil.) No explanatory information was provided with the data; therefore, the data can not be fully evaluated. The data are presented in three different forms that do not appear to describe the same light source. The light intensity data are representative of the sunlamp at a distance of 76.2 cm from the irradiated surface. Data are needed for the distance at which this study was conducted. It was not specified whether wavelengths below 280 nm were excluded. Data should be provided relating the intensity of the radiation used to that of natural sunlight.

Table 1. Determination of total individual residues remaining on TLC plates following application of either chlorothalonil or DAC-3701[a] and exposure to UV radiation.

	1.3 12-hour days exposure		32 12-hour days exposure		168 12-hour days exposure	
	Without photo-sensitizer	With photo-sensitizer	Without photo-sensitizer	With photo-sensitizer	Without photo-sensitizer	With photo-sensitizer
	Percentage of initial ^{14}C activity remaining					
Chlorothalonil residues						
Total residues remaining	100	100	66.2	78.7	46.0	55.6
DAC-3701 residues						
Total residues remaining	100	100	91.0	87.0	54.0	53.6
	Percentage of the total residues remaining					
Chlorothalonil residues						
Chlorothalonil	86.0	91.5	41.8	62.0	30.0	41.3
DAC-3701	6.3	4.6	16.6	12.1	15.6	13.3
Origin residues	3.5	1.3	21.7	12.5	27.4	22.7
DAC-3701 residues						
DAC-3701	93.5	91.6	67.0	69.1	53.9	57.5
Origin residues	4.2	4.8	22.9	16.9	33.0	20.7

[a]4-Hydroxy-2,5,6-trichloroisophthalonitrile.

CASE GS0097 CHLOROTHALONIL STUDY 5 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 05052005 GUIDELINE 40 CFR 163.62-7c

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00040541 CONTENT CAT 01

Szalkowski, M.B. 1976. Photodegradation of Daconil and its metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile, on inert surfaces. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:096466-D.

SUBST. CLASS = T; CHEM R29053 IS TRANSF. PRODUCT OF CHEM 081901

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is scientifically valid.

2. [^{14}C]Chlorothalonil and [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) are not photodegraded when irradiated as a thin film on glass beads (2 µg/bead). After irradiation for the equivalent of 14.6 days of sunlight, 77.3% of the radioactivity applied as [^{14}C]chlorothalonil remained on the inert surface, and 91.3% of this was the parent. In the [^{14}C]DAC-3701 study, 49.2% of the applied radioactivity remained after the equivalent of 28.6 days of sunlight, all of which was identified as DAC-3701.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the experiment was not conducted on soil, and insufficient information was provided regarding the light source. Photodegradation studies conducted on glass beads are not currently a Data Requirement for Registering Pesticides.

MATERIALS AND METHODS:

Benzene solutions of [^{14}C]chlorothalonil (Daconil, 3630 dpm/µg, test substance uncharacterized, source unspecified) and the degradate [^{14}C]-4-hydro-2,5,6-trichloroisophthalonitrile (DAC-3701, test substance uncharacterized, source unspecified) were each used to coat 0.2-cm diameter glass beads. The benzene was evaporated leaving a layer of chlorothalonil (<50 µ) at 2 µg/bead as determined by LSC. The treated beads were placed in a petri dish equipped with a Vycor glass cover, and glass inlet and outlet tubes which were connected to a vacuum source. Two U-shaped traps on the outlet tube contained 10 ml 1 N sodium hydroxide. The apparatus was placed 41 cm from a GE sunlamp (Type RS, 175 W) with a UV radiation peak at 297 nm and an intensity of 35 E-vitons/in^2 at a distance of 76.2 cm. Air temperature did not exceed 30 C.

Three beads were removed at intervals up to 28.6 days, placed into scintillation vials,and radioassayed by using LSC. At the end of the experiment, 1.0 ml portions of the two sodium hydroxide trap solutions were acidified using 1:1 sulfuric acid and partitioned with isopropyl ether. The extracts were analyzed by TLC in a hexane:acetone (1:1) solvent system. The TLC sections were radioassayed by LSC. At the end of the experiment, the glass beads were washed with a 1% formic acid in acetone solution and analyzed by using MS and TLC.

Volatiles evolved from the DAC-3701 treated beads during the acidification step were trapped in either sodium hydroxide:barium hydroxide or a mixture of hyamine hydroxide and scintillation fluid. Nonradioactive DAC-3701 (0.5 g) in benzene was used to coat quartz chips, which were maintained in a sealed quartz bottle and irradiated for the equivalent of 120 days. Air samples from the bottle were analyzed by using GC and MS and by using an IR differential carbon dioxide analyzer.

REPORTED RESULTS:

After exposure for the equivalent of 14.6 days in the chlorothalonil study, and 28.6 days in the DAC-3701 trial, 77.3 and 50.8% of the original ^{14}C activity, respectively, remained on the glass beads (Table 1). Apparatus washes recovered 5.5 and 4.5%, respectively, of the applied ^{14}C activity. The sodium hydroxide traps recovered 1.8 and 19.6%, respectively, of the applied ^{14}C activity. In total, 84.6 and 73.3% of the ^{14}C activity was accounted for in the chlorothalonil and DAC-3701 studies, respectively, and the remainder was assumed to have escaped through apparatus leaks. Greater than 90% of the material remaining on the glass beads was extracted and shown to be 91.3% parent compound in the chlorothalonil study. MS analysis of the DAC-3701 study showed the sample to be 100% parent compound.

TLC analysis of the sodium hydroxide trap solution in the chlorothalonil stud showed 10.5% parent compound, 31% DAC-3701 and 38% 3-cyano-2,4,5,6-tetrachlor benzamide (DS-19221). It was postulated that the two degradates were found after parent compound had entered the basic trap solution. TLC analysis of the sodium hydroxide trap solution in the DAC-3701 study showed no ^{14}C activity after acidification. It was postulated that the product could be CO_2 and further analysis confirmed this.

DISCUSSION:

1. The data submitted to describe the characteristics of the GE Sunlamp used in this study need further clarification (Reg. file no. 50534-8. Light source in photodegradation study on chlorothalonil.) No explanatory information was provided with the data; therefore, the data can not be fully evaluated. The data are presented in three different forms that do not appear to describe the same light source. The light intensity data are representative of the sunlamp at a distance of 76.2 cm from the irradiated surface. It was not specified whether wavelengths below 280 nm were excluded. Data should be provided relating the intensity of the radiation used to that of natural sunlight.

2. Recovery values and limits of detection and sensitivity for the method were not reported.

3. Negative pressure, as used in this study, will increase the rate of pesticide volatilization over that to be expected under 1 atmosphere pressure.

Table 1. Decline of ^{14}C activity from glass beads coated with [^{14}C]chlorothalonil or [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) following irradiation.

Equivalent exposure (days)	Percent of initial ^{14}C activity	
	Chlorothalonil	DAC-3701
0	100.0	100.0
1.3	104.4	92.9
3.9	90.1	90.2
6.5	--[a]	84.8
14.6	77.3	--
28.6	--	49.2

[a]--; Not determined.

CASE GS0097 CHLOROTHALONIL STUDY 7 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00040544 CONTENT CAT 01

Szalkowski, M.B. 1976. Degradation of Daconil and its metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile, in soil. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL: 096466-G.

FICHE/MASTER ID 00040545 CONTENT CAT 01

Szalkowski, M.B. 1976. Anaerobic soil metabolism of Daconil. Unpublished study received Feb. 25, 1976 under 6F1749; prepared in cooperation with Ohio State Univ., Soil Testing Laboratory, submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:096466-H.

FICHE/MASTER ID 00040546 CONTENT CAT 01

Szalkowski, M.B. 1976. Leaching of degradation products. Unpublished study received on unknown date under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:096466-I.

FICHE/MASTER ID 00087352 CONTENT CAT 01

Szalkowski, M.B. 1976. Bound residue study: Daconil. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemical, OH; CDL:097394-J.

SUBST. CLASS = S.

DIRECT RVW TIME = 23 1/2 (MH) START-DATE END DATE

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These hardcopies were combined under one review because some of the same soil used in 00040544 (aerobic study) was converted to anaerobic conditions in 00040545; 00087352 (bound residue study) was a continuation of 00040544 (aerobic study); and 00040546 (leaching study) used soil (aged) from 00040544 (aerobic study). All of these experiments were conducted by the same researcher sequentially or simultaneously.

CONCLUSIONS:

Metabolism - Aerobic Soil (00040544, 00087352)

This portion of the study cannot be validated because the soils were aged under inappropriate laboratory (greenhouse) conditions. In addition, this portion of the study does not satisfy EPA Data Requirements for Registering Pesticides (1983) because insufficient sampling was performed to establish patterns of decline of the parent compound and patterns of formation and decline of degradates, and the treated soils were not maintained at a constant temperature.

Metabolism - Anaerobic Soil (00040545)

This portion of the study cannot be validated because it cannot be ascertained that the quantity of chlorothalonil which remained in soil (15 ppm applied, 7-14% remained) after 30 days of aerobic aging under variable temperature conditions is representative of the quantity of chlorothalonil that would remain in soil 30 days after aerobic aging under constant temperature conditions. The aerobic soils were aged under inappropriate laboratory conditions before anaerobic conditions were established. In addition, this portion of the study would not satisfy EPA Data Requirements for Registering Pesticides (1983) because half-life estimates for chlorothalonil and its degradates were not provided.

Mobility - Leaching and Adsorption/Desorption (00040546)

This portion of the study cannot be validated because the chlorothalonil-treated soil was aged an excessive amount of time (only 7-14% of the parent material was present when leaching began) and the soil was not maintained at a constant temperature (greenhouse conditions) during the aging process. The DAC-3701-treated soil experiment cannot be validated because the sampling intervals and analyses for DAC-3701 aged in soil under greenhouse conditions were not reported (insufficient data to support stability or rate of degradation of [^{14}C]DAC-3701 in aerobic soil under greenhouse conditions during the 30-day aging period).

MATERIALS AND METHODS:

Metabolism - Aerobic Soil (00040544, 00087352)

Seven hundred and fifty micrograms of [^{14}C]chlorothalonil (Daconil, purity 99.3%, specific activity 3630 dpm/µg, Diamond Shamrock Corp.) or [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, purity 98.2%, specific activity 4114 dpm/µg, Diamond Shamrock Corp.) in benzene was added to the surface of 50-g samples of five air-dried soils (Table 1) placed in separate pint jars. The solvent was allowed to evaporate and the treated soils were mixed. The final concentration of each ^{14}C compound in each soil was ~15 ppm. A 3-g sample of each soil was removed immediately posttreatment.

The remaining soil was brought to 80% of field moisture capacity by the addition of appropriate volumes of water (amount unspecified), weighed and maintained in the greenhouse for 30 days. Incubation temperatures were 92-95 F during the 12-hour day and 80-85 F at night; water was added as needed to maintain moisture levels of 80% of field capacity.

Immediate posttreatment and 30-day soil subsamples (1-g samples) were air-dried and extracted with a 80:20 mixture of acetone and 0.3 N hydrochloric acid. Duplicate 0.5-ml portions of the supernatant remaining after the soils had settled were removed and quantified by using LSC. Counting efficiencies ranged between 55 and 78% (recovery of ^{14}C activity from soil).

The quantification of nonextractable residues was performed by one of two comparison methods. In Comparison Method I, radioactivity detected in the acid-acetone extracts was subtracted from the total radioactivity in unextracted samples determined by combustion analysis (percent extractability of radioactivity was determined). Comparison Method II involved a comparison of radioactivity in the acid-acetone extract to the amount of radioactivity remaining on the soil after extraction. After extraction, each soil sample was vacuum filtered and washed three times with 10-15 ml acetone. The filtered soil was allowed to air-dry, weighed, and analyzed for unextracted radioactivity by total combustion to CO_2.

The characterization of extracted residues was accomplished utilizing TLC techniques. A 10-ml portion of the acid-acetone extract was transferred to a 30-ml beaker and 0.5 ml 0.2 N HCl was added. The sample was evaporated free of acetone under a stream of clean, dry air. The remaining acid aqueou solution was quantitatively transferred to a 60-ml separatory funnel. The sample was partitioned by shaking 3-5 minutes.

To determine the partitioning of extracted residues into an organic phase (isopropyl ether), the volume of each phase was measured and 0.5 ml of each were counted in duplicate. Counting efficiency for the aqueous phase was 89-90%.

To analyze the ether phase by TLC, 15 ml of the ether was removed and concentrated to a volume less than 0.5 ml. The concentrate was applied as a 1- to 2-cm band to silica gel TLC plates with standards of nonradioactive chlorothalonil and DAC-3701. Development of the plate was accomplished in a hexane:acetone (1:1) solvent system to a distance of 15 cm from the origin. After removal from the developing chamber and evaporation of the solvent, the plates were exposed to X-ray film for 7-10 days to obtain autoradiograms to visualize any degradation products. Relative distribution of radioactivity on the plates was determined by radiochromatogram scanning.

On the basis of the R_f values of nonlabeled standard compounds applied to the plates (visualized by fluorescence under short wave UV light), autoradiograms, and radiochromatogram scanning, it was possible to section the TLC plates into significant regions. These regions were cut with scissors, deposited into scintillation vials, 20 ml of scintillation cocktail was added, and the sections were counted.

Further efforts were made to characterize the nonextractable (bound) radioactivity in [^{14}C]chlorothalonil-treated soils by determining the amount of radioactivity associated with the humin, fulvic acid and humic acid soil organic matter fractions. Four-gram samples of four soils (peat loam, silty clay loam, and two sandy loams; assumed to be 4 of the 5 soils in Table 1) were treated (amount unspecified) with [^{14}C]chlorothalonil and allowed to age 3 months. After aging, the soil samples (4-g) were ground with a mortar and pestle, extracted with 0.3 N hydrochloric acid and acetone, filtered, and radioactivity of the filtrate was quantified by using LSC. A portion (aliquot size unspecified) of the extracted soils was air dried and total radioactivity was determined by combustion. Another portion (1-2 g) of the extracted soils was reextracted three times with 1 N sodium hydroxide, the supernatants were combined, and the radioactivity remaining in the soil (stated to be associated with the humin fraction) was determined by combustion.

Radioactivity in the sodium hydroxide extracts was determined by using LSC. The humic and fulvic acid fractions, contained in the sodium hydroxide extracts, were separated by adjusting the pH of the solution to 1 to precipitate the humic acid fraction. The precipitated humic acid was redissolved in sodium hydroxide and radioactivity in both fractions was determined by using LSC. The soluble fulvic acid fraction was partitioned with isopropyl ether and the radioactivity in each phase determined by using LSC. Residues in the ether phases were identified by using TLC.

Metabolism - Anaerobic Soil (00040545)

Four subsamples (5-11 g) of three soils from the aerobic soil metabolism portion of this study (silt loam, sandy loam, and peat loam soil; Table 1), which had been aged aerobically for 30 days following treatment at 15 ppm with [^{14}C]chlorothalonil, were placed in test tubes. In two aerobically maintained tubes, soil moisture levels were adjusted to 80% of field moisture capacity and the tubes were sealed; a hypodermic needle was inserted to facilitate air exchange. Soil in the two anaerobically maintained tubes was covered with water to a depth of 2-3 cm. The atmosphere above the water was purged with nitrogen gas, and the tubes were tightly sealed. All soil samples were stored in darkness at 25 C. After 45 and 60 days one sample of each soil was removed from aerobic and anaerobic conditions and analyzed by using the methods described in the aerobic soil metabolism portion of this study. The water above the anaerobically maintained soils was partitioned with isopropyl ether, and the residue in the ether phase was characterized and quantified by using TLC and LSC.

Mobility - Leaching and Adsorption/Desorption (00040546)

Two mobility studies were conducted: 1) leaching of aged [^{14}C]chlorothalonil and its residues and 2) leaching of aged [^{14}C]DAC-3701 and its residues.

Aged [^{14}C]chlorothalonil-treated soils (Table 1) used in the aerobic soil metabolism portion of this study were layered (2-3 g) on top of columns (1.8 x 30 cm) containing untreated soils of the same type. The soils were leached daily with 0.5 inches (3.3 ml) of water per day for 45 days; leachate was collected daily and analyzed by using LSC. After the leaching period, the soils were sectioned into 5-cm segments, air dried, and ground using a mortar and pestle. Total radioactivity in each segment was determined by using combustion followed by LSC. The extractable radioactivity was characterized by using the extraction and TLC techniques described in the aerobic soil metabolism portion of this study. Nonextractable residues were determined by combustion followed by LSC.

Similar leaching studies were conducted to determine the mobility of [^{14}C]-DAC-3701.

REPORTED RESULTS:

Metabolism - Aerobic Soil (00040544, 00087352)

Immediately after treatment, >90% of the radioactivity on TLC plates was in the R_f region of the respective compounds either chlorothalonil for the [^{14}C]chlorothalonil-treated soils or DAC-3701 for [^{14}C]DAC-3701-treated soils. After 30 days of aging, the radioactivity on TLC plates of soil treated with [^{14}C]chlorothalonil was distributed among chlorothalonil (2.7-13.5%), the degradates DAC-3701 (5.1-19.3%) and 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221; 1.4-6.1%), water-soluble compounds,(19.2-24.4%) polar organic extractables (4.1-9.4%) and nonextractables (33.4-47.6%) (Table 2). The calculated half-lives of chlorothalonil (calculated using rate constant K, Table 2) in the five soils ranged from 6 to 10 days (Table 2). All of the extractable radioactivity on TLC plates of soils treated with DAC-3701 and aged for 30 days was in the R_f region of DAC-3701, indicating that further breakdown of this degradate does not occur in 30 days aging period.

Bound (unextractable) residues were associated with the humin (10.8-19.5%), humic acid (1.5-10.2%), and fulvic acid (9.4-17.7%) fractions of soil organic matter (Table 3). In the fulvic acid, 34-48% of the radioactivity that partitioned into the ether phase was identified as DAC-3701.

Metabolism - Anaerobic Soil (00040545)

The ^{14}C distribution in soil incubated anaerobically and sampled at 45 and 60 days (following 30 days of aerobic aging) is summarized in Table 4. The chlorothalonil concentrations in soils after the aerobic aging were low (4.4-

10.2%) and further reductions in the chlorothalonil concentrations during anaerobic incubation were not substantial (2.8-10.2%). The ^{14}C identified as the parent in the silt loam soil decreased from 7.4% (of applied) at the start of the anaerobic incubation to 3.6 and 2.8% after 45 and 60 days of anaerobic incubation, respectively; the respective decrease was from 10.2 to 7.5 and 6.8% in the sandy loam soil. An increase from 4.4 to 10.2% at day 45 and decline to 7.7% at 60 days (anaerobic) was reported for the peat soil. Changes in the concentrations of the DAC-3701 and DS-19221 degradates were similarly small (Table 4). In the silt loam soil the ^{14}C identified as DAC-3701 increased from 5.1% (of applied) at the start of the anaerobic incubation to 5.5% after 45 days and declined to 4.8% at 60 days of anaerobic incubation; the respective values for the sandy loam and peat loam soils were 10.9 and 17.2%, 12.0 and 5.2%, and 6.3 and 18.0%. The flood water above the silt loam, sandy loam, and peat loam soils contained an average of 9.8, 6.3, and 2.7% of the initial radioactivity, respectively, after both 45 and 60 days. Concentrations of chlorothalonil and its identified degradates were very low in the flood waters, ≤0.1% of the ^{14}C was associated with chlorothalonil, ≤1.1% DAC-3701, and ≤0.2% DS-19221. Anaerobic incubation substantially decreased (31-65% reduction) the extractable radioactivity (water and ether extracts combined) in all three soils tested (Table 4). The ^{14}C distribution of the soils incubated aerobically for 45 and 60 days (following 30 days of aerobic aging) was very similar to that observed for the anaerobic soils (Table 5).

Mobility - Leaching and Adsorption/Desorption (00040546)

Following application of ~22.5 inches of water over a 45-day period to [^{14}C]chlorothalonil-treated soils, 9.8-22.1% of the applied radioactivity was detected in the leachate (Table 6). The majority of the radioactivity remaining in the soil was distributed in the top 5 cm in the chlorothalonil-treated columns. TLC analysis of [^{14}C]chlorothalonil-treated soils identifie chlorothalonil, DAC-3701, and DS-19221 in the 0- to 5-cm segment and primaril DAC-3701 in the 5- to 10-cm segment.

Following application of ~22.5 inches of water over a 45-day period to [^{14}C]DAC-3701-treated soils, 1.4-5.3% of the applied radioactivity was detected in the leachate (Table 6). The majority of the radioactivity remaining in the soil was distributed in the top 10 cm of the DAC-3701-treate columns; an exception to this was the [^{14}C]DAC-3701-treated sandy loam soil (Texas) which contained a significant amount of radioactivity in the 10- to 30-cm sections (Table 6). TLC analysis of [^{14}C]DAC-3701-treated and aged soils identified only DAC-3701 throughout the column.

DISCUSSION:

General

The error in the counting efficiency of the method was greater than the amount of material being dealt with in these studies.

Metabolism - Aerobic Soil (00040544, 00087352)

1. Half-life calculations based on the two sampling intervals are unacceptable. Chlorothalonil's rate of degradation in soil cannot be assumed to be linear (insufficient data to support linear degradation), particularly when the soil is not maintained under constant conditions (temperature varied), and a microbial adaption period (lag time) is usually required before microbial degradation begins.

2. Soils were only sampled immediately posttreatment and after 30 days.

3. The soils from Concord, OH and Macomb, IL were reported as silty clay loams; however, they are silt loams according to USDA soil textural classification system and were reported as such in this review.

4. The soils in which the nonextractable radioactivity was characterized were assumed to be 4 of the 5 soils described in Table 1. However, only the peat loam soil can be accurately characterized because insufficient descriptions of the silty clay loam (silt loam) and the sandy loam soils were provided. It was also unclear as to whether the soils were those originally treated with 15 ppm [^{14}C]chlorothalonil and aged 30 days (then an additional 60 days) or if they were separate soil samples treated with an unspecified amount of the test substance and aged 3 months.

Metabolism - Anaerobic Soil (00040545)

1. The treated soils were aged aerobically until more than half of the parent compound had degraded; only 7-14% of the radioactivity was detected as chlorothalonil at the time soils were converted to anaerobic conditions.

2. The design of the apparatus used to incubate the aged soil aerobically for 45 and 60 days may not have adequately aerated the soil. It is suspected that the soils intended to incubate aerobically became partially anaerobic during the study.

Mobility - Leaching and Adsorption/Desorption (00040546)

1. The [^{14}C]chlorothalonil- and [^{14}C]DAC-3701-treated soils were not maintained a constant temperature during the aging period. The greenhouse conditions were insufficiently described.

2. The [^{14}C]chlorothalonil-treated soils were aged aerobically for an excessive amount of time prior to the investigation of mobility; only 7-14% of the parent compound remained in the soil at this time.

3. Sampling intervals and analyses for DAC-3701 aged in soil under greenhouse conditions were not reported (insufficient data to support the stability or rate of degradation of [^{14}C]DAC-3701 in aerobic soil under greenhouse conditions for 30 days).

4. Values of soil/water relationships (K_d) were not reported for chlorothalonil- or DAC-3701-treated soils.

Table 1. Soil characteristics.

Soil type	Location	Sand	Silt	Clay	Organic matter	pH
				%		
Silt loam[a]	Concord, OH	7.8	72.3	20.0	1.2	6.7
Sandy loam	Painesville, OH	62.2	31.0	6.8	3.2	6.0
Silt loam[a]	Macomb, IL	0.6	73.6	25.8	2.3	5.1
Sandy loam[b]	Tulia, TX	54.0	25.0	19.5	1.6	8.0
Peat loam	IA	29.7	50.0	20.3	7.2	7.0

[a]These soils were reported to be silty clay loam soils; see Discussion No. 3 under Metabolism - Aerobic Soil.

[b]The mechanical analysis for this soil adds up to only 98.5%.

Table 2. Distribution, characterization, and calculated half-life of [^{14}C]-chlorothalonil residues in five soils aged aerobically in the greenhouse for 30 days.

Soil/location	Radioactivity distribution (%)[a]							
	Chlorothalonil	DAC-3701[b]	DS-19221[c]	Water-solubles	Polar organic extractables	Nonextractables	Rate constant[d] (K)	Chlorothalonil calculated half-life (days)
Silt loam (OH)	7.4	5.1	2.3	24.4	9.4	47.6	0.087	7.97
Sandy loam (OH)	10.2	10.9	4.8	19.2	4.7	44.5	0.076	9.12
Silt loam (IL)	13.5	7.7	6.1	20.3	6.2	33.4	0.067	10.34
Sandy loam (TX)	2.7	19.3	1.4	23.5	4.1	44.3	0.120	5.77
Peat loam (IA)	4.4	17.2	5.0	21.2	5.4	38.6	0.104	6.66

[a]Percent of applied.

[b]4-Hydroxy-2,5,6-trichloroisophthalonitrile.

[c]3-Cyano-2,4,5,6-tetrachlorobenzamide.

[d]Rate constant assuming first order kinetics.

Table 3. Distribution of radioactivity between various soil fractions in nonsterile [^{14}C]chlorothalonil-treated soils (aged 3 months).

Soil type[a]	Extracted by acid acetone			Extracted into NaOH	Humin	Humus	Fulvic acid	Percent accountability
	Method I[b]	Method II[c]	Average					
	Percent of applied radioactivity							
Silt loam	80.9	76.5	78.7	13.1	10.8	2.9	10.6	103.0
Silt loam	73.9	72.6	73.2	17.8	11.6	4.7	9.9	99.4
Peat loam	66.2	65.7	65.9	19.4	16.8	--	9.4	--
Peat loam	70.1	62.9	66.5	23.2	14.9	10.1	11.2	102.7
Sandy loam	60.4	63.5	61.9	14.3	17.4	1.5	11.4	92.2
Sandy loam	50.0	52.5	51.2	18.7	19.5	4.1	12.4	87.2
Sandy loam	61.1	--	61.1	21.0	12.0	7.0	17.7	97.8
Sandy loam	60.5	59.7	60.1	35.7	13.5	10.2	10.2	94.0

[a]Duplicate samples of nonsterile soils of each soil type.

[b]Method I to determine extractability consisted of comparing radioactivity in the acid-acetone wash to applied radioactivity

[c]Method II to determine extractability of comparing radioactivity remaining on soil after acid-acetone extraction to applied radioactivity.

[d]Percent Accountability = $\frac{^{14}C \text{ extracted into acid-acetone} + ^{14}C \text{ in Humin} + ^{14}C \text{ in Humus} + ^{14}C \text{ in Fulvic Acid}}{^{14}C \text{ Applied}} \times 100$

Table 4. Distribution of radioactivity in [^{14}C]chlorothalonil treated soil aged aerobically for 30 days and then incubated anaerobically.[a]

Component	Silt loam (OH)			Sandy loam (OH)			Peat loam (IA)		
	Aerobic aging	Anaerobic incubation		Aerobic aging	Anaerobic incubation		Aerobic aging	Anaerobic incubation	
	30 days	45 days	60 days	30 days	45 days	60 days	30 days	45 days	60 days
Flood Water	--	9.5	10.2	--	5.7	7.7	--	3.1	2.5
Soil									
Aqueous extract	24.4	8.9	8.4	19.2	11.7	9.3	21.2	9.7	11.3
Ether extract	53.5	17.5	16.0	65.6	30.4	24.5	65.7	38.3	36.2
Chlorothalonil[b]	7.4	3.6	2.8	10.2	7.5	6.8	4.4	10.2	7.7
DAC-3701[b,c]	5.1	5.5	4.8	10.9	12.0	6.3	17.2	5.2	18.0
DS-19221[b,d]	2.3	2.1	1.6	4.8	3.0	1.0	5.0	14.4	4.9
Polar material[b,e]	9.4	7.1	2.6	4.7	6.0	4.1	5.4	2.2	3.5

[a]All values expressed as percent of ^{14}C applied.

[b]Total extracted from flood water and soil.

[c]4-Hydroxy-2,5,6-trichloroisophthalonitrile.

[d]3-Cyano-2,4,5,6-tetrachlorobenzamide.

[e]Origin on TLC plates.

Table 5. The distribution of radioactivity in [^{14}C]chlorothalonil treated soil aerobically incubated for 30, 45, and 60 days.[a]

Component	Silt loam (OH)			Sandy loam (OH)			Peat loam (IA)		
	30 days	45 days	60 days	30 days	45 days	60 days	30 days	45 days	60 days
Soil									
Aqueous extract	24.4	22.0	22.2	19.2	23.5	18.3	21.2	10.2	19.4
Ether extract	53.5	23.1	27.1	65.6	27.3	28.8	65.7	42.0	39.2
Chlorothalonil	7.4	5.5	6.7	10.2	6.7	7.0	4.4	12.7	4.4
DAC-3701[b]	5.1	4.9	5.5	10.9	9.3	8.4	17.2	e	21.7
DS-19221[c]	2.3	2.5	2.2	4.8	1.9	1.1	5.0	16.2	4.4
Polar material[d]	9.4	5.0	6.4	4.7	5.0	5.1	5.4	1.1	4.2

[a]All values expressed as percent of ^{14}C applied.

[b]4-Hydroxy-2,5,6-trichloroisophthalonitrile.

[c]3-Cyano-2,4,5,6-tetrachlorobenzamide.

[d]Origin on TLC plate.

[e]Data in report illegible.

Table 6. Distribution of radioactivity in leached soil columns containing aged [^{14}C]chlorothalonil and [^{14}C]DAC-3701.[a]

Soil type	Column fraction (cm)	Percent of applied radioactivity[b]	
		Chlorothalonil	DAC-3701
Silt loam (Concord, OH)	0-5	73.4	53.5
	5-10	3.9	29.7
	10-15	1.9	1.7
	15-20	1.3	0.6
	20-25	1.1	0.5
	25-30	1.0	1.0
	Leachate[c]	12.4	4.3
Sandy loam (Painesville, OH)	0-5	64.1	40.5
	5-10	9.8	33.9
	10-15	2.4	6.3
	15-20	1.6	0.7
	20-25	1.0	0.7
	25-30	0.6	0.5
	Leachate	9.8	1.4
Silt loam (Macomb, IL)	0-5	58.2	46.1
	5-10	4.7	17.2
	10-15	2.5	5.4
	15-20	2.2	6.4
	20-25	1.2	0.6
	25-30	1.1	0.4
	Leachate	22.1	2.3
Peat loam (IA)	0-5	69.5	63.7
	5-10	2.9	6.5
	10-15	3.2	4.8
	15-20	1.8	3.5[d]
	20-25	1.4	--
	25-30	1.9	--
	Leachate	11.0	2.1
Sandy loam (Tulia, TX)	0-5	--[e]	9.7
	5-10	--	9.8
	10-15	--	15.4
	15-20	--	25.3
	20-25	--	10.9
	25-30	--	3.1
	Leachate	--	5.3

[a]Columns (1.8 x 30 cm) were eluted with 0.5 inches water/day for 45 days.

[b]Recovery of radioactivity in chlorothalonil- and DAC-3701-treated columns was 89.5-95.0 and 78.4-91.3%, respectively.

[c]Total radioactivity collected over 45 days.

ENVIRONMENTAL FATE DATA REQUIREMENTS
Part 158.130
Response to Chlorothalonil Registration Standard

DEGRADATION STUDIES

161-1. Hydrolysis

Study No. 00040539 (EPA Accession No. 096466) provides much insight into the potential for chlorothalonil to hydrolyze. SDS Biotech has another study underway which should provide the additional information requested by the Registration Standard. However, that study is not scheduled for completion until about mid-1985.

PHOTODEGRADATION

161-2. Photodegradation In Water

Resubmitted herewith is a study entitled, "Photodegradation of Daconil in Aqueous Systems", which was previously submitted in Pesticide Petition No. 6F1749, pp. J34-J35 (EPA Accession No. 096466).

161-3. Photodegradation in Soil

Resubmitted herewith are three studies which were previously submitted as part of Pesticide Petition No. 6F1749, pp. J46-J109 (EPA Accession No. 096466).

The propensity of chlorothalonil to bind to soil should minimize any potential for photodegradation in soil.

161-4. Photodegradation in Air

Submitted herewith in the Product Chemistry Section of this response to the Chlorothalonil Registration Standard is a study entitled, "Determination of Vapor Pressure of 2,4,5,6-Tetrachloroisophthalonitrile (Chlorothalonil, DS-2787)", (Document No. 416-3EI-80-0162-001). Due to the very low vapor pressure of chlorothalonil, a photodegradation study in air should not be required.

METABOLISM STUDIES

162-2. Anaerobic Soil

SDS Biotech is conducting an anaerobic aquatic study which should be completed about mid-1985. This study, according to EPA Guidelines, should satisfy both anaerobic soil and anaerobic aquatic data requirements.

MOBILITY STUDIES

163-1. Leaching and Adsorption/Desorption

Although several studies have been previously submitted (refer to Data Requirement Listing for the Owner Submission Method of Support) to the EPA providing substantial information, an aged soil leaching study is being conducted by SDS Biotech. A protocol for this study is submitted herewith. Initiation of the study has been delayed due to a move of SDS Biotech's research investigators to different laboratory facilities. Results of this study are now expected to be available near the end of 1985.

A satisfactory adsorption/desorption study for chlorothalonil has been submitted previously. A satisfactory aged soil leaching study on the metabolite, SDS-3701, was submitted February 25, 1976 (Pesticide Petition No. 6F1749, Section J) in a study entitled, "Degradation of Daconil and Its Metabolite, 4-Hydroxy-2,5,6-trichloroisophthalonitrile in Soil: Part III, Leaching of Degradation Products".

163-2. Volatility (Lab)

A study entitled "Determination of Vapor Pressure of 2,4,5,6-Tetrachloroisophthalonitrile (Chlorothalonil, DS-2787)" (Document No. 416-3EI-80-0162-001) is submitted herewith in the Product Chemistry Section. Due to the very low vapor pressure of chlorothalonil, additional laboratory volatility studies should not be required. The strong potential for adsorption of chlorothalonil onto soil is also considered to greatly reduce the potential for volatility.

163-3. Volatility (Field)

Because of the very low vapor pressure of chlorothalonil, field studies should not be required.