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DYNAMAC
CORPORATION

CHLOROTHALONIL

TASK 1: REVIEW AND EVALUATION OF INDIVIDUAL STUDIES

Contract No. 68-01-6679

Final Report

December 2, 1983

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

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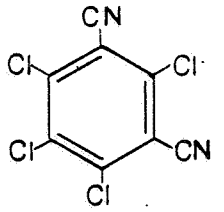
CHLOROTHALONIL

CHLOROTHALONIL, BRAVO, DACONIL 2787,
EXOTHERM TERMIL, FORTURF



Tetrachloroisophthalonitrile

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2	Szalkowski, M.B. 1976. Photodegradation of Daconil in aqueous systems.
3	Wolfe, A.L. 1972. The effect of ultraviolet radiation on 4-hydroxy-2,5,6-trichloroisophthalonitrile in aqueous solutions.
4	Szalkowski, M.B. 1975. Photodegradation of Daconil and 4-hydroxy-2,5,6-trichloroisophthalonitrile on silica gel plates.
5	Szalkowski, M.B. 1976. Photodegradation of Daconil and its metabolite, 4-hydroxy2,5,6-trichloroisophthalonitrile, on inert surfaces.
6	Szalkowski, M.B. 19??. Photodegradation and mobility of Daconil and its major metabolite on soil thin films.
7	Szalkowski, M.B. 1976. Degradation of Daconil and its metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile, in soil.
	Szalkowski, M.B. 1976. Anaerobic soil metabolism of Daconil.
	Szalkowski, M.B. 1976. Leaching of degradation products.
	Szalkowski, M.B. 1976. Bound residue study: Daconil.
8	Szalkowski, M.B., J.J. Mannion, D.E. Stallard, et al. 1979. Quantitation and characterization of the biotransformation products of 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in soil.
9	Stallard, D.E., and A.L. Wolfe. 1967. The fate of 2,4,5,6-tetrachloroisophthalonitrile (Daconil 2787) in soil.
10	Wolfe, A.L. 1971. C^{14} Daconil 2787 degradation in soil.

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Study	
11	Wolfe, A.L., and D.E. Stallard. 1968. The fate of DAC-3701 (4-hydroxy-2,5,6-trichloroisophthalonitrile) in soil.
12	Szalkowski, M.B. 1976. Effect of microorganisms upon the soil metabolism of Daconil and 4-hydroxy-2,5,6-trichloroisophthalonitrile.
13	Szalkowski, M.B., and D.E. Stallard. 1980. Adsorption of chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) DS-2787.
14	Wolfe, A.L., and D.E. Stallard. 1965. Residue of tetrachloroisophthalonitrile (Forturf) in soil resulting from foliar application to established turf.
15	Stallard, D.E., A.L. Wolfe, and W.C. Duane. 1972. Evaluation of the leaching of chlorothalonil under field conditions and its potential to contaminate underground water supplies.
16	Szalkowski, M.R., D.E. Stallard, and R.T. Bachand, Jr. 1979. Absorption and translocation of 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil) metabolites in soil by leafy, root and fruiting crops--A laboratory rotational crop study: Research Report R-78-0020.
17	Szalkowski, M.B., J.P. Marciniszyn, J.C. Killeen, Jr., et al. 1981. Accumulation, distribution and depuration of ^{14}C-residues of ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in channel catfish (Ictalurus punctatus) under static aquatic conditions: Document No. 077-3EI-80-0205-003.
18	Szalkowski, M.B., J.P. Marciniszyn, J.C. Killeen, Jr., et al. 1981. Characterization and quantitation of ^{14}C-residues in water and fish exposed to ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) in a flow-through aquatic system: Document No. 268-3EI-79-0031-002.
	Szalkowski, M.B., and D.E. Stallard. 1980. Characterization of ^{14}C-residues in water and fish exposed to ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) in a flowthrough aquatic system.
	Szalkowski, M.B., D.E. Stallard, and R.T. Bachand, Jr. 1979. Residue accumulation study in bluegill sunfish with ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) under flow-through conditions: Protocol No. RM-78-0017.
	Szalkowski, M.B., D.E. Stallard, J.A. Ignatoski, et al. 1980. Accumulation, distribution and depuration of ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitril (DS-3701) in bluegill sunfish (Lepomis macrochirus) under flow through aquatic conditions: Document No. 115-3EI-80-0176-001.

Study	
19	Szalkowski, M.B., D.E. Stallard, J.A. Ignatoski, et al. 1980. Accumulation, distribution and depuration of ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in bluegill sunfish (Lepomis macrochirus) under flow-through aquatic conditions: Document No. 079-3EI-80-0120-001.
	Szalkowski, M.B., D.E. Stallard, and R.T. Bachand, Jr. 1979. Residue accumulation study in bluegill sunfish with ^{14}C-2,4,5, 6-tetrachloroisophthalonitril (chlorothalonil) under flow-through conditions: Protocol No. RM-78-0018.
	Szalkowski, M.B., J.P. Marciniszyn, J.C. Killeen, Jr., et al. 1981. Characterization and quantitation of ^{14}C-residues in water and fish exposed to ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in a flow-through aquatic system: Document No. 116-4EI-81-0016-003.
20	Sleight, B.H. 1972. Exposure of fish to ^{14}C-labeled chlorothalonil (DAC-2787, tech.): accumulation, distribution, and elimination of residues.
21	Sleight, B.H. 1972. Exposure of fish to ^{14}C-labeled DAC-3701: accumulation, distribution, and elimination of residues.
22	Johnston, E.F. 1981. Soil disappearance studies with Benlate fungicide and Bravo 500 F fungicide, alone and in combination: Document No. AMR-06-81.
23	Capps, T.M., J.P. Marciniszyn, A.F. Markes, and J.A. Ignatoski. 1982. Document No. 555-4EF-81-0261-001, Section J, Vol. VI.

CASE GS0097 CHLOROTHALONIL STUDY 1 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 0510

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00040539 CONTENT CAT 01

Szalkowski, M.B. 1976. Hydrolysis of Daconil and its metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile, in the absence of light at pH levels of 5, 7, and 9. Updated method. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:096466-B.

SUBST. CLASS = T; CHEM R29053 IS TRANSF. PRODUCT OF CHEM 081901
OTHER SUBJECT DESCRIPTORS SEC: EFB -30-051015

DIRECT RVW TIME = 11 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. Ring-labeled [^{14}C]chlorothalonil, at 0.5-1.5 ppm, was stable to hydrolysis for up to 72 days in aqueous solutions buffered at pH 5 and 7 and maintained at room temperature. In these solutions, >94 and 96.3% of the applied radioactivity remained as unchanged parent compound after 49 and 72 days of incubation, respectively.

   At pH 9, chlorothalonil hydrolyzed with half-lives of 33-43 days and 28-72 days in solutions treated with ring-labeled [^{14}C]chlorothalonil at 0.52 and 1.5 ppm, respectively. After 72 days of incubation, pH 9 buffered solutions treated with chlorothalonil at 1.5 ppm contained 36.4% chlorothalonil, 48.9% 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19211), and 11.3% 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701).

The degradate, DAC-3701 at 1000 ppm, was stable to hydrolysis in aqueous solutions buffered at pH 5, 7, and 9; ~99% of the applied radioactivity was identified as DAC-3701 after 72 days of incubation at room temperature.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the hydrolysis of chlorothalonil and DAC-3701 in aqueous buffer solutions (pH 5, 7, and 9), and by identifying DS-19221 and DAC-3701 as hydrolysis products of chlorothalonil at pH 9. DS-19221 was shown to be formed in greater amounts than DAC-3701. However, no data were provided on the decline of DS-19221 in water.

MATERIALS AND METHODS:

Hydrolysis was studied using ring-labeled [^{14}C]chlorothalonil (Daconil, Diamond Shamrock Corp., specific activity 3630 dpm/µg, 99.3% radiochemical purity), the degradate [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, Diamond Shamrock Corp., specific activity 4114 dpm/µg, 98.2% radiochemical purity), and benzene solutions (50 µg/ml) of nonradioactive chlorothalonil and DAC-3701 (99.8 and 98.0% pure, respectively, source unspecified).

Three buffers were prepared as follows: pH 5, 23.85 ml of 0.1 N NaOH and 50.00 ml 1 M potassium hydrogen phthalate diluted to 100 ml; pH 7, Fisher Scientific buffer solution; and pH 9, 21.30 ml 0.1 N NaOH and 50.00 ml 1 M boric acid diluted to 100 ml.

To each of three flasks, stock solutions (3 ml) of nonradioactive chlorothalonil were added and the benzene was evaporated. A 6 ml volume of the appropriate buffer and 294 ml of water were added to each flask to make a final concentration of 0.50 ppm. The pH 9 buffered solution was also fortified with 0.02 ppm [^{14}C]chlorothalonil to make a total concentration of 0.52 ppm. The flasks were maintained at room temperature and in darkness. Two additional samples were prepared in a similar manner using either [^{14}C]chlorothalonil at 1.5 ppm or a mixture of nonradiolabeled and [^{14}C]DAC-3701 at 1000 ppm. Sterile glassware and sterile distilled water were used in all preparations; sample sterility was maintained by the use of aseptic techniques.

At appropriate intervals (Tables 1 and 2), samples for analysis were prepared by acidifying 10-15 ml of each sample with 10 drops of sulfuric acid (1:1; presumably diluted with water) and extracting with 20-30 ml isopropyl ether. Total ^{14}C activity was determined in the aqueous and ether phases of the sample extracts by using LSC. The ether extracts were concentrated to dryness, diluted to a known volume (unspecified) and analyzed by using GLC equipped with an electron capture detector.

TLC analysis was conducted on concentrated ether extracts and non-labeled standards by using one of three solvent systems: 1) benzene:acetone (8:2) followed by benzene:methanol (2:1); 2) hexane:acetone (1:1); or 3) benzene:acetone (9:1). The spots on the plates were visualized by fluorescence and analyzed by using autoradiography. The radioactive spots were separated and assayed by LSC.

REPORTED RESULTS:

In the samples treated at 0.5 ppm, the chlorothalonil concentration decreased by ~80% (as determined by GLC) after 89 days in the pH 9 buffered solutions (Table 1). The pH 9 buffered solution contained 24% chlorothalonil, 22% DAC-3701, and 54% 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221) as determined by TLC and LSC. The identification of DS-19221 was confirmed by GLC and MS. The decline of chlorothalonil in the pH 9 buffer followed first order kinetics. Unidentified, nonextractable water soluble residues were ≤1.3%. No hydrolysis occurred in solutions at pH 5 and pH 7 containing chlorothalonil at 0.5 ppm for 49 days; 89-day samples were not analyzed. The water solubility of the radioactivity was observed to increase by 50.5% in the pH 9 buffer and ~17% in the pH 5 and pH 7 buffers over a 72-day period in solutions treated with chlorothalonil at 1.5 ppm (applied as [^{14}C]chlorothalonil in excess of its water solubility). Chlorothalonil hydrolysis was ≤9.6% in the pH 5 and pH 7 buffered solutions at up to 72 days after treatment. At pH 9, 36.4% of the applied chlorothalonil remained in solution; the degradates DS-19221 and DAC-3701 were detected (day 72) at 48.9 and 11.3%, respectively, as determined by TLC and LSC (Table 2). Unidentified, nonextractable water-soluble residues were ≤5.1%. DAC-3701, at ~1000 ppm, was found to be stable to hydrolysis at pH 5, 7, and 9. Only parent compound was found after 72 days.

DISCUSSION:

1. The pH 5 buffer listed 50.00 ml of 1 M $KHC_8H_4O_8$, which was assumed to be erroneous, and was interpreted in this report as potassium hydrogen phthalate.

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

Table 1. Effect of time and pH upon the decline of chlorothalonil (ppm) in aqueous solutions.[a]

Sampling interval (days)	pH 5	pH 7	pH 9
0	0.43	0.43	0.40
14	0.44	0.40	0.36
33	0.39	0.45	0.33
43	0.44	0.42	0.22
49	0.48	0.42	0.23
89	--[b]	--	0.08

[a]Application rate 0.5 ppm for pH 5 and 7 and ~0.52 ppm for pH 9.

[b]--; not determined.

Table 2. Effect of time upon the decline of chlorothalonil and formation of hydrolysis products under various pH conditions.[a]

Sampling interval (days)	pH 5				pH 7				
	Total residues in solution (ppm)	Chlorothalonil	DS-19221[b]	DAC-3701[c]	Total residues in solution (ppm)	Chlorothalonil	DS-19221	DAC-3701	Total residues in solution (ppm)
		%				%			
0	0.89	97.4	0.8	0.8	0.96	90.4	0.3	5.7	0.95
7	0.87	97.4	1.6	0.3	0.90	96.8	0.3	2.5	1.02
14	0.91	--[d]	--	--	0.92	--	--	--	1.16
28	0.94	95.2	4.3	0.2	0.94	95.3	1.1	1.6	1.30
72	1.04	98.9	0.4	0.0	1.13	96.3	2.1	0.9	1.43

[a]Application rate 1.5 ppm.

[b]DS-19221; 3-cyano-2,4,5,6-tetrachlorobenzamide.

[c]DAC-3701; 4-hydroxy-2,5,6-trichloroisophthalonitrile.

[d]--; not determined.

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

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is scientifically valid.

2. Ring-labeled [^{14}C]chlorothalonil was not degraded in acid solution (0.1 N HCl) after 90 hours of exposure to 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.

3. This study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because the exposure period for chlorothalonil in aqueous 0.1 N HCl solution was insufficient to estimate a half-life, photodegradawas 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 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 R.S., 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 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 establish a decline curve for chlorothalonil in the pH 7 buffered solution.

4. The experiment was not stated to have been conducted at 25 ± 1 C.

5. The wavelength distribution and intensity of the light source were not provided; however, in Study 4 (00040542) the reported peak for this sunlamp was 297 nm and the intensity was 35 E-vitons/in^2 at a distance of 30 inches.

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

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		0.1N 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 3 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 00087281 CONTENT CAT 01

Wolfe, A.L. 1972. The effect of ultraviolet radiation on 4-hydroxy-2,5,6-trichloro-isophthalonitrile in aqueous solutions. Unpublished study received Aug. 11, 1970 under 1F1024; submitted by Diamond Shamrock Chemical Co., Cleveland, OH; CDL:09333-A.

SUBST. CLASS = T; CHEM R29121 IS TRANSF. PRODUCT OF CHEM 081901

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

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CONCLUSION:

Degradation - Photodegradation in Water

This study is scientifically invalid because photolysis was studied in non-sterile tap water and dark controls were not used. Additionally, this study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test solutions were not buffered or maintained at 25 ± 1 C, a materials balance was not conducted, and insufficient information was provided regarding the light source.

MATERIALS AND METHODS:

4-Hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, Diamond Shamrock Corp., pure compound, purity unspecified), a known degradate of chlorothalonil, was dissolved in tap water (0.020 g/400 ml). Fifty milliliters of the stock solution was placed eight inches below a Sears 275 watt sunlamp which delivered 35 E-vitons/in^2 at a distance of 30 inches. Under the experimental conditions, 1 hour of exposure to the sunlamp at 8 inches was calculated to approximate 41 hours of midsummer sunlight or 3.4 12-hour days of sunlight. Solutions were maintained at 18 and 40 C for up to 3 hours. At 18 C, pH 6 solutions were prepared with 0.05 N H_2SO_4 and at 40 C with 0.05 N HCl. All solutions at pH 7 and 8 were prepared with 0.05 N NaOH. At 40 and 18 C, samples were taken after 1, 2, and 3 hours and after 1 and 2 hours of irradiation, respectively

Samples were combined with 10 ml isopropyl ether and 5 drops of 50% H_2SO_4 and shaken. One milliliter of the ether extract was combined with 1 ml of the alkylating agent PTT reagent (1-n-propyl-3-p-tolyltriazine in pure ethyl ether, 1.8 mg/ml) and the reaction mixture was allowed to stand for 30 minutes. The solvent was removed with a stream of dry air. To ensure complete propylation, an additional 3 ml of alkylating agent (PTT reagent) was added, and the mixture was allowed to stand (10 minutes). The solvent was again evaporated, and the sample was brought up to an appropriate volume in benzene and analyzed for DAC-3701 by using electron-capture GC. Residues were characterized by using TLC with an ethyl acetate:methylene dichloride: acetic acid:acetone:methanol (8:8:2:1:1) solvent system.

REPORTED RESULTS:

The photodegradation of DAC-3701 is shown in Table 1. Analysis by TLC indicated the presence of DAC-3701 and at least three unidentified degradates.

DISCUSSION:

1. Dark controls were not used and a materials balance was not conducted.

2. Tap water was used to prepare the test solutions instead of sterile distilled or deionized water.

3. Application rates for the pH 6 and 8 test solutions were not confirmed.

4. At least 3 degradation products were separated by TLC, but they were not identified.

5. The wavelength distribution was not reported.

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

Table 1. Photodegradation of DAC-3701 in aqueous nonbuffered solutions.[a]

Exposure time (hr)	Temperature (C)	DAC-3701 (ppm)		
		pH 6	pH 7	pH 8
0	40	--[b]	52	--
1	40	36	21	21
2	40	5	5	10
3	40	2	1	4
0	18	--	53	--
1	18	24	24	26
2	18	10	11	11

[a]One hour of irradiation approximates 41 hours midsummer sunlight.

[b]--; not determined.

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

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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 characterized as to its composition of wavelengths below 297 nm.

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 wit 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 analyzed 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 light source was not characterized as to its composition of wavelengths below 297 nm.

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 30 inches. 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 study showed 10.5% parent compound, 31% DAC-3701 and 38% 3-cyano-2,4,5,6-tetrachloro 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 light source was not characterized as to its composition of wavelengths below 297 nm.

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 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 metabo-. lite 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

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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 mobility 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 located by using chromatography, 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 light source was not characterized as to its composition of wavelengths below 297 nm.

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 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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CONCLUSIONS:

Metabolism - Aerobic Soil (00040544, 00087352)

1. This portion of the study is scientifically valid.

2. [^{14}C]Chlorothalonil was calculated to degrade with half-lives of 7.97, 9.12, 10.34, 5.77, and 6.66 days in Ohio silt loam, Ohio sandy loam, Illinois silt loam, Texas sandy loam, and Iowa peat loam soils, respectively. After 30 days of aerobic incubation (80.6-95 F, 80% of field moisture capacity) of [^{14}C]chlorothalonil-treated soils, the percentage of radioactivity identified as chlorothalonil was 7.4, 10.2, 13.5, 2.7, and 4.4% in the Ohio silt loam, Ohio sandy loam, Illinois silt loam, Texas sandy loam, and Iowa peat loam soils, respectively. Remaining soil radioactivity was distributed among nonextractable residues (32.7-48.6%), water soluble compounds (18.5-25.8%), polar organic extractables (3.2-10.6%), and the degradates, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) (4.2-21.0%) and 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221) (0.5-6.6%) (00040544).

   Bound 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. In the fulvic acid, 34-48% of the radioactivity partitioned into the ether phase was identified as DAC-3701 (00087352).

3. This 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 is scientifically invalid because an insufficient quantity of chlorothalonil remained (7-14%) in the aged, treated soils at the time anaerobic conditions were established to adequately assess degradation. 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)

1. This portion of the study is scientifically valid.

2. After leaching aged (30-day) silt loam, sandy loam, and peat loam soil columns (30-cm height) with 22.5 inches of water, 58-73% of the applied radioactivity was found in the top 5 cm of soil, 3-10% at the 5- to 10-cm depth, 2-3% at the 10- to 15-cm depth, and <2.3% in the remaining 15- to 30-cm depth. Chlorothalonil and its degradates, DAC-3701 and DS-19221, were identified in the top 5 cm of soil; however only DAC-3701 was found below this depth. In

columns containing aged [^{14}C]DAC-3701-treated soils, the majority of the radioactivity was found in the top 15 cm of soil with the exception of a sandy loam soil in which radioactivity was concentrated at the 15- to 30-cm depth.

3. This portion of the study partially satisfies EPA Data Requirements for Registering Pesticides (1983) by providing information on the mobility of the chlorothalonil degradate DAC-3701 in two sandy loam soils, two silt loam soils, and a peat loam soil. However, data on the mobility of aged chlorothalonil do not fulfill requirements because the 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 during the aging process.

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 of five air-dried soils (Table 1) placed in separate pint jars The solvent was allowed to evaporate, and the treated soils were mixed to yield a final concentration of 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 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 were air-dried and extracted with an 80:20 mixture of acetone and 0.3 N hydrochloric acid. Duplicate 0.5-ml portions of the supernatant remaining after soils had settled were removed and quantified by using LSC. Counting efficiencies ranged between 55 and 78%. 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 subjected to combustion analysis. In Comparison Method II, the soil remaining from the acid-acetone extraction was analyzed for unextracted radioactivity by total combustion to $^{14}CO_2$. The extracted residues were partitioned into aqueous and organic (isopropyl ether) phases, and identified and quantified using TLC, autoradiography, and radiochromatogram scanning, followed by LSC. Counting efficiencies for the aqueous and ether phases were 74-85 and 89-90%, respectively.

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 soils (peat loam, silty clay loam, and two sandy loams; assumed to be 4 of the 5 soils in Table 1) were treated with [^{14}C]-chlorothalonil and allowed to age 3 months. After aging, soil subsamples 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 of the extracted soils was air dried and total radioactivity was determined by combustion. Another portion 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)

Subsamples of three treated soils from the aerobic soil metabolism portion of this study (silt loam and sandy loam soils from Ohio and peat loam soil from Iowa; 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 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 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. Soil samples were removed after 45 and 60 days, and quantified 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 ether phase was characterized and quantified by using TLC and LSC.

Mobility - Leaching and Adsorption/Desorption (00040546)

Aged [^{14}C]chlorothalonil- and [^{14}C]DAC-3701-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.

REPORTED RESULTS:

Metabolism - Aerobic Soil (00040544, 00087352)

Immediately after treatment, >90% of the radioactivity on TLC plates was in the R_f region of chlorothalonil and DAC-3701 in soils treated with [^{14}C]chlorothalonil and [^{14}C]DAC-3701, respectively. After 30 days of aging, the radioactivity on TLC plates of soil treated with [^{14}C]chlorothalonil was distributed among chlorothalonil, the degradates DAC-3701 and 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221), water-soluble compounds, polar organic extractables and nonextractables (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. In the fulvic acid, 34-48% of the radioactivity partitioned into the ether phase was identified as DAC-3701.

Metabolism - Anaerobic Soil (00040545)

The ^{14}C distribution in soil incubated anaerobically for 45 and 60 days (following 30 days of aerobic aging) is summarized in Table 3. The chlorothalonil concentrations in soils after the aerobic aging were low and further reductions in the chlorothalonil concentrations during anaerobic incubation were not substantial. 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 2.8% after 60 days of anaerobic incubation; this decrease was from 10.2 to 6.8% in the sandy loam soil. An increase from 4.4 to 7.7% was reported for the peat soil. Changes in the concentrations of the DAC-3701 and DS-19221 degradates were similarly small (Table 3). 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 the extractable radioactivity (water and ether extracts combined) in all three soils tested (Table 3). 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 4).

Mobility - Leaching and Adsorption/Desorption (00040546)

Following application of ~22.5 inches of water over a 45-day period to [^{14}C]-chlorothalonil- and [^{14}C]DAC-3701-treated soils, 9.8-22.1 and 1.4-5.3% of the applied radioactivity was detected in the leachate, respectively (Table 5) The majority of the radioactivity remaining in the soil was distributed in

the top 5 cm in the chlorothalonil-treated columns and in the top 10 cm of the DAC-3701-treated 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 10-30 cm sections (Table 5). TLC analysis of [^{14}C]-chlorothalonil-treated soils identified chlorothalonil, DAC-3701, and DS-19221 in the 0- to 5-cm segment and primarily DAC-3701 in the 5- to 10-cm segment. TLC analysis of [^{14}C]DAC-3701-treated and aged soils identified only DAC-3701 throughout the column.

DISCUSSION:

Metabolism - Aerobic Soil (00040544, 00087352)

1. Treated soils were not incubated at a constant temperature.

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 treated soils were not maintained at a constant temperature and were aged aerobically for longer than one half-life of the parent compound prior to the investigation of mobility; only 7-14% of the parent compound remained in the soil at this time.

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

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]							
	Chloro-thalonil	DAC-3701[b]	DS-19221[c]	Water-solubles	Polar organic extractables	Nonex-tractables	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 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 4. 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 5. 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.

CASE GS0097 CHLOROTHALONIL STUDY 8 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 05

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00029407 CONTENT CAT 01

Szalkowski, M.B., J.J. Mannion, D.E. Stallard, et al. 1979. Quantitation and characterization of the biotransformation products of 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in soil. Unpublished study received Feb. 19, 1980 under 677-313; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:099248-E.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: EFB -30-050520 EFB -30-050525

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. [^{14}C]Chlorothalonil is degraded at an unknown rate in soil to 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701), 3-cyano-2,4,5,6-tetrabenzamide (DS-19221), trichloro-3-carboxybenzamide, 3-cyanotrichlorohydroxybenzamide, and 3-cyano-trichlorobenzamide. The soil was incubated at 24 C and 15% moisture content for more than 13 weeks.

3. This portion of the study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by identifying the five aforementioned degradates of chlorothalonil in aerobic soil. However, this portion of the study does not satisfy data requirements for rates of degradation because the pattern of decline of the parent compound and patterns of formation and decline of degradates were not established.

Mobility - Leaching and Adsorption/Desorption

This portion of the study is scientifically invalid because the test soil was ground and sieved to 0.59 mm, thus reducing the particle size and altering the soil characteristics. Additionally, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because the length of the soil column was not specified, and the chlorothalonil-treated soil was repeatedly retreated and aged for an excessive amount of time prior to leaching.

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

A sandy loam soil (61.3% sand, 30.4% silt, 8.3% clay, 1.6% organic matter, pH 5.6) was air dried, ground with a mortar and pestle, and sieved to ≤0.59 mm. The soil was treated with [^{14}C]chlorothalonil (Diamond Shamrock Corp., purity 99.5%, specific activity 32.8 mCi/mM) to yield 10 ppm, mixed, and moistened with water. The soil was then stored at 24 ± 1 C in a sealed container. The soil was re-treated with 10 ppm [^{14}C]chlorothalonil each week for 13 weeks and maintained at a moisture content of 15% (by weight). At the end of the 13-week period, the soil was stored at 24 ± 1 C until ~15% of the parent compound remained intact as determined by the quantitative characterization techniques described below.

Samples of the treated soil were air dried and combusted, and the released $^{14}CO_2$ was quantified by using LSC.

Mobility - Leaching and Adsorption/Desorption

A 20-g air-dried sample of the aged [^{14}C]chlorothalonil treated soil produced in the aerobic soil metabolism portion of this study was added to a chromatographic column (inside diameter 2.5 cm) and eluted 16 times with 50 ml of distilled water. Duplicate 5 ml aliquots of each leachate fraction were analyzed by LSC. The remainder of the leachate was evaporated to dryness. The residue was dissolved in methanol and analyzed by LSC. The leachate was also characterized by TLC and autoradiography. The residues were spotted onto TLC plates, developed 20 mm in methanol, and then scraped from the TLC plate and assayed individually by combustion and LSC. In addition, the TLC spots were rechromatographed to obtain pure compounds for analysis by MS.

The soil was extracted by stirring with acidified acetone. The mixture was filtered and the filter cake was reextracted twice. The combined extracts were analyzed by LSC. The extracted soil was air dried and analyzed by combustion and LSC as described above.

In order to generate sufficient quantities of [^{14}C]chlorothalonil residues, an additional portion (200 g) of treated soil was placed into a chromatograph column (inside diameter 5.5 cm) and eluted with distilled water, and the eluate was analyzed by TLC and MS.

REPORTED RESULTS:

Metabolism - Aerobic Soil

After repeated treatments and aging, the [^{14}C]chlorothalonil-treated soil contained 86.3% of the applied radioactivity, which was present as chlorothalonil, five degradation products, and unextractable residues (Table 1).

Mobility - Leaching and Adsorption/Desorption

After a modified soil column was eluted 16 times with 50 ml aliquots of distilled water, 40% of the residues leached through a soil column, 27% were unextractable, and 28% were extractable. The extractable residues consisted primarily of chlorothalonil, whereas the leachate contained primarily the degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) (Table 2).

DISCUSSION:

Metabolism - Aerobic Soil

1. Test protocols used in this study were not designed to establish the rate of chlorothalonil degradation or rates of formation and decline of degradates.

2. The test soil was ground and passed through a 0.59 mm sieve, thus reducing the particle size and altering the soil characteristics.

Mobility - Leaching and Adsorption/Desorption

1. The length of the soil column was not reported.

2. The soil was repeatedly treated and then aged for an excessive amount of time prior to column preparation for leaching; only 15% of the parent compound remained intact. In addition, the test soil was ground and sieved (0.59 mm) prior to treatment, thus altering its physical characteristics by reducing the particle size.

Table 1. Characterization and quantitation of [^{14}C]chlorothalonil residues in aged soil.

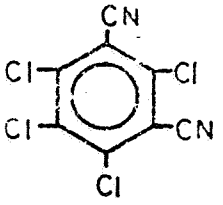
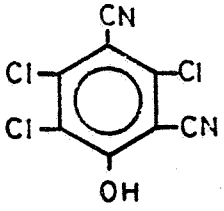
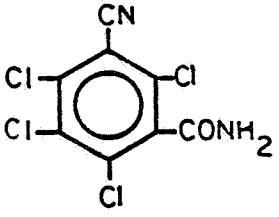
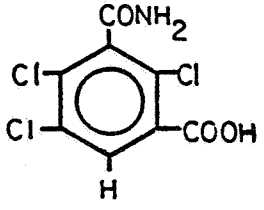
Chemical structure	Chemical name	Percent of applied chlorothalonil
	Unextractable residues	26.8
	2,4,5,6-Tetrachloroisophthalonitrile (chlorothalonil)	15.5
	4-Hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701)	22.3
	3-Cyano-2,4,5,6-tetrabenzamide (DS-19221)	10.4
	Trichloro-3-carboxybenzamide (or other isomeric form) (Unknown I)	4.3

Table 1. Characterization and quantitation of [^{14}C]chlorothalonil residues in aged soil. (continued)

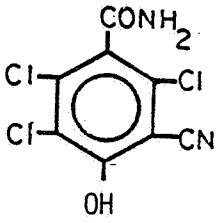
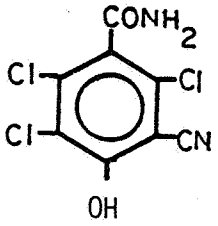
Chemical structure	Chemical name	Percent of applied chlorothalonil
	3-Cyanotrichlorohydroxybenzamide (or other isomeric form) (Unknown II)	3.8
	3-Cyanotrichlorobenzamide (or other isomeric form) (Unknown III)	3.2

Table 2. Chromatographic distribution of radioactivity in aged, leached soil and leachate.

Residue	Percent of total radioactivity on chromatogram	
	Soil	Leachate
Chlorothalonil	49.3	4.3
DAC-3701	16.0	43.9
DS-19221	11.6	17.8
Unknown I	2.9	8.6
Unknown II	4.5	6.3
Unknown III	3.6	5.3
Other	12.1	13.8

CASE GS0097 CHLOROTHALONIL STUDY 9 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 0505

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00087332 CONTENT CAT 01

Stallard, D.E., and A.L. Wolfe. 1967. The fate of 2,4,5,6-tetrachloroisophthalonitrile (Daconil 2787) in soil. Unpublished study received May 17, 1967 under 7F0599; submitted by Diamond Alkali Co., Cleveland, OH; CDL:090770-J.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: EFB-30-050510 EFB-30-050525 EFB-30-050520

DIRECT RVW TIME = 18 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. Chlorothalonil (WP) is degraded with half-lives of 4 to >40 days in soils ranging in texture from sand to silty clay loam, at 76-100 F and 6% soil moisture. Increasing either the soil moisture content (0.6-8.9%) or incubation temperature (76-100 F) enhanced chlorothalonil degradation. Soil pH (pH 6.5-8.0) had no effect on the degradation rate of chlorothalonil; however, soil sterilization greatly reduced the degradation rate. [^{14}C]Chlorothalonil degradation in silty clay loam soil yielded small amounts (8.7% of applied radioactivity) of an unidentified degradate and major amounts (69.4% of applied radioactivity) of the degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701), after 46 days of incubation at 36 C.

3. These aerobic soil metabolism studies do not fulfill EPA Data Requirements for Registering Pesticides (1983) because:

Experiment 1 - the test substance used was not technical grade or purer, and a materials balance was not provided; Experiment 2 - the purity of the test substance was not reported, and a materials balance was not provided; Experiment 3 - The test substance was uncharacterized, the soil moisture content was not reported, the incubation temperature was >30 C, and a materials balance was not provided; Experiment 4 - the test substance was uncharacterized, the test soil was not characterized, the soil moisture content was below 75% of field capacity, the incubation temperature was >30 C, and a materials balance was not provided; Experiment 5 - The test substance was uncharacterized, the test soil was not characterized, the soil moisture content was below 75% of field capacity, the incubation temperature was >30 C, and a materials balance was not provided; Experiment 6 - the test substance was uncharacterized, the soil moisture content was not reported, the incubation temperature was >30 C, and a materials balance was not provided; Experiment 7 - the soil moisture content was not reported, and the incubation temperature was >30 C.

Field Dissipation - Terrestrial

This portion of the study is scientifically invalid because the sampling intervals were insufficient to assess the dissipation of chlorothalonil in soil and contamination of control samples was not explained. In addition, these field dissipation studies would not fulfill EPA Data Requirements for Registering Pesticides (1983) because:

Georgia - characteristics of the test soil used were not reported, meteorological data such as soil and air temperature and rainfall were not provided, and the patterns of formation and decline of degradates were not determined; Mississippi - characteristics of the test soil used were not reported, meteorological data such as soil and air temperature and rainfall were not provided, and the patterns of formation and decline of degradates were not determined; Ohio - characteristics of the test soil used were not reported, meteorological data such as soil and air temperature and rainfall were not provided, and the patterns of formation and decline of degradates were not determined; South Dakota - meteorological data such as soil and air temperature and rainfall were not provided, and the patterns of formation and decline of degradates were not determined.

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

Experiment 1

Chlorothalonil (Daconil 2787, WP, Diamond Shamrock Corp., purity unspecified) was added to 2 kg of a Lismore silty clay loam soil (18.5% sand, 51.3% silt, 30.2% clay, pH 6.6, CEC 36.37 meq/100 g, 5.6% organic matter, 10% moisture) to give a concentration of 20-30 ppm. Treated soils were sampled immediately, transferred to glass jars, sealed with aluminum-lined screw caps, and incubated at 76, 86, or 100 F. Duplicate soil samples were removed at five intervals over a 38-day period and quantified by using a microcoulometric GC method.

Prior to GC analysis, the soil samples (100-g aliquots) were extracted by shaking for 2 hours with 250 ml of methylene chloride, and the extract was filtered. The extracts were evaporated to dryness, dissolved in xylene or benzene, and then an aliquot (20 µl) was injected into the GC apparatus. Recovery of chlorothalonil from spiked soil samples averaged 102%.

Experiment 2

Samples (1000-g) of Lismore silty clay loam soil (11.3% moisture) were placed in glass jars and fortified at 20 or 40 ppm with chlorothalonil (Daconil 2787, pure crystals, Diamond Shamrock Corp.). Treated soils were sampled immediatel and the jars were tightly capped and incubated at 76, 86, and 100 F. Samples were removed at intervals of 7, 14, and 36 days posttreatment and quantified by using GC as described previously in Experiment 1. Recovery of chlorothalonil from spiked soil samples averaged 86%.

Experiment 3

Samples of a Lismore silty clay loam soil were autoclaved (conditions unspecified), fortified at ~50 ppm with chlorothalonil (Daconil 2787, test substance uncharacterized, Diamond Shamrock Corp.), and maintained at 100 F (soil moisture unspecified). Soils were sampled at intervals of 1 hour and 2 and 7 days posttreatment, and quantified by using GC as described previously in Experiment 1.

Experiment 4

Soil samples (Table 1) were adjusted to 6.0% moisture, fortified at ~40 ppm with chlorothalonil (Daconil 2787, test substance uncharacterized, Diamond Shamrock Corp.), and sampled immediately. The treated soils were then incubated at 98 F; each was sampled once at 7, 14, 15, or 21 days and quantified by using GC as described previously in Experiment 1.

Experiment 5

Samples of Yohola and Portageville sandy loam soils, and a Lismore silty clay loam soil (Table 1) were adjusted to ~6%, ~3%, and ~1% moisture, and fortified with ~40 ppm of chlorothalonil (Daconil 2878, test substance uncharacterized, Diamond Shamrock Corp.). The treated soils were sampled immediately, incubated at 98 F, resampled after 21 days, and quantified by using GC as described previously in Experiment 1.

Experiment 6

Three samples of a Lismore silty clay loam soil were weighed into glass jars and the pH was adjusted to 6.5, 7.2, and 8.0 by adding NaOH, KH_2PO_4, and/or water. The samples were then fortified with ~45 ppm of chloro-

thalonil (Daconil 2787, test substance uncharacterized, Diamond Shamrock Corp.), incubated at 98 F, sampled at 2 hours and 5, 15, and 43 days posttreatment, and analyzed as described previously in Experiment 1.

Experiment 7

A 50-g sample of Lismore silty clay loam soil was treated with [^{14}C]chlorothalonil (Daconil 2787, specific activity 1.8 mCi/g, Diamond Shamrock Corp., purity unspecified) at 100 ppm and incubated at 36 C (soil moisture unspecified).

At intervals of 7, 35, and 46 days, soil samples were removed, extracted with acetone, and quantified by using a gas flow counter (~22% counting efficiency). The parent compound and degradates were separated by using TLC. The TLC plates were developed with benzene:chloroform:acetonitrile (5:5:2, v:v:v).

Field Dissipation - Terrestrial

Field dissipation studies were conducted at four geographical locations; Georgia, Mississippi, Ohio, and South Dakota as follows:

In Georgia, chlorothalonil (Daconil 2787, 75% WP, Diamond Shamrock Corp.) was applied to bermudagrass plots (soil uncharacterized) at 2 and 4 oz/1000 ft^2 (~4 and 8 lb ai/A) eight times between August 6, 1965 and October 13, 1965. Eight soil cores (9 x 0.75 inches) were taken from five treated plots and two control plots on a monthly basis beginning on December 8, 1965, ~2 months following the last application. The sample cores were divided into three 3-inch sections and composited.

The soil samples were air dried and extracted once with acetone using a solvent to soil ratio (v:w) of 1.75-2.5/1. The extracts were evaporated to dryness, redissolved in benzene, and quantified by using a microcoulometric GC. Recovery from spiked soil samples was 103 ±9%.

In Mississippi, chlorothalonil was sprayed on a 4-year-old bermudagrass sod (soil uncharacterized) at 2 and 4 oz/1000 ft^2 (~4 and 8 lb ai/A). Eight applications were made on the following dates in 1965: May 5 and 21; June 4 and 18; July 7 and 29; and August 13 and 26. Six soil core (9 x 0.75 inch) samples were taken on December 2, January 3, and February 1, divided into three 3-inch segments and composited. The soil samples were analyzed analyzed for chlorothalonil as described above; results were corrected for a mean recovery of 91%.

In Ohio, chlorothalonil was applied (November 8, 1964) at ~15 lb ai/A to each of three steel drums buried into the soil with drainage holes in the bottoms and containing 180 lb of well mixed sandy loam soil (soil not further characterized). One steel drum was left untreated to serve as a control. Five soil cores (18 x 0.75 inch) were taken from each drum on four sampling dates (June 18, September 15, November 15, 1965 and June 20, 1966), divided into 6-inch segments, and analyzed for chlorothalonil as described above. The limits of detection were 0.1 and 0.02 ppm for samples collected June 18 and September 15, 1965, respectively; recovery efficiency for samples collected September 15, was 71%.

In South Dakota, chlorothalonil was applied at 14 lb ai/A to a Lismore silty clay loam [0- to 16-inch profile: 18.0% sand, 50.6% silt, 31.4% clay, pH 6.2, CEC 35.02 meq/100 g; 5.6% organic matter (0- to 5-inch depth)]. Nine soil cores (10 x 0.75 inch) were taken and divided into 2-inch segments at 1 and 2 months posttreatment. Soil samples were analyzed as described above; recovery efficiency and sensitivity were not reported.

REPORTED RESULTS:

Metabolism - Aerobic Soil

Experiment 1

Half-lives of the parent compound (75% WP) were ~12, 7.5, and 6 days in silty clay loam soil incubated at 76, 86, and 100 F, respectively (Table 2). Temperature increased the rate of chlorothalonil degradation in silty clay loam soil.

Experiment 2

Chlorothalonil was degraded rapidly (degradation essentially complete after 36 days of incubation in tightly sealed glass jars) in silty clay loam soil fortified at 20 or 40 ppm; chlorothalonil degradation was more rapid at 100 F than at either 86 or 76 F (Table 2).

Experiment 3

Chlorothalonil degraded from 50 to 47 ppm 1 hour after the fortification of autoclaved silty clay loam soil, and 31 and 20 ppm after 2 and 7 days, respectively. As compared with a half-life of 2-3 days in unsterilized silty clay loam soil, the half-life of chlorothalonil in sterilized soil at 100 F was ~5 days.

Experiment 4

Half-lives for chlorothalonil in Lismore silty clay loam, Yohola sandy loam, Portageville sandy loam, Clarkton sand, silt loam, loam, and sandy loam soils were 4, 9, 9, 14, 36, 38, and >40 days, respectively (Table 1). Half-

lives for chlorothalonil in four unspecified soils ranged from 6 to 24 days. The soils were maintained at constant temperature (98 F) and moisture (6.0%).

Experiment 5

Half-lives for chlorothalonil in two sandy loam soils and a silty clay loam soil were greatest (>70 days) in samples containing the least amount of moisture (Table 3). Soil moisture content directly influenced the persistence of chlorothalonil in the two sandy loam soils and the silty clay loam soil.

Experiment 6

Half-lives for chlorothalonil in silty clay loam soil were <5 days at pH 6.5, 7.2, and 8.0 (Table 4).

Experiment 7

The distribution of radioactivity between the parent compound, Product A, Product B, and unextractable substances in silty clay loam soil was 26.6, 8.5, 43.5, and 21.5%, respectively, after 7 days of incubation; 3.8, 13.0, 64.3, and 18.9%, respectively, after 35 days of incubation; and 0, 8.7, 69.4, and 21.9%, respectively, after 46 days of incubation (Table 5). Product A was present in insufficient amounts to permit complete characterization; however, Product B was shown by a comparison of IR spectra and melting point to be identical to 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) Data were presented showing that Product A probably has the formula, $C_8HN_2OCl_3$ which is the same as that for DAC-3701. However, this compound appears to have a structure different from DAC-3701 since no hydroxyl group has been detected by MS. TLC confirms this observation by showing that Product A is less polar than DAC-3701. The exact structure of Product A has not been determined.

Field Dissipation - Terrestrial

The results reported for all four experiments are shown in Table 6.

Georgia

The average half-life for chlorothalonil at the lower rate (~4 lb ai/A) was 38 days and 56 days at the higher rate (~8 lb ai/A). Concentrations of chlorothalonil were found to be negligible after 10 months at the lower rate and 14 months at the higher rate. An identification of degradation products study in Georgia indicated the presence of trace amounts of a halogenated product similar in retention time to trimethylsilyl ether derivative of DAC-3701 (x-hydroxytrichloroisophthalonitrile).

Mississippi

A half-life of 26 days was calculated from the data obtained from the 98-130 day samples.

Ohio

The half-life of chlorothalonil between June and November was ~51 days.

South Dakota

The total amount of chlorothalonil found in the 2 month soil sample (0-10 inches) was 2.1% of the amount applied. It is apparent that chlorothalonil applied to soil of high organic content is almost quantitatively degraded within 1 month after application.

DISCUSSION:

Metabolism - Aerobic Soil

1. Experiment 1 - the test substance used was not technical grade or purer, and a materials balance was not provided.

2. Experiment 2 - the purity of the test substance was not reported, and a materials balance was not provided.

3. Experiment 3 - the test substance was uncharacterized, the soil moisture content was not reported, the incubation temperature was >30 C, and a materials balance was not provided.

4. Experiment 4 - the test substance was uncharacterized, the test soil was not characterized, the soil moisture content was below 75% of field capacity, the incubation temperature was >30 C, and a materials balance was not provided.

5. Experiment 5 - the test substance was uncharacterized, the test soil was not characterized, the soil moisture content was below 75% of field capacity, the incubation temperature was >30 C, and a materials balance was not provided.

6. Experiment 6 - the test substance was uncharacterized, the soil moisture content was not reported, the incubation temperature was >30 C, and a materials balance was not provided.

7. Experiment 7 - the soil moisture content was not reported, and the incubation temperature was >30 C.

Field Dissipation - Terrestrial

1. Characteristics of the test soils used in Georgia, Mississippi, and Ohio were not reported. Meteorological data such as soil and air temperature and rainfall were not provided.

2. Pre- and immediate postapplication soil samples were not collected and sampling did not commence in most of the studies until the majority of the applied (theoretical) chlorothalonil had dissipated.

3. Contamination of control samples in the Ohio experiment was not explained.

Table 1. The degradation of chlorothalonil in 11 soils.

Soil type	Source	pH	Chlorothalonil concentration (ppm) 0 days	14 days	Half-life estimates (days)
Lismore silty clay loam	SD	6.9	43	12[a]	4
--[b]	TX	8.2	42	8	6
Yohola sandy loam	LA	8.2	48	8[c]	9
Portageville sandy loam	MO	5.9	45	15	9
Clarkton sand	MO	6.9	45	23	14
--	TX	5.9	39	22	18
--	TX	7.8	54	34	18
--	SC	6.0	50	27[c]	24
Silt loam	TN	6.3	52	35[d]	36
Loam	TN	5.6	47	32[d]	38
Sandy loam	LA	6.5	41	41[d]	>40

[a]7 days incubation.

[b]Soil types were not specified.

[c]15 days incubation.

[d]21 days incubation.

Table 2. The effect of temperature on the degradation of chlorothalonil in a silty clay loam soil; first and second experiments.

Incubation time (days)	Chlorothalonil (ppm)								
	Sealed jars[a]			"Tightly" sealed jars[b]					
	20-30 ppm			20 ppm			40 ppm		
	76 F	86 F	100 F	76 F	86 F	100 F	76 F	86 F	100 F
0	23	29	20	22.6	20.0	19.4	36.9	37.4	38.5
6-7	20	13	6.7	7.5	4.2	3.7	14.0	10.2	4.4
10	15	10	6.1	--[c]	--	--	--	--	--
14	11	7.4	3.1	5.5	0.9	0.1	12.0	3.8	1.3
21	5.8	2.2	1.5	--	--	--	--	--	--
36-38	3.3	1.2	0.9	1.5	NR[d]	NR	5.3	NR	NR

[a]WP formulation used.

[b]"Pure crystals" used.

[c]--; Samples not collected.

[d]ND; data not reported.

Table 3. The effect of soil moisture on the degradation of chlorothalonil in three soils.

Soil	Moisture content (%)	Chlorothalonil (ppm) Sampling interval (days) 0	21	Half-life estimates (days)
Yohola sandy loam	0.6	45	46	>70
	3.6	46	25	24
	6.6	52	21	16
Portageville sandy loam	1.0	40	40	>70
	4.0	37	30	70
	7.0	46	26	26
Lismore silty clay loam	2.9	42	44	>70
	5.9	44	29	35
	8.9	43	5	6

Table 4. The effect of pH on the degradation of chlorothalonil in silty clay loam soil.

Incubation time	Average concentration of chlorothalonil (ppm) in soil		
	pH 6.5	pH 7.2	pH 8.0
2 hours	49	47	44
5 days	24	21	16
15 days	14	16	10
43 days	7	7	7

Table 5. Distribution of radioactivity (% of applied) in a silty clay loam soil treated with [^{14}C]chlorothalonil at 100 ppm and incubated at 36 C.

Sampling interval (days)	Chlorothalonil	Product "A"[a]	Product "B"[b]	Unextractable
7	26.6	8.5	43.5	21.5
35	3.8	13.0	64.3	18.9
46	ND	8.7	69.4	21.9

[a]Present in insufficient amounts to permit characterization.

[b]Shown by comparison of IR spectra and melting point to be identical to 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701).

Table 6. Concentration of chlorothalonil in soils treated with Daconil (75% WP).

Location	Application rate	Sampling interval (days)	Chlorothalonil (ppm) Sampling depth (inches) 0-3	3-6	6-12
Georgia	16 oz/1000 sq. ft.[a]	56	9.9	1.8	1.2
		97	3.7	0.4	0.2
		125	3.5	0.21	0.16
		217	0.69	0.04	0.16
		285	0.10	--[b]	--
		365	ND[c]	--	--
	32 oz/1000 sq. ft.[a]	56	25.7	5.5	3.4
		97	19.5	2.2	1.7
		125	15.7	1.0	0.6
		217	8.4	0.25	0.28
		285	1.4	--	--
		365	0.5	--	--
Mississippi	16 oz/1000 sq. ft[a]	98	ND	0.08	0.08
		130	ND	ND	ND
	32 oz/1000 sq. ft.[a]	98	0.79	0.03	0.05
		130	0.33	0.02	0.03

			Sampling depth (inches) 0-6	6-12	12-18
Ohio	15 lb ai/A	221	7.8	<0.01	<0.01
		310	3.02	0.03	0.24
		371	0.9	0.2	0.1
	Control	221	<0.01	<0.01	<0.01
		310	1.62	0.11	<0.02

			Sampling depth (inches) 0-2	2-4	4-6	6-8	8-10
South Dakota	14 lb ai/A	30	<0.05	<0.05	<0.05	<0.05	<0.05
		60	0.20	0.05	0.07	0.02	0.13

[a]Eight 2 or 4 oz/1000 sq. ft. bimonthly applications totaling 16 or 32 oz/1000 sq. ft., respectively; samples collected following the last application.

[b]Samples not collected or not analyzed for chlorothalonil.

CASE GS0097 CHLOROTHALONIL STUDY 10 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00087284 CONTENT CAT 02

Wolfe, A.L. 1971. C^{14} Daconil 2787 degradation in soil. Unpublished study received Aug. 11, 1970 under 1F1024; submitted by Diamond Shamrock Chemical Co., Cleveland, OH; CDL:093333-D.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

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CONCLUSION:

Metabolism - Aerobic Soil

This study is scientifically invalid because treated soils were sampled only once; therefore, the pattern of decline of chlorothalonil could not be assessed. Additionally, this study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because soil moisture content (9-10%) was significantly below the recommended 75% of field capacity level, and patterns of formation and decline of degradates were not determined. However, useful information was provided by identifying 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) as a degradate of chlorothalonil.

MATERIALS AND METHODS:

[^{14}C]Chlorothalonil (Daconil 2787, 4.5 x 10^6 dpm, source and purity unspecified) was applied at 10 ppm to 100 g of a Lismore silty clay loam soil (pH 6.9). The treated soil was maintained at 9-10% moisture for 10 days at 95 F (35 C). The soil was removed at the end of the incubation period for subsequent analysis.

Soil samples were extracted with 200 ml of water and two 100 ml washes. Soil samples were then extracted with 150 ml of acetone and 10 ml of 50% sulfuric acid, followed by two 150-ml acetone extractions, followed by three 50 ml acetone washes. These extracts were partitioned using hexane and isopropyl ether in order to separate the parent compound, the degradate 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701), and other water-soluble residues. Each of these fractions was quantified by using LSC (80% ^{14}C counting efficiency).

REPORTED RESULTS:

At the end of the 10-day incubation, 7.3, 17.7, and 63.9% of the applied radioactivity was recovered as chlorothalonil, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701), and other unidentified water-soluble compounds, respectively; ~11% of the ^{14}C was nonextractable.

DISCUSSION:

1. Soil moisture content was maintained below the recommended level of 75% of field capacity.

2. Treated soil was not sampled immediately posttreatment or at any other interval than the end of the 10-day incubation period (sampling was insufficient and the study was not conducted long enough).

3. Soil was not incubated at a constant temperature between 18 and 30 C and complete soil characteristics were not provided.

4. The pattern of decline of [^{14}C]chlorothalonil and patterns of formation and decline of degradates were not determined.

CASE GS0097 CHLOROTHALONIL STUDY 11 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00087286 CONTENT CAT 01

Wolfe, A.L., and D.E. Stallard. 1968. The fate of DAC-3701 (4-hydroxy-2,5,6-trichloro-isophthalonitrile) in soil. Unpublished study received Aug. 11, 1970 under 1F1024; submitted by Diamond Shamrock Chemical Co., Cleveland, OH; CDL:093333-F.

SUBST. CLASS = T; CHEM R29121 IS TRANSF. PRODUCT OF CHEM 081901
OTHER SUBJECT DESCRIPTORS SEC: EFB -30-050525

DIRECT RVW TIME = 7 1/2 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Soil

This portion of the study is scientifically invalid because the test protocol was unacceptable; soils were sampled at an insufficient number of intervals to construct a decline curve for the degradation of 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701; a degradate of chlorothalonil) in soil. In addition, this portion of the study would not satisfy EPA Data Requirements for Registering Pesticides (1983) because the test soils were not completely characterized, the purity of the test substance was not reported, treated soils were not maintained at a constant temperature between 18 and 30 C or at 75% of field capacity, and a materials balance was not conducted.

Mobility - Leaching and Adsorption/Desorption

1. This portion of the study is scientifically valid.

2. The chlorothalonil degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) is mobile in sand, loam, silty clay loam, and clay soils. After eluting 6-inch soil column with the equivalent of 5 inches of water, 57, 84, 10, and 84% of the applied DAC-3701 was recovered in the leachate of the sand, loam, silty clay loam, and clay soil columns, respectively.

3. This portion of the study does not satisfy EPA Data Requirements for Registering Pesticides (1983) because the test substance and test soils were not adequately characterized, the length of the soil column was inadequate (6 inches in height), and the soil was not analyzed for DAC-3701 residues, therefore precluding a determination of the distribution of DAC-3701 residues in the soil column.

Field Dissipation - Terrestrial

This portion of the study is scientifically invalid due to insufficient sampling intervals; therefore, the dissipation of chlorothalonil could not be assessed. In addition, this portion of the study would not satisfy EPA Data Requirements for Registering Pesticides (1983) because the test soil was incompletely characterized; field test data, including rainfall and irrigation amounts, and soil and air temperatures were not provided; and the patterns of formation and decline of degradates were not addressed.

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

4-Hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, 'pure' standard solution, Diamond Shamrock Corp.), a degradate of chlorothalonil, was dissolved in methanol (concentration unspecified), placed in glass jars, and evaporated to dryness. Samples (500 g) of five soils (Table 1), adjusted to 8% moisture holding capacity, were added to the jars and DAC-3701 at 40 or 100 ppm was incorporated into the soil by tumbling the jar at 2 rpm for 4 hours. The jars were tightly capped and maintained in an oven at 35-37 C. Subsamples (150 g) were removed immediately posttreatment and at two additional intervals between 1 and 5 months for analysis.

The soils were adjusted to pH 2 with 50% sulfuric acid, and extracted with diethyl ether. Following solvent evaporation, a diazomethane reagent was added to form the methyl ether of DAC-3701, which was quantified by using GC. Recoveries of DAC-3701 from soil samples fortified at 40 ppm ranged from 74 to 90%.

Mobility - Leaching and Adsorption/Desorption

Four soils (Table 2) were air dried and passed through a Number 20 sieve to remove stones and coarse sand. The sieved soils were poured into a 1.8 x 40 cm chromatographic column to a depth of 5 inches. An additional aliquot of soil which had been previously treated with 100 µg of DAC-3701 ('pure'

standard solution, Diamond Shamrock Corp.) was added to the column bringing the total soil height to 6 inches. Each column was leached with distilled water at rates shown in Table 2. Water samples representing 5 inches (30 ml) and 42 inches (252 ml) of leachate were collected and analyzed for DAC-3701 using the method described in the aerobic soil metabolism portion of this study.

Field Dissipation - Terrestrial

Two Okeelanta peaty muck (soil not further characterized) celery plots were treated with chlorothalonil (Daconil 2787, 75% WP, Diamond Shamrock Corp.) at 0.75 lb ai/A 20 times at 4 day intervals between November 13, 1967 and January 29, 1968. The total quantity of chlorothalonil applied to the plots was 15 lb ai/A. Soil samples were collected on January 30, 1968, 1 day following the last treatment. Twelve core samples (12 inches deep) were taken from each of the two plots. The cores were divided into three segments (0-3, 3-6, and 6-12 inches) and composited. The samples were analyzed for chlorothalonil and a degradate 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701).

The soils were air dried, extracted with a distilled water: 50% sulfuric acid:acetone (2:2:21) mixture, and centrifuged. The supernatant was concentrated, adjusted to pH 2 by using 50% sulfuric acid, and partitioned between distilled water and ether. The aqueous layer was repartitioned with ether, and the ether phases were combined, evaporated to dryness, and redissolved in ether. Chlorothalonil and DAC-3701 were separated by using LC, the DAC-3701 was methylated, and chlorothalonil and methylated DAC-3701 were quantitatively analyzed by using GC equipped with a microcoulometric or electron capture detector.

REPORTED RESULTS:

Metabolism - Aerobic Soil

Based on two sampling intervals, the chlorothalonil degradate DAC-3701 had estimated half-lives of 36, 53, 64, 141, and 220 days in sandy loam, sand, silty clay loam, loam, and clay soils, respectively (Table 1). This compound degraded faster in the coarse-textured soils than in finer-textured soils. No degradation products of DAC-3701 (including 4,6-dihydroxy-2,5-dichloroisophthalonitrile, 2-hydroxy-3,4,6-trichloro-5-carboxybenzonitrile, and 4-hydroxy-2,5,6-trichloroisophthalic acid) were detected in any of the test soils.

Mobility - Leaching and Adsorption/Desorption

After eluting 6-inch high soil columns with the equivalent of 47 inches of water, 80, 100, 100, and 81% of the applied DAC-3701 was found in the leachate from the sand, clay, loam, and silty clay loam soil columns, respectively (Table 2).

Field Dissipation - Terrestrial

The average (2 replications) concentration of chlorothalonil found in the 0- to 3-, 3- to 6-, and 6- to 12-inch depths of a peaty muck soil 1 day following the last of twenty 0.75 lb ai/A applications was 6.1, 3.6, and 0.45, ppm; respective DAC-3701 concentrations at these depths were 3.05, 0.4, and 0.1 ppm. The amount of chlorothalonil and DAC-3701 recovered from the soil represented ~12 and 7%, respectively, of the theoretical total application.

DISCUSSION:

Metabolism - Aerobic Soil

1. Complete characteristics of the test soils were not reported.

2. Treated soils were maintained above 30 C and below the test standard moisture content of 75% of 0.33 bar moisture.

3. Soils were not sampled pretreatment, or at a sufficient number of intervals posttreatment to establish a decline curve for DAC-3701; sampling did not extend beyond two half-lives in three of the five test soils.

4. Materials balance data were not provided.

5. There was no apparent use of experimental controls or any replication of treatments or analyses.

Mobility - Leaching and Adsorption/Desorption

1. The test substance and test soils were not completely characterized.

2. The soil column was only 6 inches in height and was leached with an excessive amount of water (47 inches).

3. Following leaching, the column soil was not analyzed for the test substance.

Field Dissipation - Terrestrial

1. Soil characteristics and meteorological data were not reported.

2. Adequate decline curves for chlorothalonil and its degradates could not be constructed on the basis of one sampling interval.

Table 1. The degradation of DAC-3701[a] in five soils under aerobic conditions.

Sand	Source	pH	Treatment (ppm)	DAC-3701 (ppm) Sampling interval (days) 76	158	Half-life estimates (days)
Portageville sandy loam	MO	5.9	40	--[b]	2	36
Clarkton sand	MO	6.9	40	20 (31 days)	11 (75 days)	53
Lismore silty clay loam	SD	6.9	100	78 (30 days)	28 (123 days)	67
Lake County loam	OH	--	40	26	21	141
Clay	GA	--	40	32	26	220

[a]DAC-3701 (4-hydroxy-2,5,6-trichloroisophthalonitrile) is a known degradate of chlorothalonil.

[b]Data not provided.

Table 2. The percent of applied DAC-3701[a] leaching through 6-inch columns containing various soils.

Soil	Source	Flow rate (ml/hr)	DAC-3701 (% of applied) Leachate (inches) 5	42	Total (47)
Clarkston sand	MO	35	57	23	80
Clay	GA	12	84	16	100
Lake County loam	OH	16	84	16	100
Lismore silty clay loam	SD	36	10	71	81

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

CASE GS0097 CHLOROTHALONIL STUDY 12 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00087351 CONTENT CAT 01

Szalkowski, M.B. 1976. Effect of microorganisms upon the soil metabolism of Daconil and 4-hydroxy-2,5,6-trichloroisophthalonitrile. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:097394-I.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: EFB -30-05052005 EFB -30-05052010

DIRECT RVW TIME = 13 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. [^{14}C]Chlorothalonil is degraded with half-lives of 22-31, 7-16, 7-16, and 0-7 days in nonsterile silt loam, peat loam, Texas sandy loam, and Ohio sandy loam soils, respectively. The rate of chlorothalonil degradation was slower in sterile soils, with half-lives of 60-90, 22-31, 7-16, and 16-22 days in the respective soils. [^{14}C]Chlorothalonil is degraded to 4-hydroxy-2,5,6-trichloroisophthalonitrile (up to 32% of the applied radioactivity at 60 days posttreatment) and 3-cyano-2,4,5,6-tetrachlorobenzamide (up to 7.4% of the applied radioactivity at 7 and 16 days posttreatment). Unextractable residues increased in both sterile and nonsterile soils over the study period, accounting for 40-42, 52-62, 63-75, and 56-63% of the applied radioactivity by day 90 in the silt loam, peat loam, Texas sandy loam, and Ohio sandy loam soils, respectively. The soils were incubated at 25 C and 80% of field capacity in the dark.

3. This study fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the degradation of chlorothalonil and on the formation and decline of two chlorothalonil degradates in silt loam, peat loam, and two sandy loam soils for 90 days.

MATERIALS AND METHODS:

Duplicate 4-g samples of sterile (autoclaved twice for 30 minutes at 50 psi and 270 F) and nonsterile soils (Table 1) contained in 20 ml glass scintillation vials were treated with ring-labeled [^{14}C]chlorothalonil in a benzene solution (specific activity 3630 dpm/µg, 99.3% pure, Diamond Shamrock Corp.). The Illinois silt loam, Iowa peat loam, and Texas sandy loam soils were treated at 39 ppm; the Ohio sandy loam was treated at 3.9 ppm. The soil samples were covered with aluminum foil to prevent light exposure and were maintained at 25 C and at 80% of field capacity (distilled water additions).

Two sterile and two nonsterile soil samples were removed at 0, 7, 16, 22, 31, 60, and 90 days posttreatment, air dried, and ground with a mortar and pestle. The samples (~2 g) were extracted one time with 30 ml of acetone: HCl (80:20) and duplicate 0.5-1.0 ml aliquots of the supernatant were radioassayed by using LSC.

A 15-ml portion of the remaining supernatant was evaporated free of acetone under a stream of air, and the remaining acid aqueous portion was transferred to a 60-ml separatory funnel and partitioned into isopropyl ether (20 ml). Duplicate 0.5 ml portions of each phase were quantified by using LSC.

A 15-ml portion of the ether phase was concentrated to a volume <0.5 ml, and applied along with known standards to silica-gel TLC plates. The plates were developed with hexane:acetone (1:1) to a distance 15 cm from the origin, allowed to dry, visualized under UV light, and autoradiographed. Radioactive sections of the TLC plates were then quantified by using LSC.

In a second experiment, [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, specific activity 4114 dpm/µg, 98.2% pure, Diamond Shamrock Corp.) was applied at 4.3 ppm to the four test soils (Table 1). Procedures and protocols were the same as described above.

REPORTED RESULTS:

Chlorothalonil concentrations detected in sterile and nonsterile soils are shown in Tables 2 and 3, respectively.

In nonsterile soils, half-lives for chlorothalonil ranged from 22-31, 7-16, 7-16, and 0-7 days in the silt loam, peat loam, Texas sandy loam, and Ohio sandy loam soils, respectively. In sterile soils, half-lives for chlorothalonil ranged from 60-90, 22-31, 7-16, and 16-22 days in the silt loam, peat loam, Texas sandy loam, and Ohio sandy loam soils, respectively.

Concentrations of 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) in sterile and nonsterile [^{14}C]chlorothalonil-treated soils reached a maximum of 10-30% of the applied radioactivity at 16-60 days posttreatment. Another degradate, 3-cyano-2,4,5,6-tetrachlorobenzamide, accounted for <7.4% of the applied radioactivity in sterile or nonsterile soils at any sampling interval.

[^{14}C]4-Hydroxy-2,5,6-trichloroisophthalonitrile-treated soils showed no degradation in any of four test soils after the 90-day test period.

DISCUSSION:

1. The test soil reported to be a silty clay loam is a silt loam according to the USDA soil texture classification system.

2. It was stated that no degradation of DAC-3701 occurred in soils treated with [^{14}C]DAC-3701 at 4.3 ppm; however, no data were presented to support this position.

Table 1. Soil characteristics.

Soil type	Origin	Sand	Silt	Clay	Organic matter	pH
				%		
Silt loam[a]	Macomb, IL	0.6	73.6	25.8	2.3	5.1
Peat loam	IO	29.7	50.0	20.3	7.2	7.0
Sandy loam	Tulia, TX	54.0	25.0	19.5	1.6	8.0
Sandy loam	Painesville, OH	62.2	31.0	6.8	3.2	6.0

[a]Reported as a silty clay loam; see Discussion No. 1.

Table 2. Chlorothalonil degradation (% of applied) in sterile soils.[a]

Sampling interval (days)	Chlorothalonil	DAC-3701[b]	DS-19221[c]	Water soluble	Nonextractable
		Silt loam soil			
0	95.3	0	0	1.3	2.1
7	94.9	1.9	0	0.7	2.6
16	86.6	2.1	0.1	3.3	8.0
22	88.1	2.8	0	1.8	4.6
31	80.9	3.1	0	3.2	9.5
60	78.4	4.3	0	1.7	11.0
90	45.0	5.5	0.1	5.2	40.3
		Peat loam soil			
0	90.8	0	0	1.5	7.5
7	74.3	3.5	0.6	3.1	19.5
16	64.0	7.2	0.3	3.5	26.0
22	54.2	10.4	0.4	3.0	28.4
31	51.3	9.4	0.1	3.8	31.6
60	19.5	13.7	1.5	3.0	41.3
90	13.9	7.6	0.5	6.8	61.9
		Texas sandy loam soil			
0	99.5	0	0	0.9	0.4
7	67.4	3.1	0.1	0.8	28.0
16	50.2	4.3	0.5	1.0	42.3
22	42.7	5.5	1.4	1.7	46.0
31	41.7	9.2	0.5	2.7	44.4
60	21.0	8.2	0.4	1.3	62.2
90	8.1	5.6	0.1	4.5	74.8
		Ohio sandy loam soil			
0	83.5	0	0	1.6	13.1
7	90.5	5.1	0.3	2.7	1.9
16	61.3	6.2	1.3	14.3	24.5
22	41.5	6.4	3.0	12.0	30.1
31	67.2	4.8	0.7	9.0	13.0
60	24.9	7.6	1.5	11.1	35.4
90	5.7	4.2	2.3	18.6	62.9

[a]Average of duplicate samples.

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

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

Table 3. Chlorothalonil degradation (% of applied) in non-sterile soils.[a]

Sampling interval (days)	Chlorothalonil	DAC-3701[b]	DS-19221[c]	Water soluble	Nonextractable
			Silt loam soil		
0	94.8	0	0	1.2	3.5
7	80.9	8.1	0.4	3.3	7.7
16	67.2	12.0	1.0	8.5	15.4
22	62.4	13.2	0.7	5.7	12.1
31	46.5	16.0	1.4	7.1	16.4
60	51.1	13.4	1.9	5.2	16.9
90	33.3	10.5	1.0	9.5	41.7
			Peat loam soil		
0	97.6	0	0	1.8	3.2
7	61.6	13.6	3.1	3.7	17.5
16	42.4	23.8	3.9	7.4	22.6
22	34.3	24.5	4.4	6.7	24.8
31	23.9	28.1	4.9	14.3	24.5
60	14.4	31.9	5.2	6.6	28.7
90	6.0	18.0	2.8	12.2	51.9
			Texas sandy loam soil		
0	100.2	0	0	0.7	0.2
7	60.2	15.1	1.0	5.2	17.1
16	36.4	26.2	1.7	7.0	35.2
22	30.7	26.1	1.3	10.0	26.3
31	26.0	23.3	1.8	8.3	34.6
60	12.8	27.4	2.3	8.4	32.6
90	4.6	13.5	0.8	10.5	62.8
			Ohio sandy loam soil		
0	92.2	0	0	1.1	3.4
7	44.8	12.5	7.4	19.8	25.5
16	32.2	15.0	7.4	22.5	31.3
22	21.1	11.2	5.1	22.8	26.2
31	11.2	7.3	6.1	26.5	35.4
60	10.8	11.6	2.6	17.2	34.5
90	4.8	6.3	3.1	24.5	56.0

[a]Average of duplicate samples.

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

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

CASE GS0097 CHLOROTHALONIL STUDY 13 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050515

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00029406 CONTENT CAT 01

Szalkowski, M.B., and D.E. Stallard. 1980. Adsorption of chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) DS-2787. Unpublished study received Feb. 19, 1980 under 677-313; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL: 099248-D.

SUBST. CLASS = S.

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

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CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This study is scientifically invalid because the test soils were sieved to 60 mesh (<0.25 mm), thus removing the medium and coarse sand and altering the soil characteristics. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing adsorption coefficients (Freundlich K values) which were correlated with the organic matter content for Texas clay loam, Ohio sandy loam, Nebraska silt loam, Iowa loam, Minnesota silt loam, and Michigan loamy sand soils.

MATERIALS AND METHODS:

Samples of six soils (Table 1), and a muck, sea sand, and montmorillonite clay were air dried and passed through a 0.25 mm sieve. A stock solution of ring-labeled [^{14}C]chlorothalonil (99.7% pure, specific activity 32.8 mCi/mM, Diamond Shamrock Corp.) in benzene was prepared and added to five flasks at a volume equivalent to 32, 67, 102, 137, and 172 µg of chlorothalonil. The benzene was evaporated, and distilled water (350 ml) was added to each flask to yield concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 ppm.

Portions (1 g) of the test soils were weighed into flasks, and 10-ml aliquots of the test solutions containing [^{14}C]chlorothalonil were added. The flasks were sealed, and the soils were equilibrated by shaking the flasks for 20 hours. After equilibration, the samples were centrifuged, and the radioactivity in the supernatant was quantified by using LSC. Freundlich K values were calculated by using the standard Freundlich isotherm equation.

REPORTED RESULTS:

The clay and organic matter contents of soils were the major factors affecting chlorothalonil adsorption. Freundlich K values were correlated to the soil organic matter content. The K values for the six soils tested were 11.83, 15.96, 22.88, 43.38, 111.35, and 471.85 for the Michigan loamy sand, Texas clay loam, Ohio sandy loam, Nebraska silt loam, Minnesota silt loam, and Iowa loam soils, respectively (Table 2).

Freundlich K values obtained for sea sand, muck, and montmorillonite clay were 0.33, 201.09, and 1342.76, respectively.

DISCUSSION:

1. The adsorption of chlorothalonil to soil was not representative of actual environmental conditions because the soil was sieved to 60 mesh, thus removing the medium and coarse sand and altering the soil characteristics. Soils whose characteristics have been altered in this manner will have higher K values than unaltered soil.

2. The peat loam soil was not properly classified. A peat soil has an organic matter content of >50% (Glossary of Soil Science Terms, Soil Science Society of America, October 1979). Since the peat loam soil had an organic matter content of only 7.2%, it should be classified as a loam soil and was reported as such in this review.

3. Soil characteristics for the muck soil were not presented.

Table 1. Characteristics of soils used in a study of chlorothalonil adsorption.

Location	Soil type	pH	Organic matter	Sand	Silt	Clay
			%			
Texas	Clay loam	7.5	0.8	44.6	27.8	27.6
Ohio	Sandy loam	5.6	1.6	61.3	30.4	8.3
Nebraska	Silt loam	5.6	1.9	1.4	71.5	27.1
Iowa	Loam[a]	7.0	7.2	29.7	50.0	20.3
Minnesota	Silt loam	5.6	3.4	13.7	63.7	22.6
Michigan	Loamy sand	6.6	1.8	79.0	14.0	7.0

[a]Reported as a peat loam, see Discussion No. 2.

Table 2. Freundlich isotherm constants and adsorption coefficients for chlorothalonil absorbed onto various soils.

Media	K (µg/g)	1/n	Q (µg/g)
Sand	0.33	0.69	--[a]
Michigan loamy sand	11.83	0.75	629
Texas clay loam	15.96	0.72	1,995
Ohio sandy loam	22.88	1.01	1,404
Nebraska silt loam	43.38	0.61	2,271
Minnesota silt loam	111.35	1.05	3,275
Muck	201.09	1.26	--[a]
Iowa loam	471.85	1.15	6,590
Clay	1,342.76	0.69	--[a]

[a]Q = K x 100/% organic matter; Q was not calculated for adsorbing media containing no organic matter or for which the organic matter content was unknown.

CASE GS0097 CHLOROTHALONIL STUDY 14 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 06 - WETTABLE POWDER (WP OR W)

FICHE/MASTER ID 00087300 CONTENT CAT 01

Wolfe, A.L., and D.E. Stallard. 1965. Residue of tetrachloroisophthalonitrile (Forturf) in soil resulting from foliar application to established turf. Unpublished study received Dec. 21, 1965 under unknown admin. no.; submitted by Diamond Shamrock Chemical Co., Cleveland, OH; CDL:110552-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 3 1/2 (MH) START-DATE END DATE

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CONCLUSION:

Field Dissipation - Terrestrial

This study is scientifically invalid because soils were sampled at an insufficient number of intervals to construct a decline curve for chlorothalonil dissipation from soil, and the method of analysis was neither referenced nor described. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because patterns of formation and decline of degradates were not assessed; the test soil was not characterized; and meteorological data, including rainfall and irrigation amounts were not provided.

MATERIALS AND METHODS:

Chlorothalonil (Forturf, 75% WP, Diamond Shamrock Corp.) was applied at 2 or 4 oz product/1000 sq. ft. (~4 or 8 lb ai/A) to a bermudagrass sod plot (4 x 15 ft) every 2 weeks from May 4 to August 26, 1965 (nine applications). Three months after the last application (Dec. 2, 1965), six soil core samples (0.75 inches diameter x 9 inches deep) were taken and divided into 3-inch segments for analysis. The method of analysis was not reported.

REPORTED RESULTS:

Bermudagrass sod plot soil samples treated with chlorothalonil at 2 oz/1000 sq. ft. at 2-week intervals for nine applications contained chlorothalonil concentrations ≤0.07 ppm. At 4 oz/1000 sq. ft., at 2 week intervals for nine applications, concentrations of chlorothalonil were 0.72, 0.03, and 0.05 ppm at depths of 0-3, 3-6, and 6-9 inches, respectively, 3 months after the last application.

DISCUSSION:

1. Soil samples were collected only once (3 months posttreatment); therefore, a decline curve for chlorothalonil could not be generated.

2. The method of analysis was neither reported nor referenced.

3. Soil characteristics, and rainfall and irrigation data were not reported.

4. The patterns of formation and decline of degradates were not assessed.

CASE GS0097 CHLOROTHALONIL STUDY 15 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 06 - WETTABLE POWDER (WP OR W)

FICHE/MASTER ID 00087296 CONTENT CAT 01

Stallard, D.E., A.L. Wolfe, and W.C. Duane. 1972. Evaluation of the leaching of chlorothalonil under field conditions and its potential to contaminate underground water supplies. Unpublished study received Feb. 25, 1976 under 6F1749; submitted by Diamond Shamrock Co., Cleveland, OH; CDL:098072-R.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 1/2 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Terrestrial

1. This portion of the study is scientifically valid.

2. The half-life of chlorothalonil (75% WP) in a sandy loam soil was between 1 and 2 months following the last of five consecutive weekly applications totaling 15 lb ai/A. Little movement of chlorothalonil (<0.01-0.17 ppm) below the 0- to 3-inch depth occurred throughout the 8 month study. Small amounts (<0.01-0.21 ppm) of the degradate, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) were found in soil samples collected up to 5 months posttreatment. No chlorothalonil or DAC-3701 was detected (<1 ppb) in a nearby stream up to 7 months posttreatment, or in ground water samples (10-foot depth) up to 8 months posttreatment. Cumulative rainfall over the study period was 26.22 inches.

3. This portion of the study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the dissipation of chlorothalonil (75% WP) in a sandy loam soil.

MATERIALS AND METHODS:

Chlorothalonil (Bravo, 75% WP, Diamond Shamrock Corp.) was applied weekly at 3 lb ai/A to a test plot (400 x 327 ft) of weed-free sandy loam soil (61.3% sand, 8.3% clay, 30.4% silt, 2% organic matter) for five consecutive weeks. A second field plot served as a control. At the center of each field plot a 1.25 inch diameter iron pipe was driven 12 feet into the ground to obtain ground water samples (water table was ~10 feet below soil surface). Ground water was sampled prior to the initial application of chlorothalonil and immediately following each application for five consecutive weeks then on a monthly basis for 7 months. Soil samples were taken on the same schedule except that no sample was obtained in February (3 months after the last treatment) due to frozen ground conditions. Soil was sampled to a depth of 12 inches (20 0.75-inch cores) and divided and composited in four 3-inch increments. Water from a nearby stream (300 ft south and 15 ft downslope) was sampled at 143 and 172 days after treatment. Rainfall and temperature data were collected for the 8-month study period (Table 1).

Water samples (1,000 g by weight) were partitioned with sulfuric acid and isopropyl ether. The aqueous phase was discarded and the ether phase was evaporated under nitrogen. The residue was dissolved in benzene and analyzed for chlorothalonil by using GC equipped with an electron capture detector. The extract containing the degradation product, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701), was prepared for analysis by evaporating the benzene solution of the chlorothalonil sample to dryness, dissolving the thalonil sample to dryness, dissolving the residue in isopropyl ether and adding 1 ml of PTT reagent (0.18 g of 1-n-propyl-3-p-tolyltriazene per 100 ml pure isopropyl ether). The propylated sample was quantified by using GC. The recovery of chlorothalonil ranged from 80 to 110% with a mean of 96%; recovery of DAC-3701 ranged from 60 to 130% with a mean of 96%. The detection limit of the method was reported as 1 ppb for both compounds.

Soil samples were air dried, passed through a 10 mesh sieve (<2 mm), and 100 g from each depth was extracted with acetone (240 ml) and 10 ml of sulfuric acid (1:1). The acetone was evaporated from a 100 ml aliquot under a stream of nitrogen until only a water:acid mixture remained, which was extracted with aqueous isopropyl ether. The aqueous phase was discarded, the ether phase was evaporated to dryness, and analysis was continued as described for water samples. Recovery for the soil analyses were not reported; detection limit was 0.01 ppm.

REPORTED RESULTS:

No detectable concentrations (<1 ppb) of chlorothalonil or DAC-3701 were found in any of the water samples.

In soil, the maximum concentration of chlorothalonil (2.24 ppm) occurred in the top 3 inches after the second application of chlorothalonil (Table 1).

The degradate, DAC-3701, was detected in soil samples immediately following the last chlorothalonil application at 0.05 ppm (6- to 9-inch depth); 1 month posttreatment at 0.05 ppm (0- to 3-inch depth) and 0.02 ppm (6- to 9- and 9- to 12-inch depths); 2 months posttreatment at 0.21 ppm (0- to 3-inch depth) and 0.02 ppm (3- to 6-inch depth); and 5 months posttreatment at 0.08 ppm (0- to 3-inch depth).

DISCUSSION:

1. Maximum field dissipation of chlorothalonil would be expected during this study because of the excessive precipitation (>26 inches) during the study period.

2. Control data were not reported throughout the experimental period.

3. The preapplication soil sample of October 8, 1971 detected chlorothalonil residues of 0.21 ppm at the 6- to 9-inch depth; therefore, the accuracy of reported values below 0.21 ppm is questionable.

4. The chlorothalonil degradate, 3-cyano-2,4,5,6-tetrabenzamide (DS-19221) was not analyzed for in either soil or water samples.

Table 1. Concentration (ppm) of chlorothalonil in a sandy loam soil following several applications of chlorothalonil (75% WP).

Sampling date	Cumulative chlorothalonil application (lb ai/A)	Cumulative rainfall (inches)	Average monthly air temperature (F)	Chlorothalonil (ppm) Sampling depth (inches) 0-3	3-6	6-9	9-12
10-8-71	0	--	59.9	0.05	ND[a]	0.21	0.02
10-8-71	3.0	--	59.9	0.69	0.17	0.01	0.04
10-14-71	6.0	0.63	59.9	2.24	0.14	ND	ND
10-21-71	9.0	0.69	59.9	1.65	0.06	0.02	0.05
10-29-71	12.0	0.81	59.9	1.10	ND	ND	0.07
11-5-71	15.0	0.84	41.4	0.75	ND	ND	ND
12-2-71	15.0	2.61	38.1	0.45	0.02	0.02	0.02
1-6-72	15.0	6.70	27.3	ND	ND	ND	ND
3-29-72	15.0	12.29	34.8	0.13	ND	ND	ND
4-26-72	15.0	15.79	46.0	0.02	ND	ND	ND
5-23-72	15.0	19.17	58.6	ND	ND	ND	ND
6-29-72	15.0	26.22	62.7	0.01	ND	ND	0.05

[a]ND; not detectable (<0.01 ppm).

CASE GS0097 CHLOROTHALONIL STUDY 16 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 20 TOPIC 150525 GUIDELINE 40 CFR 163.62-11b

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00029409 CONTENT CAT 01

Szalkowski, M.R., D.E. Stallard, and R.T. Bachand, Jr. 1979. Absorption and translocation of 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil) metabolites in soil by leafy, root and fruiting crops--A laboratory rotational crop study: Research Report R-78-0020. Unpublished study received Feb. 19, 1980 under 677-313; Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:099248-G.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: RCBR-20-1510 RCBR-20-1515

DIRECT RVW TIME = 15 (MH) START-DATE END DATE

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CONCLUSIONS:

Confined Accumulation - Rotational Crops

1. This study is scientifically valid.

2. Residues of [^{14}C]chlorothalonil and its degradation products [^{14}C]4-hydroxy-2,5,6-trichloroisothalonil (DS-3701) and [^{14}C]3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221) found in aerobic soil 14 weeks after treatment (10.4 ppm) were uptaken by rotated lettuce, green beans and carrots under confined conditions. Amounts of the above respective residues found in green beans and carrots 63 and 90 days after planting were: green beans; pod and beans - 0.03, 0.35 and 0.03 ppm; carrot roots - 0.02, 0.07 and 0.06 ppm; carrot tops - 0.05, 0.11 and 0.09 ppm. Quantities of unidentified but characterized ^{14}C-residues found in lettuce 63 days after planting were: Total ^{14}C-residues 1.19 ppm; Extractable ^{14}C-residue 1.06 ppm; Unextractable ^{14}C-residue <0.01 ppm; water-soluble ^{14}C-residue 0.86 ppm and ether-soluble ^{14}C-residue <0.18 ppm. No plateau for residues in the rotated crops was reached throughout the 2 to 3 months confined accumulation study.

3. This study fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the uptake of aged [^{14}C]chlorothalonil and its residues (DS-3701 and DS-19221) in aerobic soil by rotated lettuce, green beans and carrots under confined conditions. The results of this study indicate that field accumulation studies on rotational crops are required to establish rotation restrictions or to determine if tolerances are needed for rotational crops.

MATERIALS AND METHODS:

A sandy loam soil (62.2% sand, 6.8% clay, 31.0% silt, 3.2% organic matter, pH 6.0) was sieved to 590 µm, treated with [^{14}C]chlorothalonil (99.7% purity, Diamond Shamrock Corp.) to yield a concentration of 10.4 ppm, and aged for 14 weeks in the dark at 16-29 C, 15% moisture (by weight), and 94% relative humidity. After the aging period <3% of the test material remained as intact [^{14}C]chlorothalonil. Subsamples (1.3 kg) of the aged soil were transferred to each of six plastic planting pots (15-cm diameter x 15-cm deep). Two plastic pots were then planted with Grand Rapids lettuce, two with Nantes carrots, and two with Tendergreen beans. Petri dishes were placed under the pots to catch any leachate resulting from daily watering. Plants were maintained at 27-29 C during daylight and 16-24 C during a 10-hour dark cycle. Plant samples were taken for analysis at 15, 30, 45, and 63 and/or 90 days after planting.

The plant tissue samples were placed in tared beakers of suitable sizes and oven-dried at 95 C for 2 to 4 hours. The plant tissues were re-weighed to determine the oven-dried tissue weight. After oven-drying, all dried plant tissues were subsequently ground to a fine powder using a mortar and pestle.

All soil samples were prepared for analysis by air-drying in a laboratory fume hood for 16 hours and grinding to a fine powder using a mortar and pestle

Analyses for the total ^{14}C-residue in soil and plant tissue samples were conducted using total combustion techniques. Duplicate 0.2 g samples of air-dried soil or 0.05 g samples of oven-dried plant tissue were combusted to $^{14}CO_2$ using a biological oxidizer. The resulting $^{14}CO_2$ was trapped in 15 ml of a carbon dioxide absorbing solution consisting of Instafluor liquid scintillation counting cocktail:hydroxide of hyamine (4:1, v:v). Total $^{14}CO_2$ in the trapping solution was determined by liquid scintillation counting at ambient temperature using LSC. Combustion and trapping efficiencies were determined to be 98% to 100% by combusting untreated, control soil or plant tissue samples amended with known amounts of [^{14}C]chlorothalonil.

Counting efficiencies ranged from 54% to 70% with a background ^{14}C-radioactivity of 19 cpm. Samples with radioactivity less than twice the background level were considered as containing ^{14}C-residues below the detectable limit.

To determine extractable ^{14}C-residues, 1.0 g of an air-dried soil sample or 0.1 g of an oven-dried plant tissue sample was weighed into a 50 ml flask. A 25 ml portion of acetone:0.3 N hydrochloric acid (80:20, v:v) was added. A Teflon-coated magnetic stirring bar was added, the flask was sealed with a ground glass stopper and the ^{14}C-residues was extracted by magnetic stirring for 30 minutes. The entire contents of the flask were transferred to a centrifuge tube and centrifuged for 20 minutes at 5 ± 1 C. After centrifugation, the supernatant was removed and transferred to a graduated cylinder. The volume of the supernatant was measured and recorded. The sample pellet was returned to the extraction flask, 25 ml of acetone:0.3 N hydrochloric acid (80:20, v:v) was added and the sample was extracted and centrifuged as previously described. The supernatant resulting from the second extraction was removed from the centrifuge tube, transferred to a separate graduated cylinder and the volume was measured and recorded.

To quantitatively determine the amount of extractable ^{14}C-residue, duplicate 0.5-ml portions of each supernatant were separately transferred to scintillation vials and a 15-ml portion of Aquasol liquid scintillation cocktail was added. The vials were capped and the contents were mixed by inverting as previously described. The samples were counted using LSC. All samples were corrected for background radiation, counting efficiency (68% to 81%), and dilution factors. Using these techniques, the total extractable ^{14}C-residue was calculated as µg [^{14}C]chlorothalonil equivalents per gram of sample.

After extraction, the extracted plant tissue or soil was allowed to air-dry in a laboratory fume hood for 16 hours. The dried sample was mixed by grinding with a mortar and pestle. The unextractable ^{14}C-residue was quantified indirectly as $^{14}CO_2$ by subjecting 0.2 g extracted soil sample or 0.05 g extracted plant tissue sample to total combustion and trapping the resulting $^{14}CO_2$. Radioactivity in the trapping solution was quantified by LSC.

Supernatants containing the extractable ^{14}C-residue, were quantitatively transferred to a round bottom flask. The flask was placed in a thermostatically controlled water bath maintained at 38 ± 2 C. The acetone was removed from the extract using a Buchler rotary flash evaporator operated under reduced pressure.

After evaporation of the acetone, the resulting aqueous solution was quantitatively transferred to a 60 ml separatory funnel using two 5-ml to 10-ml washings with distilled water. A 25-ml portion of isopropyl ether was added to the separatory funnel and the ^{14}C-residue was partitioned between the aqueous and the isopropyl ether phases by shaking for 2 minutes. The phases were allowed to separate. The volume of each phase was measured and recorded. Each phase was subsequently assayed for radioactivity by LSC of duplicate 0.5-ml portions. The ^{14}C-residue remaining in the aqueous phase was designated as "water-soluble" ^{14}C-degradates of ^{14}C-chlorothalonil.

The ^{14}C-residue partitioned from the aqueous phase into isopropyl ether was further characterized by TLC and quantitated by LSC. The isopropyl ether phase was concentrated to a known volume using a stream of clean, dry air. A portion of the concentrated extract was applied as a 1.0-cm band onto a silica gel thin layer chromatographic plate containing a fluorescent indicator at a distance of 2.0 cm from the bottom of the plate. A 50-µl portion of an acetone solution containing approximately 1 mg/ml each of chlorothalonil and its two known degradates (Table 1) was applied onto the chromatographic plate adjacent to each sample extract in a similar manner to serve as reference standards. The chromatogram was developed by ascending chromatography to a measured distance of 150 mm to 165 mm from the site of sample application (origin) in a chromatographic chamber containing a hexane:acetone (1:1, v:v) solvent system. After development, the chromatographic plate was removed from the chromatographic chamber and allowed to air-dry in a laboratory fume hood. The standard reference compounds were visualized on the chromatogram by their absorbance of ultraviolet light. The R_f value of each standard reference compound was then calculated.

The distribution of radioactivity on each chromatogram was quantitatively determined. Each chromatogram was sectioned into regions based upon the R_f value of the reference standards of chlorothalonil and its known degradates. Each section was cut with scissors, deposited into scintillation vials, 18 ml of the scintillation cocktail was added and the radioactivity in each section was quantitated by LSC.

The entire scheme of analytical procedures used is summarized in Figure 1.

DISCUSSION:

1. The results of this study indicate that field accumulation studies on rotational crops are required to establish crop rotation restrictions or to determine if tolerances are needed for rotational crops.

2. A small grain crop was not included in the rotated crops.

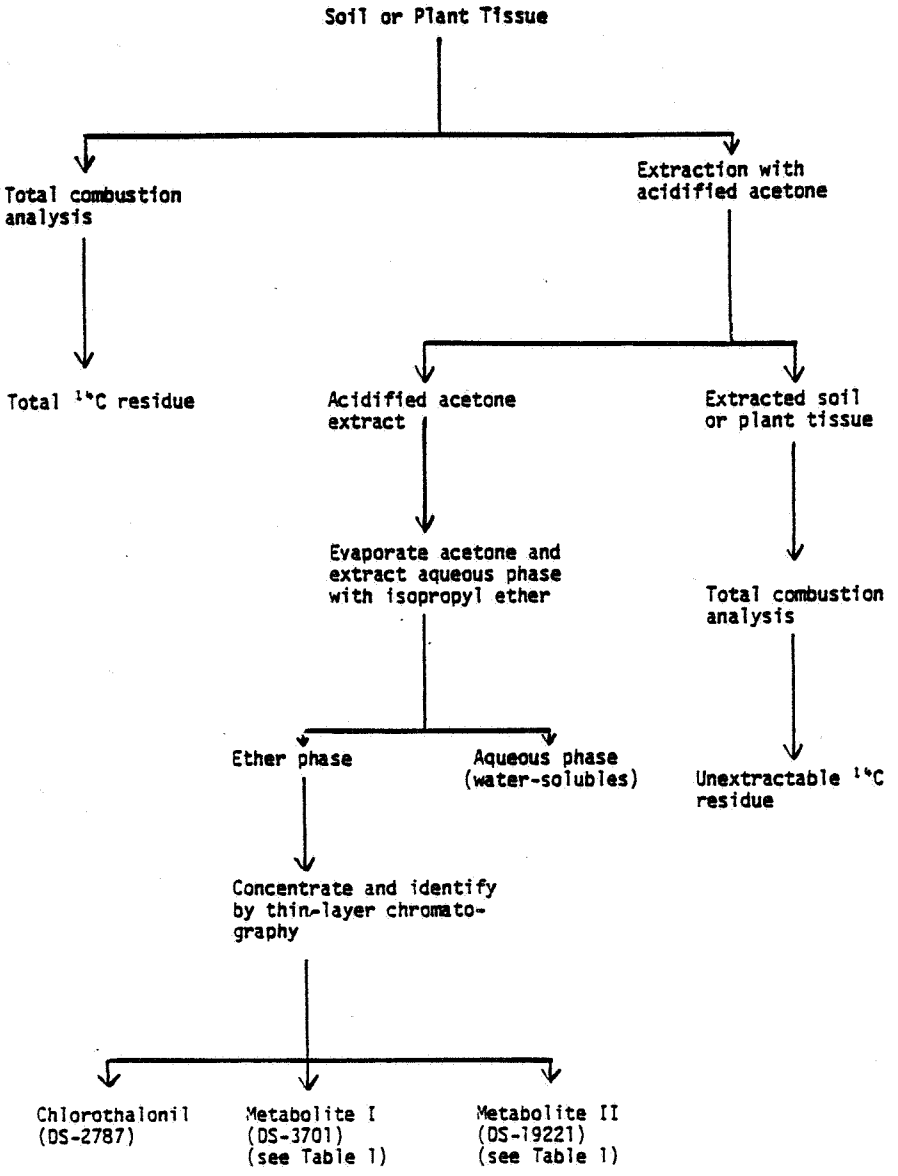

Figure 1. Scheme for characterization and quantitation of the ^{14}C residues in soil and plants.

Table 1. Distribution of ^{14}C residues in soil treated with [^{14}C]-chlorothalonil and aged for 14 weeks.

Residue	Percent of applied ^{14}C
Unextractable	43.8
Water-solubles	37.8
[^{14}C]4-Hydroxy-2,5,6-trichloro-isophthalonitrile (DS-3701; Degradate I)	21.6
Chlorothalonil	2.9
[^{14}C]3-Cyano-2,4,5,6-tetrachloro-benzamide (DS-19221; Degradate II)	<2.0

Table 2. Quantitation and characterization of ^{14}C residues in lettuce leaves grown in soil treated with [^{14}C]chlorothalonil and aged for 14 weeks prior to planting.

Time (days)	[^{14}C]Chlorothalonil equivalents (ppm)[a]				
	Total ^{14}C residues	Extractable ^{14}C residues	Unextractable ^{14}C residues	Water-soluble ^{14}C residues	Ether-soluble ^{14}C residues
30	0.46	0.53	<0.01	0.35	<0.18
45	0.96	0.84	<0.01	0.84	<0.18
63	1.19	1.06	<0.01	0.86	<0.18

[a]Values given are the averages of duplicate tests.

Table 3. Quantitation, distribution, and characterization of the ^{14}C residues in carrot plants 90 days after planting in [^{14}C]chlorothalonil-treated soil aged for 14 weeks prior to planting.

	[^{14}C]Chlorothalonil equivalents (ppm)[a]					
Sample	Total ^{14}C residues	Extractable ^{14}C residues	Water-soluble ^{14}C residues	Intact [^{14}C]chlorothalonil	Degradate I[b]	Degradate II[c]
Roots	0.40	0.34	0.28	0.02	0.07	0.06
Tops	2.20	2.34	2.11	0.05[d]	0.11	0.09

[a]Values given are the averages of duplicate tests.

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

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

[d]This value for one test only; no duplicate was analyzed.

Table 4. Quantitation, distribution, and characterization of the ^{14}C residues in the aerial portions of bean plants grown for 30 or 63 days in soil treated with [^{14}C]chlorothalonil and aged 14 weeks prior to planting.

Bean sample[b]	[^{14}C]Chlorothalonil equivalents (ppm)[a]					
	Total ^{14}C residues	Extractable ^{14}C residues	Unextractable ^{14}C residues	Water-soluble ^{14}C residues	Ether-soluble ^{14}C residues	Intact [^{14}C]chlorothalonil
30 Days						
Section 1	2.21	2.31	0.07	1.32	0.77	0.04
Section 2	1.24	1.31	0.03	0.76	0.41	0.01
Section 3	1.13	1.24[e]	0.03[e]	0.67[e]	0.42[e]	--[f]
Section 4	0.75	1.01[e]	0.02[e]	0.44[e]	0.41[e]	0.01
63 Days						
Section 1	6.78	6.68	0.14	2.60	1.75	0.02
Section 2	3.72	3.47[e]	0.09[e]	2.45[e]	0.88[e]	<0.01[e]
Section 3	5.40	4.92	0.09	3.56	1.02	0.02
Section 4	7.85	5.64	0.08	3.23	0.93	<0.01[e]
Section 5	4.35	1.13[e]	<0.02[e]	--[f]	--[f]	--[f]
Fruit-5th node (1 pod & beans)	0.87	0.67	0.03	0.30	0.47	0.03

[a]Values given are the averages of duplicate samples, except where otherwise noted.

[b]Section 1: hypocotyl + first internode + primary leaves.
Section 2: second internode + first trifoliate leaf.
Section 3: third internode + second trifoliate leaf.
Section 4: fourth internode + third trifoliate leaf.
Section 5: fifth internode + fourth trifoliate leaf.

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

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

[e]Only one sample analyzed.

[f]No samples analyzed.

CASE GS0097 CHLOROTHALONIL STUDY 17 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 10

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00086631 CONTENT CAT 01

Szalkowski, M.B., J.P. Marciniszyn, J.C. Killeen, Jr., et al. 1981. Accumulation, distribution and depuration of ^{14}C-residues of ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in channel catfish (Ictalurus punctatus) under static aquatic conditions: Document No. 077-3EI-80-0205-003. Unpublished study received Nov. 12, 1981 under 677-313; prepared in cooperation with Analytical Bio Chemistry Laboratories, Inc., submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:070467-D.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS PRIM: EEB-35-05000043 SEC: EEB-35-05100043 EEB-35-05050043 EEB-35-05150043 EFB-30-1010 EFB-30-1005

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

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CONCLUSION:

Laboratory Accumulation - Fish

This study is scientifically invalid because of the unacceptable test protocol; fish were exposed at too high a concentration of the test substance (10 ppm), resulting in fish stress and mortality. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because [^{14}C]chlorothaloni residues were not characterized, and a static exposure system was used.

MATERIALS AND METHODS:

Nonsterile sandy loam soil (73% sand, 23% silt, 4% clay, 0.1% organic matter, pH 8.2, CEC 9.5 meq/100 g) was treated with [^{14}C]chlorothalonil (analytical grade, purity 98%, specific activity 3548 dpm/µg, Diamond Shamrock Corp.) at 10 ppm, and maintained aerobically for 30 days at 22 ± 2 C. After the 30-day aging period, tanks containing treated or untreated soil were filled with well water [dissolved oxygen 9.3 ppm, pH 8.2, hardness ($CaCO_3$) 255 ppm] and aerated continuously for 3 days. Following the 3-day equilibration period, 255 channel catfish (Ictalurus punctatus) were added to each tank and maintained under static conditions for 26 days. Channel catfish remaining after this time were transferred to depuration tanks for 14 days.

Soil samples taken at appropriate intervals (Table 1) during the aging and accumulation periods were combusted, and the resulting ^{14}C collected and quantified by using LSC. Water samples were taken at intervals (Table 1) during the accumulation and depuration periods, allowed to settle for 15 minutes, and the ^{14}C concentration quantified by using LSC. All soil and water samples analyzed were composites of 5-8 samples taken from random locations throughout each tank.

At appropriate intervals during the accumulation and depuration periods, five channel catfish were removed from each tank. Two of these fish were homogenized whole. The remaining three fish were dissected into edible and viscera portions which were then pooled and homogenized. Duplicate subsamples of tissue homogenates (edible tissue, viscera, and whole fish) were combusted, and the ^{14}C trapped and quantified by using LSC.

Minimum detection limits were 0.0061 mg/kg whole fish, 0.0091 mg/kg edible tissue, 0.0069 mg/kg viscera, 0.018 mg/kg soil, and 0.0041 mg/l water. Recovery values averaged 97, 83, 78, and 91% for soil, edible tissue, whole fish, and viscera, respectively. Recovery values for water were not reported.

REPORTED RESULTS:

After 3 days of exposure to [^{14}C]chlorothalonil under static conditions, ^{14}C accumulation in whole channel catfish, edible tissue, and visceral tissues had reached maximum levels of 1.9, 0.83, and 2.4 mg/kg, respectively (Table 1). Radioactive residues in fish tissue reached a plateau by day 7 of exposure, and by the end of the accumulation period (day 26) were 0.95 mg/kg for whole fish, 0.33 mg/kg for edible tissue, and 1.4 mg/kg for viscera. Carbon-14 tissue concentrations steadily declined during the depuration period. By day 14, ^{14}C residues were 0.061 mg/kg for edible tissue and 0.079 mg/kg for both whole fish and viscera, representing clearance rates of 82, 92, and 94%, respectively. The maximum bioconcentration factor was 16X for whole fish, 9.4X for edible tissue, and 25X for visceral tissue.

DISCUSSION:

1. The accumulation portion of the study was terminated 4 days ahead of schedule because several of the treated fish died and the surviving fish were observed to be stressed and surfacing. Treated and untreated fish collected on day 26 of the accumulation phase were sent to Wildlife Vaccines, Inc., Colorado, and were found to have no disease causing parasites or bacteria. It was concluded that fish mortality and stress were due to the test substance. The purpose of fish accumulation studies is to determine the accumulation and elimination of the test substance in viable fish; this study is unacceptable for this purpose.

2. The test substance was not maintained at a constant concentration throughout the study.

3. On days 7, 14, 22, and 26 of accumulation and days 3 and 14 of depuration, ten additional fish were removed from both treated and control tanks for the purpose of characterization of the ^{14}C residues. However, the methods and results of residue characterization were not provided in this report.

Table 1. [^{14}C]Chlorothalonil residues in soil, water, and channel catfish tissue during a static bioaccumulation study.

Incubation period (days)		Soil (mg/kg)	Water (mg/l)	Edible tissue (mg/kg)	Whole fish (mg/kg)	Viscera (mg/kg)
Aging	0	7.7	--	--	--	--
	30	8.9	--	--	--	--
Uptake	0	6.8	0.069	--	--	--
	1	6.3	0.088	0.83	1.4	2.2
	3	6.0	0.12	0.65	1.9	2.4
	7	5.4	0.19	0.42	0.74	0.93
	10	5.6	0.22	0.31	0.80	1.1
	14	5.5	0.25	0.28	0.54	0.81
	22	5.6	0.31	0.36	0.89	0.88
	26	6.9	0.34	0.33	0.95	1.4
Depuration	1	--	--	0.36	0.82	0.73
	3	--	--	0.19	0.40	0.35
	7	--	--	0.081	0.090	0.10
	10	--	--	0.059	0.070	0.081
	14	--	--	0.061	0.079	0.079

CASE GS0097 CHLOROTHALONIL STUDY 18 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 1010

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00086633 CONTENT CAT 01

Szalkowski, M.B., J.P. Marciniszyn, J.C. Killeen, Jr., et al. 1981. Characterization and quantitation of ^{14}C-residues in water and fish exposed to ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) in a flow-through aquatic system: Document No. 268-3EI-79-0031-002. Unpublished study received Nov. 12, 1981 under 677-313; prepared in cooperation with Analytical Bio Chemistry Laboratories, Inc., submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:097467-F.

FICHE/MASTER ID 00029417 CONTENT CAT 06

Szalkowski, M.B., and D.E. Stallard. 1980. Characterization of ^{14}C-residues in water and fish exposed to ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) in a flow-through aquatic system. Unpublished study received Feb. 19, 1980 under 677-313; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:099248-O.

FICHE/MASTER ID 00029416 CONTENT CAT 06

Szalkowski, M.B., D.E. Stallard, and R.T. Bachand, Jr. 1979. Residue accumulation study in bluegill sunfish with ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) under flow-through conditions: Protocol No. RM-78-0017. Unpublished study received Feb. 19, 1980 under 677-313; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:099248-N.

FICHE/MASTER ID 00086632 CONTENT CAT 01

Szalkowski, M.B., D.E. Stallard, J.A. Ignatoski, et al. 1980. Accumulation, distribution and depuration of ^{14}C-4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) in bluegill sunfish (Lepomis macrochirus) under flow through aquatic conditions: Document No. 115-3EI-80-0176-001. Unpublished study received Nov. 12, 1981 under 677-313; prepared in cooperation with Analytical Bio Chemistry Laboratories, Inc., submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:070467-E.

SUBST. CLASS = T; CHEM R29121 IS TRANSF. PRODUCT OF CHEM 081901 OTHER SUBJECT DESCRIPTORS PRIM: EEB-35-05000043 SEC: EEB-35-05050043 EEB-35-05100043 EEB-35-05150043

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

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CONCLUSION:

Laboratory Accumulation - Fish

This study is scientifically invalid because fish were exposed to an impractical working concentration of the test substance, resulting in fish and mortality. If a lower exposure concentration had been used, this study would have partially fulfilled EPA Data Requirements for Registering Pesticides (1983) by providing information on the accumulation and depuration of DS-3701 (chlorothalonil degradate) in bluegill sunfish tissue in a flow-through exposure system.

MATERIALS AND METHODS:

Bluegill sunfish (Lepomis macrochirus), acclimated in culture tanks for >14 days to 22 C, were transferred to test aquaria designed for flow-through exposure conditions (500 ml water/minute/aquarium). Ring-labeled [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile, a chlorothalonil degradate (DS-3701, radiochemical purity 101%, specific activity 3075 dpm/µg), was introduced intermittently into the system to maintain an exposure concentration of 0.1 ppm throughout the 28-day accumulation period. After 28 days, the water [dissolved oxygen 9.3 ppm, pH 7.7, hardness ($CaCO_3$) 260 ppm] in each aquarium was replaced with untreated well water for a 14 day depuration period.

Fish and water samples were taken at 1, 3, 7, 10, 14, 22, and 28 days during the accumulation period, and at day 1, 3, 7, 10, and 14 of depuration. Water was also sampled at day 0 of each phase.

Eight fish were collected on each sampling date. Six of these fish were separated into edible and visceral tissue, and these tissue portions were pooled and homogenized with dry ice. An aliquot of each portion was combusted and the ^{14}C trapped and quantified by using LSC. The two remaining fish were homogenized whole and assayed for radioactivity by combustion and LSC. Fish samples were then stored frozen until analysis by TLC.

Thawed homogenized fish samples were extracted three times with acetone:3 N hydrochloric acid (80:20, v:v), centrifuged, the supernatants combined, and evaporated free of acetone. The remaining aqueous sample was acidified with 3 N hydrochloric acid to a pH <2, extracted twice with petroleum ether: diethyl ether (1:1, v:v), and the phases separated. A portion of the ether phase was concentrated, diluted with ether, and reconcentrated. Following extraction, the remaining fish tissue was dried and assayed for ^{14}C by combustion and LSC.

A portion of each water sample was assayed for total radioactivity in duplicate by using LSC; the remaining sample was stored frozen. Water samples were thawed, acidified with 3 N hydrochloric acid to a pH <2, extracted twice with petroleum ether:diethyl ether (1:1, v:v), and the phases were separated. A portion of the organic phase was concentrated, diluted with acetone, and reconcentrated.

LSC was performed on the original fish extract, and also on the aqueous phase, organic phase, and organic concentrate of fish and water extracts. Residues in the organic concentrates were characterized by using TLC. Recovery of radioactivity from combusted samples ranged from 93-100%. The detection limits were 0.014 ppm for whole fish, 0.016 ppm for edible tissue, 0.021 ppm for viscera, and 0.00093 ppm for water.

Radioactive residues in both water and fish were characterized using TLC. For TLC analysis, 100-150 µl portions of the water or fish extracts were applied as 2-cm bands to silica-gel TLC plates along with known standards. The TLC plates were developed by ascending chromatography to a distance of 165 mm from the origin using hexane:acetone (1:1). The TLC plates were visualized using UV light and autoradiographed. Radioactive zones were scraped from the plates and quantified using LSC.

REPORTED RESULTS:

Radioactive residues in bluegill sunfish exposed for 28 days to [^{14}C]-DS-3701 at 0.1 ppm, under flow-through conditions were 0.48 ppm, 0.19 ppm, and 0.81 ppm for whole fish, edible tissue, and viscera, respectively (Table 1). Corresponding bioconcentration factors were 4.4, 1.7, and 7.4X. During 14 days in untreated water, the depuration rate constant was 0.061 ppm per day. By day 10 of the depuration phase, fish had eliminated 100% of accumulated residues. Radioactive residues were identified as [^{14}C]DS-3701.

DISCUSSION:

During the study, a total of 47 of the 240 fish died in the exposure tanks (~20%); all of these fish had severe eye tissue damage. No disease causing parasites or bacteria (as determined by Wildlife Vaccines, Inc., Colorado) were found in affected fish; therefore, it was concluded that fish mortality was a result of the test substance.

Table 1. Concentration (ppm) of [^{14}C]DS-3701 in water and bluegill sunfish during bioaccumulation and depuration.

Phase/Day		Water	Whole fish	Edible	Viscera
Accumulation	0	0.099			
	1	0.11	0.24	0.094	0.37
	3	0.11	0.43	0.19	0.76
	7	0.11	0.39	0.14	0.56
	10	0.11	0.32	0.15	0.59
	14	0.11	0.48	0.15	0.81
	22	0.11	0.28	0.11	0.53
	28	0.094	0.48	0.19	0.81
Depuration	0	0.018			
	1	0.002	0.30	0.12	0.70
	3	ND[a]	0.056	0.036	0.16
	7	ND	0.020	ND	0.022
	10	ND	ND	ND	ND
	14	ND	ND	ND	ND

[a]Less than 0.00093 ppm for water, 0.014 ppm for whole fish, 0.016 ppm for edible, and 0.021 ppm for visceral tissue.

CASE GS0097 CHLOROTHALONIL STUDY 19 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC TOPIC

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00086629 CONTENT CAT 01

Szalkowski, M.B., D.E. Stallard, J.A. Ignatoski, et al. 1980. Accumulation, distribution and depuration of ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in bluegill sunfish (Lepomis macrochirus) under flow-through aquatic conditions: Document No. 079-3EI-80-0120-001. Unpublished study received Nov. 12, 1981 under 677-313; prepared in cooperation with Analytical Bio Chemistry Laboratories, Inc., submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:070467-B.

FICHE/MASTER ID 00029411 CONTENT CAT 06

Szalkowski, M.B., D.E. Stallard, and R.T. Bachand, Jr. 1979. Residue accumulation study in bluegill sunfish with ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil) under flow-through conditions: Protocol No. RM-78-0018. Unpublished study received Feb. 19, 1980 under 677-313; submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:099248-I.

FICHE/MASTER ID 00086630 CONTENT CAT 01

Szalkowski, M.B., J.P. Marciniszyn, J.C. Killeen, Jr., et al. 1981. Characterization and quantitation of ^{14}C-residues in water and fish exposed to ^{14}C-2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil, DS-2787) in a flow-through aquatic system: Document No. 116-4EI-81-0016-003. Unpublished study received Nov. 12, 1981 under 677-313; prepared in cooperation with Analytical Bio Chemistry Laboratories, Inc., submitted by Diamond Shamrock Agricultural Chemicals, Cleveland, OH; CDL:070467-C.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS PRIM: EEB-35-05000043 SEC: EEB-35-05100043 EEB-35-05200043

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

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study is scientifically valid.

2. Radioactive residues accumulate in bluegill sunfish tissues reaching a plateau (3.0 ppm) after 14 days of exposure to [^{14}C]chlorothalonil at 0.008 mg/l in a flow-through exposure system. At day 30 of the exposure period ^{14}C residues were 1.9 ppm, 0.55 ppm, and 3.7 ppm for whole fish, edible tissue, and viscera, respectively. Corresponding bioconcentration factors were 264, 76, and 514 times the mean exposure concentration of 0.0072 mg/l. Accumulated [^{14}C]chlorothalonil was depurated rapidly; after 14 days in untreated water, chlorothalonil residues had declined to 0.38, 0.30, and 0.54 ppm in whole fish, edible, and visceral tissues, respectively. Of the residues accumulated in fish after 30 days of exposure, 0.041 ppm was characterized to be chlorothalonil while the degradates 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) and 3-cyanotrichlorohydroxybenzamide (DS-19221) were not detected (<0.04 ppm). The majority of the accumulated residues were unextractable (35-69%) or unidentified polar, water soluble residues (28-47%).

3. This study fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the accumulation and depuration of [^{14}C]chlorothalonil in bluegill sunfish in a flow-through exposure system, and on the identification of DAC-3701 and DS-19221 as metabolites.

MATERIALS AND METHODS:

Bluegill sunfish (Lepomis macrochirus; average weight and length, 4.9 g and 69 mm, respectively), acclimated for >14 days in culture tanks to 22 C, were transferred to test aquaria designed for flow-through exposure conditions (500 ml water/minute/aquarium). Ring-labeled [^{14}C]chlorothalonil (analytical grade, purity 99.9%, specific activity 29369 dpm/µg, Diamond Shamrock Corp.) was introduced intermittently into the system to maintain an exposure concentration of 0.008 mg/l throughout the 30 day accumulation period. Untreated fish maintained in a similar aquarium served as a control. The water characteristics were pH <8.0, dissolved oxygen 9.3 ppm, and hardness ($CaCO_3$) 260 ppm. After 30 days, the water in each aquarium was replaced with untreated well water for a 14-day depuration period. Fish and water samples were taken at 1, 3, 7, 10, 14, 22, and 30 days during the accumulation period, and at day 1, 3, 7, 10, and 14 of depuration. Water was also sampled at day 0 of each phase.

Residues in samples collected on days 7, 14, 22, and 30 of accumulation and days 3 and 14 of depuration were characterized. Water samples were acidified with 3 N HCl to a pH <2 and extracted twice with petroleum ether:diethyl ether (1:1). Radioactivity of the original water sample and the aqueous and organic phases of the extracts were determined by using

LSC (detection limit 0.00005 mg/l). Water samples were also acidified to a pH <2 by using 3 N HCl, diluted with n-butyl alcohol, evaporated to dryness, diluted with methanol, reevaporated to 1 ml, and characterized by using TLC (detection limit 0.002 µg/ml). Fish samples (whole fish, edible tissue, and viscera) were homogenized with dry ice, combusted, and the resultant $^{14}CO_2$ trapped and quantified by using LSC (LSC detection limits for edible tissue, viscera, and whole fish were 0.0028, 0.0036, and 0.0022 mg/kg, respectively). Homogenized fish were also extracted three times with acetone:0.3 N HCl (80:20), the extracts combined, and a portion assayed for radioactivity by using LSC. The remaining extract was evaporated free of acetone, acidified to a pH <2 with 3 N HCl, extracted twice with petroleum ether:diethyl ether (1:1), and the aqueous and organic phases assayed by using LSC. The organic phase was diluted with n-butyl alcohol, evaporated to dryness, and rediluted with methanol. The aqueous phase was diluted with n-butyl alcohol, evaporated to dryness, and rediluted with methanol. Both phases were assayed for radioactivity by using LSC and characterized by using TLC (detection limit 0.04 µg/ml).

REPORTED RESULTS:

Radioactive residues in bluegill sunfish exposed for 30 days to [^{14}C]chlorothalonil, at 0.008 mg/l, in a flow-through exposure system were 1.9 ppm, 0.55 ppm, and 3.7 ppm for whole fish, edible tissue, and viscera, respectively (Table 1). Corresponding bioconcentration factors were 264, 76, and 514 times the mean exposure concentration of 0.0072 mg/l. Maximum [^{14}C]chlorothalonil levels of 3.1 ppm (whole fish), 0.73 ppm (edible tissue), and 5.8 ppm (viscera) occurred at day 14 of accumulation. After 14 days in untreated flowing water, [^{14}C]chlorothalonil levels were 0.38 ppm in whole fish, 0.30 ppm in edible tissue, and 0.54 ppm in viscera, representing 80%, 45%, and 85% elimination of accumulated ^{14}C residues. Less than 6% of the radioactive residues accumulated in fish were characterized to be chlorothalonil or its known degradates, DAC-3701 and DS-19221 (Table 2). Unextractable ^{14}C residues accounted for 35-69% of the total radioactivity, and 28%-47% was characterized to be polar, water soluble ^{14}C residues.

DISCUSSION:

Experimental procedures and protocols were adequate to evaluate the accumulation and depuration of [^{14}C]chlorothalonil in bluegill sunfish tissue.

Table 1. Concentration (ppm) of [^{14}C]residues as chlorothalonil equivalents in water and bluegill sunfish during bioaccumulation and depuration.

Phase/Day		Water	Whole fish	Edible tissue	Viscera
Accumulation	0	0.0070	--[a]	--	--
	1	0.0064	1.8	0.14	3.8
	3	0.0079	1.8	0.20	1.9
	7	0.0066	2.7	0.72	4.3
	10	0.0073	2.5	0.51	5.4
	14	0.0076	3.0	0.70	5.8
	22	0.0071	2.4	0.53	4.3
	30	0.0075	1.9	0.55	3.7
Depuration	0	0.0011	--	--	--
	1	0.0011	1.4	0.48	2.2
	3	ND[b]	0.81	0.35	1.2
	7	ND	0.57	0.26	0.77
	10	ND	0.48	0.26	0.75
	14	ND	0.38	0.30	0.54

[a]--; not sampled.

[b]ND; not detected, detection limit 0.00005 ppm.

Table 2. Characterization of [^{14}C]chlorothalonil residues in fish tissues.

Day[a]	Total ^{14}C-residues	Unextractable	Chlorothalonil	DAC-3701	DS-19221	Origin-I[b]	Zone III[c]	Origin-II[d]	Zone IV[e]
Whole Fish									
7-A	2.96	1.20	ND[f]	ND	ND	0.055	ND	0.463	0.641
14-A	3.44	1.96	0.031	ND	0.037	0.064	0.080	0.822	0.305
22-A	2.57	1.23	0.100	ND	ND	0.056	ND	0.460	0.231
30-A	2.29	1.25	0.041	ND	ND	0.033	ND	0.497	0.230
3-D	0.848	0.487	0.011	ND	ND	ND	ND	0.141	ND
14-D	0.395	0.274	ND	ND	ND	ND	ND	0.067	ND
Fillet									
7-A	0.898	0.439	ND	ND	ND	0.019	ND	0.214	ND
14-A	0.739	0.385	0.042	ND	ND	0.013	ND	0.187	ND
22-A	0.596	0.308	ND	ND	ND	0.012	ND	0.104	0.078
30-A	0.630	0.352	0.016	ND	ND	0.006	ND	0.150	ND
3-D	0.378	0.231	0.013	0.004	ND	ND	ND	0.078	ND
14-D	0.287	0.156	ND	ND	ND	ND	--	0.045	0.119
Viscera									
7-A	4.78	1.68	ND	ND	ND	0.141	ND	1.32	0.505
14-A	6.24	3.28	0.053	ND	0.031	0.191	ND	1.52	0.825
22-A	5.13	2.40	0.064	ND	ND	0.116	ND	1.19	0.404
30-A	4.79	2.58	0.049	ND	0.018	0.110	ND	1.04	0.197
3-D	1.19	0.676	0.043	ND	ND	0.014	ND	0.268	0.092
14-D	0.607	0.317	ND	ND	0.030	ND	ND	0.101	ND

CASE GS0097 CHLOROTHALONIL STUDY 20 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Sleight, B.H. 1972. Exposure of fish to ^{14}C-labeled chlorothalonil (DAC-2787, tech.): accumulation, distribution, and elimination of residues. Unpublished study prepared for Diamond Shamrock Corporation by Bionomics, Inc., Accession No. 099248.

SUBST. CLASS =

DIRECT RVW TIME = 3 (MH) START-DATE END DATE

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study is scientifically valid.

2. At very low concentrations of chlorothalonil (0.003 ppm) in water, bluegill sunfish accumulate around 200 times the ambient water concentration of chlorothalonil in edible tissues. Viscera tissues contain ~15 times more (radioactive) residues than muscle tissue. A residue plateau was reached after 3-10 days and depuration was rapid, with a half-life of about 10 days.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because radioactive residues were not identified, total residues in whole fish were not determined, and visceral tissues were analyzed only on day 28 of exposure.

MATERIALS AND METHODS:

Bluegill sunfish (Lepomis macrochirus; average length and weight of 2-3 inches and 3 g, respectively) were held in hatchery facilities (conditions unspecified) for >15 days prior to the initiation of the study. Cumulative mortality during this time was <2%. Flow-through aquatic exposure systems were prepared using two 30-l aquaria equipped with continuous-flow proportional dilution apparatus, as described by Mount and Brungs (1967. Water Res. 1:21). Aerated well water (pH 7.1, total hardness ($CaCO_3$) 40 ppm, dissolved oxygen >0.5 ppm, temperature 18 ± 0.5 C) was provided to each aquarium at a flow rate of 6 l/hr.

One hundred bluegill were placed in each aquarium and acclimated for 5 days. After the acclimation period, one aquarium was continuously treated with [^{14}C]chlorothalonil (specific activity 2105 dpm/µg; source and purity unspecified) in acetone, at 0.01 ppm. The second aquarium served as an untreated control.

Duplicate 500-ml water samples and five fish were taken from each aquarium prior to exposure and at 1, 3, 7, 10, 14, 21, and 28 days of exposure.

After the exposure period, the fish remaining in the treated aquarium (number of fish unspecified) were transferred to an aquarium containing untreated water for a 14-day depuration period. Fish were sampled at 1, 3, 7, 10, and 14 days of depuration.

Fish were eviscerated, and the edible portion (muscle) analyzed for [^{14}C]-chlorothalonil residues radiometrically. The relative distribution of residues in edible and nonedible tissues was determined only at 28 days of exposure. Relative amounts of polar and nonpolar residues were also determined at this interval.

Fish tissue radioassays were performed by drying duplicate samples of fish tissue (0.5-1.0 g) for ~24 hours on filter discs at 3 C. Each dried sample (300-500 mg) was combusted. The $^{14}CO_2$ evolved from the combustion was trapped as carbonate in ethanolamine, and the ethanolamine was transferred to a scintillation vial. The $^{14}CO_2$ trapping vessel was then rinsed with methanol and counting fluid, and the rinses were also transferred to the scintillation vial. Standard reference material was oxidized with control fish to determine recovery values; recovery values ranged from 98-101%.

To determine polar and nonpolar residues, separate hexane and methanol extractions were made of fish tissue. Fish samples were blotted dry, weighed, and homogenized for 3 minutes (22,000 rpm) with 30 g of anhydrous granular sodium sulfate, 16 g of Celite (filter aid), and 150 ml of hexane. The extract was filtered, and reextracted twice with 100 ml portions of hexane. The extracts were combined, evaporated to a volume of 1-3 ml, and quantified by using LSC. This procedure was then repeated using separate fish tissue samples, substituting methanol for hexane. The detection limit was 0.005 ppm for fish tissue.

Water samples (500 ml) were extracted four times with methylene chloride (50, 25, 25, and 25 ml volumes). The extracts were combined, concentrated to a volume of 20 ml, and quantified by using LSC. Recovery of DAC-3701 from water samples was 94%. The detection limit was 0.001 ppm for water samples.

REPORTED RESULTS:

Accumulation of [^{14}C]chlorothalonil residues in the edible portion of bluegill tissue reached a plateau of 0.72 ± 0.34 ppm after ~10 days of exposure (average exposure concentration was 0.003 ppm). Mean chlorothalonil residues were ≤0.59 ± 0.14 ppm from day 14 of exposure to day 28 (Table 1). Chlorothalonil residues in nonedible tissues after 28 days of exposure were ~15 times the concentration of residues in edible tissues, with a mean residue level of 8.6 ± 2.7 ppm. About 16% of the residues were extractable by hexane (nonpolar), and about 18% were extractable by methanol (polar). Chlorothalonil residues accumulated by day 28 (0.59 ± 0.14 ppm) had declined by ~50% after 10 days of depuration (0.30 ± 0.14 ppm) and by ~62% after 14 days of depuration (0.25 ± 0.07 ppm) (Table 2).

DISCUSSION:

1. Radioactive residues were not identified.

2. The exposure concentration in the water (0.003 ppm) was much lower than the intended level (0.01 ppm). This was probably due to adsorption of chlorothalonil to plastic tubing in the dilutor and/or an inaccurate dilutor, resulting in a 30% error.

3. Total residues in whole fish were not determined, and viscera was analyzed only on day 28 of exposure.

Table 1. Mean ^{14}C residues in water and in the edible portion of bluegills continuously exposed to [^{14}C]chlorothalonil for 28 days.

Day	Measured concentration (ppm) in water	Average residue level[a] (ppm) in fish
0	0.0032	--
1	0.0031	0.23 ± 0.06
3	0.0029	0.48 ± 0.10
7	0.0024	0.54 ± 0.17
10	0.0033	0.72 ± 0.34
14	0.0030	0.48 ± 0.13
21	0.0029	0.56 ± 0.20
28	0.0031	0.59 ± 0.14

[a]Mean (±SD) usually based on 10 radiometric analyses; the minimum number of observations was 8. Detectable limit = 0.005 mg/kg. Average exposure level = 0.003 mg/l.

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Table 2. Mean ^{14}C residues in the edible portion of bluegills during 14-day depuration period.

Day	Average residue level[a] (ppm)
1	0.59 ± 0.14
3	0.51 ± 0.18
7	0.40 ± 0.13
10	0.30 ± 0.14
14	0.25 ± 0.07

[a]Mean (±SD) usually based on 10 radiometric analyses; the minimum number of observations was 8. Detectable limit = 0.005 mg/kg.

CASE GS0097 CHLOROTHALONIL STUDY 21 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Sleight, B.H. 1972. Exposure of fish to ^{14}C-labeled DAC-3701: accumulation, distribution, and elimination of residues. Unpublished study prepared for Diamond Shamrock Corporation by Bionomics, Inc., Accession No. 099248.

SUBST. CLASS =

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study is scientifically valid.

2. Chlorothalonils' degradation product, 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701) accumulated in bluegill sunfish exposed to water containing the degradate at 0.005 and 0.61 ppm. [^{14}C]DAC-3701 residues in the edible portion of bluegill reached a plateau by day 3 of exposure to 0.005 ppm (0.19 ± 0.02 ppm) and by day 28 of exposure to 0.61 ppm (48.9 ± 11.0 ppm). Elimination of [^{14}C]-DAC-3701 residues from bluegill was 50% complete within 7 days.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because DAC-3701 radioactive residues were not identified or characterized, and sufficient whole body residues were neither determined nor characterized.

MATERIALS AND METHODS:

Bluegill sunfish (Lepomis macrochirus; average length and weight of 2-3 inches and 3 g, respectively) were held in hatchery facilities (conditions unspecified) for >15 days prior to the initiation of the study. Cumulative mortality during this time was <2%. Flow-through aquatic exposure systems were prepared using three 30-l aquaria equipped with continuous-flow proportional dilution apparatus, as described by Mount and Brungs (1967. Water Res. 1:21). Aerated well water (pH 7.1, total hardness ($CaCO_3$) 40 ppm, dissolved oxygen >5.0 ppm, temperature 18 ± 0.5 C) was provided to each aquarium at a flow rate of 6 l/hr.

One hundred bluegill were placed in each aquarium and acclimated for 5 days. After the acclimation period, two of the aquaria were continuously treated with a major degradation product of chlorothalonil, [^{14}C]4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701, specific activity 14.5 or 1587 dpm/µg, source unspecified) in acetone, at 0.01 and 1 ppm. The third aquarium served as an untreated control.

Duplicate 500-ml water samples and five fish were taken from each aquarium prior to exposure and at 1, 3, 7, 10, 14, 21, and 28 days of exposure. Water and fish were also sampled from the aquarium treated with DAC-3701 at 1 ppm at 35, 42, and 49 days of exposure.

After the exposure periods (28 and 49 days for the 0.01 and 1.0 ppm exposure concentrations, respectively) the fish remaining in the DAC-3701-treated aquaria (number of fish unspecified) were transferred to aquaria containing untreated water for a 28-day depuration period. Fish were sampled at 1, 3, 7, 10, 14, 21, and 28 days of depuration.

Fish were eviscerated, and the edible portion (muscle) analyzed for [^{14}C]-DAC-3701 residues radiometrically. The relative distribution of residues in edible and nonedible tissues was determined only at 28 days of exposure (0.01 ppm) and 49 days of exposure (1 ppm). Relative amounts of polar and nonpolar residues were also determined at these intervals (28 and 49 days).

Fish tissue radioassays were performed by drying duplicate samples of fish tissue (0.5-1.0 g) for ~24 hours on filter discs at 3 C. Each dried sample (300-500 mg) was combusted. The $^{14}CO_2$ evolved from the combustion was trapped as a carbonate in ethanolamine, and the ethanolamine was transferred to a scintillation vial. The $^{14}CO_2$ trapping vessel was then rinsed with methanol and counting fluid, and the rinses were also transferred to the scintillation vial. Standard reference material was oxidized with control fish to determine recovery values; recovery values ranged from 98-101%.

To determine polar and nonpolar residues, separate hexane and methanol extractions were made of fish tissue. Fish samples were blotted dry, weighed, and homogenized for 3 minutes (22,000 rpm) with 30 g of anhydrous granular sodium sulfate, 16 g of Celite (filter aid), and 150 ml of hexane. The

extract was filtered, and reextracted twice with 100-ml portions of hexane. The extracts were combined, evaporated to a volume of 1-3 ml, and quantified by using LSC. This procedure was then repeated using separate fish tissue samples, substituting methanol for hexane. Detection limits were 0.01 and 0.75 mg/kg for fish tissue at the 0.01 and 1 ppm treatment concentrations, respectively.

Water samples (500 ml) were extracted four times with equal volumes of methylene chloride (amount unspecified). The extracts were combined, concentrated to a volume of 10 ml, and quantified by using LSC. Recovery of DAC-3701 from water samples was 34%. Detection limits were 0.002 and 0.30 mg/l for water samples from the 0.01 and 1 ppm treatment concentrations, respectively.

REPORTED RESULTS:

The control group suffered no mortality during the experiments, nor did the groups exposed to DAC-3701 at 0.01 ppm. The fish exposed at the high concentration became lethargic and exhibited discoloration after 16 days; about 18% mortality was observed after 28 days in the fish exposed at the high concentration. Water samples contained the compound at actual average exposure levels of around 0.005 and 0.61 ppm instead of 0.01 and 1 ppm, respectively, as shown in Table 1. Fish exposed at a nominal concentration of 0.01 ppm reached peak accumulation levels (0.19 ± 0.02 ppm) in edible tissues between the 1st and 3rd days (Table 2). The maximum accumulation level of edible fish tissues exposed at the nominal concentration of 1 ppm was 48.9 ± 11.0 ppm, reached on the 28th day of exposure (Table 1). Thereafter the accumulated concentration declined. On the average, nonedible tissues bioconcentrated five times as much as edible tissues. About half of the residues were eliminated within 7 days during depuration (Table 3). Less than 4% of the residues in fish exposed at the nominal 1 ppm concentration for 49 days remained after 28 days of depuration.

Of the residues remaining in the edible tissues of fish exposed to DAC-3701 at the high concentration, about 1% was extractable by hexane and about 34% was extractable with methanol. Corresponding values for fish exposed at the lower concentration were 8% (hexane) and 24% (methanol), respectively.

DISCUSSION:

1. Analysis for residues in edible and nonedible portions were only conducted for the 28 and 49 day samples for the 0.01 and 1 ppm exposure levels, respectively. Whole body residues were not determined for any of the sampling intervals for either of the exposure levels.

2. Radioactive residues were not characterized.

3. Actual concentrations of DAC-3701 in the water in this study are questionable because a 34% recovery rate from the water was reported. The report used the nominal water concentrations for calculations of bioconcentration factors, thus yielding data based on nominal water values. Bioconcentration factors reported in this review were calculated using actual measured water concentrations.

4. Determination of DAC-3701 residue accumulation in bluegill at an exposure concentration of 0.61 ppm may yield unreliable results because the compound is toxic to fish (18% mortality rate).

Table 1. [^{14}C]DAC-3701 residues measured in the water during continuous exposure of bluegill sunfish.

Day	Measured concentration (ppm) (Nominal) 0.01 ppm	(Nominal) 1.0 ppm
0	0.005	0.69
1	0.004	0.77
3	0.004	0.50
7	0.005	0.52
10	0.006	0.44
14	0.005	0.49
21	0.005	0.58
28	0.004	0.45
35	--	0.50
42	--	0.42
49	--	0.44

Table 2. Mean measured ^{14}C residues (mg/kg) in the edible portion of bluegill sunfish (Lepomis macrochirus) during continuous exposure to [^{14}C]DAC-3701.

	Nominal exposure concentration (mg/l)[a]	
	0.01	1.0
Day	Average[b] residue concentration	Average[b] residue concentration
1	0.16 ± 0.02	2.2 ± 0.5
3	0.19 ± 0.02	3.1 ± 0.7
7	0.15 ± 0.02	6.8 ± 1.3
10	0.15 ± 0.02	15.6 ± 3.6
14	0.10 ± 0.05	18.3 ± 6.5
21	0.09 ± 0.02	25.2 ± 5.0
28	0.07 ± 0.02	48.9 ± 11.0
35	--	31.9 ± 17.0
42	--	20.6 ± 9.5
49	--	21.2 ± 7.6

[a]Actual exposure concentration average 0.005 and 0.61 mg/l throughout the course of the experiment.

[b]Average (±SD) based on 6-10 radiometric analyses. Minimum detectable limits were 0.75 mg/kg (high concentration) and 0.01 mg/kg (low concentration).

Table 3. Mean measured ^{14}C residues (mg/kg) in the edible portion of bluegill sunfish during the depuration period following either 28 or 49 days of exposure to [^{14}C]DAC-3701 at 0.01 and 1.0 mg/l, respectively.

	Nominal exposure concentration (mg/l)[a]	
	0.01	1.0
Day	Average[b] residue concentration	Average[b] residue concentration
1	0.04 ± 0.01	20.0 ± 3.4
3	0.04 ± 0.01	24.7 ± 7.6
7	<0.02	11.8 ± 6.6
10	<0.01	13.5 ± 8.8
14	<0.01	<3.8 ± 3.7
21	--	2.0 ± 0.6
28	--	<1.8 ± 0.5

[a]Actual exposure concentrations averaged 0.005 and 0.61 mg/l, respectively.

[b]Average (±SD) based on 6-10 radiometric analyses. Minimum detectable limits of 0.75 mg/kg (high concentration) and 0.01 mg/kg (low concentration).

CASE GS0097 CHLOROTHALONIL STUDY 22 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC 30 TOPIC 050515 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 04 - FLOWABLE CONCENTRATE (F)

FICHE/MASTER ID 00071058 CONTENT CAT 01

Johnston, E.F. 1981. Soil disappearance studies with Benlate fungicide and Bravo 500 F fungicide, alone and in combination: Document No. AMR-06-81. Unpublished study received Feb. 27, 1981 under 352-354; submitted by E.I. du Pont de Nemours & Co., Wilmington, DE; CDL:244633-B.

SUBST. CLASS = S.

DIRECT RVW TIME = 3 (MH) START-DATE END DATE

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CONCLUSIONS:

Dissipation - Combination Products and Tank Mix Uses

1. This study is scientifically valid.

2. Chlorothalonil is degraded with a half-life of 1-3 months in sandy loam and silt loam soils when applied alone or in combination with benomyl.

3. Compliance to EPA Data Requirements for Registering Pesticides (1983) is not being evaluated because data requirements for combination products and tank mix uses are currently not being imposed for this Standard.

MATERIALS AND METHODS:

Chlorothalonil (Bravo 500 F, 4.17 lb/gal FlC, source unspecified) was applied at 8.34 lb ai/A alone and in combination with benomyl (Benlate, 50% WP, source unspecified, 1.35 lb ai/A) to 150-g aliquots of Fallsington sandy loam (56% sand, 29% silt, 15% clay) and Flanagan silty clay loam (5% sand, 64% silt, 31% clay) soils. The treated soils were mixed thoroughly and incubated at 80% of moisture capacity in a greenhouse. Soil samples were collected at 0 and 14 days and 1, 3, and 6 months posttreatment.

To determine chlorothalonil levels the samples were air dried and extracted with acidified acetone. The acetone was evaporated under vacuum at 40 C. The residue was redissolved in 0.4 M $NaHCO_3$ and the solution adjusted to pH 4.5. The $NaHCO_3$ solution was extracted twice with ethyl acetate and the extracts were concentrated. The oily residue was diluted with toluene and analyzed for chlorothalonil by using a GC equipped with an electron capture detector. Recovery values for chlorothalonil averaged 98.5% with a limit of detection of 0.01 ppm. Benomyl levels were determined using the method of Kirkland, et al. 1973. (J. Agric. Food Chem. 21:368). Recovery values for benomyl averaged 77% with a limit of detection of 0.05 ppm.

REPORTED RESULTS:

The dissipation rate of chlorothalonil in Fallsington sandy loam and Flanagan silt loam soils was the same when chlorothalonil was applied alone or tank mixed with benomyl (Table 1).

DISCUSSION:

1. The test soil reported as a Flanagan silt loam is a silty clay loam according to the USDA soil textural classification system.

2. Patterns of formation and decline of degradates were not established.

3. A two month sample should have been taken to more accurately estimate the half-life of chlorothalonil applied individually and in combination with benomyl.

Table 1. Chlorothalonil concentrations (ppm) in soils when applied alone or in combination with benomyl.

Treatment	Application rate (lb ai/A)	Sampling interval 0 days	14 days	1 month	3 months	6 months
		Fallsington sandy loam				
Chlorothalonil	8.34	17.5	14.5	10.2	3.5	0.7
Chlorothalonil[a] Benomyl	8.34 1.35	18.5	15.0	10.5	3.8	0.5
		Flanagan silty clay loam[b]				
Chlorothalonil	8.34	18.5	12.0	9.4	1.3	0.5
Chlorothalonil[a] Benomyl	8.34 1.35	18.5	13.0	8.3	8.4	0.2

[a]Tank mixture.

[b]Reported as a silt loam; see Discussion No. 3.

CASE GS0097 CHLOROTHALONIL STUDY 23 PM 400 08/03/82

CHEM 081901 Chlorothalonil

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Capps, T.M., J.P. Marciniszyn, A.F. Markes, and J.A. Ignatoski. 1982. Document No. 555-4EF-81-0261-001, Section J, Vol. VI. Submitted by Diamond Shamrock Corp.

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SIGNATURE: DATE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Chlorothalonil has a moderately high potential to be adsorbed to silt, silty clay loam, and sandy loam soils, and a relatively low mobility. Adsorption of chlorothalonil to sand was low. Adsorption K constants were 26, 29, 20, and 3 for the silty clay loam, silt, sandy loam, and sand soils, respectively.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing data on the mobility of chlorothalonil unaged in silt, silty clay loam, sandy loam, and sand soils. Mobility data for DAC-3701, a major degradate of chlorothalonil, was not provided.

MATERIALS AND METHODS:

Four concentrations (~0.1, 0.2, 0.4, and 0.5 µg/ml) of ring-labeled [^{14}C]chlorothalonil (SA = 375,564 dpm/µg) in 0.03 N calcium sulfate (pH 7.0) were applied to samples of sieved silty clay loam, silt, sand, and sandy loam soils (Table 1). The soils were air dried and sieved as follows: clay and silt soils were sieved through a 250 µm screen prior to use; sand and sandy loam soils were sieved through a 400 µm sieve prior to use.

Equilibration times were established by treating soil samples with the [^{14}C]chlorothalonil and shaking them for various lengths of time (1, 3, 5, and 8 hours for the silt soils and an additional sample at 24 hours for the sand soils). After equilibration, the samples were centrifuged, and portions of the supernatant were quantified by LSC.

To determine adsorption, 2.0-g samples of each soil were treated with 8.0 ml of test solution at each concentration. The samples were shaken in a shaker bath for the previously established equilibration time, centrifuged and the radioactivity in the supernatant quantitated by LSC. The adsorption/desorption phases involving the sandy soils, were based on a 24-hour period.

Immediately after adsorption, a portion of each supernatant was removed and the same amount of 0.03 N $CaSO_4$ blank added back to the supernatant. The samples were then shaken for an additional equilibration period equivalent to those established for the adsorption phase. After equilibration, the samples were centrifuged and the radioactivity in the supernatant quantified by LSC. This desorption phase was carried out twice.

REPORTED RESULTS:

Approximately 90% of the chlorothalonil in solution was adsorbed within 1 hour for silty clay loam and silt soils. For the sandy loam and sand soils, 84% and 47% of the chlorothalonil were adsorbed, respectively, and 8 hours were required to establish equilibrium. The adsorption constants (K) and percent desorption are shown in Table 2.

DISCUSSION:

1. This study was submitted to supercede a soil adsorption/desorption study reviewed by EFB on October 21, 1980 (data were contained in accession number 071096). The new submission provides updated information on the effect of sieving at <500 µm on soil characteristics. The new information (Table 1) shows that the soil characteristics remain the same when sieved below 500 µm; therefore, the adsorption characteristics of the test soils were not altered, and K values were not appreciably affected. This study did not, however, provide mobility data for 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC-3701). Since DAC-3701 is a major degradate of chlorothalonil, an adsorption constant must be determined for it, as well as for chlorothalonil.

2. Mobility data for DAC-3701, a major degradate of chlorothalonil, was not provided. Chlorothalonil adsorption K constants were 26, 29, 20, and 3 for the silty clay loam, silt, sandy loam, and sand soils, respectively (Table 1). Desorption of chlorothalonil from the respective soils was 1.8-2.9, 1.8-3.2, 4.2-6.6, and 9.5-28.4%.

Table 1. Soil characteristics.

Soil	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
			%			
Sandy loam	63.6	28.4	8.0	3.5	6.1	10.95
after sieving[a]	65.5	30.4	4.0	3.2	5.7	12.64
Sand	96.0	--	4.0	0.6	6.8	1.50
after sieving[a]	96.0	--	4.0	0.6	6.4	1.80
Silty	8.0	84.0	8.0	0.8	7.7	10.30
after sieving[b]	10.0	82.0	8.0	0.7	7.5	10.00
Silty clay loam	12.0	62.0	26.0	3.2	6.6	25.10
after sieving[b]	6.0	64.0	30.0	3.2	6.6	24.90

[a]Passed through a 500 µm sieve prior to use.

[b]Passed through a 250 µm sieve prior to use.

Table 2. Chlorothalonil adsorption (K) constants and percent desorption in soil.

Soil texture	Chlorothalonil adsorption constants (K)	Percent desorption of chlorothalonil (range for 2 desorption steps)
Silty clay loam	26	1.8 - 2.9
Silt	29	1.8 - 3.2
Sandy loam	20	4.2 - 6.6
Sand	3	9.5 - 28.4