

FTSanders:ow
July 15, 1971

Evaluation of Environmental Data for
Registration of Chlorothalonil (2,4,5,6-
tetrachloroisophthalonitrile)
PP No. 1F1024
Submitted by Diamond Shamrock Chemical Corp.
Filed May 4, 1971

I. Introduction

1. Chlorothalonil is also referred to as Daconil 2787.

II. Discussion of Data

1. Determination of Daconil 2787 in Soil

The method is based on the extraction of Daconil 2787 from soil using either dichloromethane or acetone. The residue of Daconil 2787 is determined microcoulometrically after separation by vaporphase chromatography. Recoveries of 86-116% were obtained from fortified soil.

2. Section I and II
Degradation of Daconil 2787 in Soil (Laboratory Tests)

(a) Effect of pH

To study the effect of pH on the degradation of Daconil 2787, 3 samples of 11smore silty clay loam soil (S. Dakota) were weighed into a glass jar. The moisture level of each soil sample was held constant and the pH levels were adjusted as described below. Each soil sample was fortified with approximately 45 ppm Daconil 2787 and incubated at 98°F.

Incubation	Daconil 2787 Residue, PPM		
	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

It appears that the degradation of Daconil 2787 is not critically dependent upon the pH of soil within the limits of pH range of this experiment. See conclusion.

(b) Effect of Water

In this series of experiments, three samples of soil from each of three locations were prepared to contain 6%, 3%, and a minimum amount of water. Each sample was fortified with approximately 40 ppm Daconil 2787. All samples were incubated at 98°F for 21 days.

Source	Soil Type	Daconil 2787 Residue, PPM			Half-life (Days)
		H ₂ O%	0-Day	21 Days	
Louisiana	Yohola Sandy Loam	0.6	45	46	>70
"	" " "	3.6	46	25	24
"	" " "	6.6	52	21	16
Missouri	Portageville Sandy Loam	1.0	40	40	>70
"	"	4.0	37	30	70
"	"	7.0	46	26	26
S. Dakota	Lismore Silty Clay Loam	2.9	42	44	70
"	"	5.9	44	29	35
"	"	8.9	43	5	6

Note: The greater the moisture content the less extracted over a period of time? We should have samples run every 6-12 hours for 21 days.

It is apparent that Daconil 2787 is not readily degraded in soil that contains little or no free moisture. Conversely, Daconil 2787 is degraded more rapidly when soil contains 6% water than when it contains 3% water.

(c) Half-life of Daconil 2787 in Unsterilized Soil

The moisture level of each soil was adjusted to 6.0%. Fortification of Daconil 2787 was 40 ppm and incubation temperature was 98°F.

Location	Soil Type	pH	Daconil 2787 PPM Parent		
			0 day	14 days	Half life (day)
S. Dakota	Lismore Silty Clay Loam	6.9	43	12**	4
Texas (Valley)	-----	8.2	42	8	6
Louisiana	Yohola Sandy Loam	8.2	48	8*	9
Missouri	portageville Sandy Loam	5.9	45	15	9
"	Clarkton Sand	6.9	45	23	14
Texas (Upland)	-----	5.9	39	22	18
" (McGregor)	-----	7.8	54	34	18
S. Carolina	-----	6.0	50	27*	24

Location	Soil Type	pH	0 day	14 days	Half life (day)
Tennessee	Collins Silt Loam	6.3	52	35***	36
"	(Loring silt and Dexter loam)	5.6	47	32***	38
Louisiana	Commerce Sandy Loam	6.5	41	41***	40

*15 days incubation

** 7 days "

***21 days "

The half-life of Daconil 2787 ranges from 4 to 40 days. It is evident from this experiment that the half-life of Daconil 2787 is valid only when stated in respect to a given type of soil and at a given moisture level.

(d) Autoclaved Soil

Samples of control soil were first autoclaved, then fortified with Daconil 2787 at approximately 50 ppm and held at a constant temperature of 100°F. Samples were then analyzed:

One hour after fortification	-----	47 ppm
Two days	" "	-----31 ppm
7 days	" "	-----20 ppm

There is a decline in the amount of Daconil 2787 in autoclaved S. Dakota soil. The half-life is approximately five days in sterilized soil with incubation temperatures at 100°F. 2 to 3 days in unsterilized S. Dakota soil. See half-life of Daconil 2787 in soil for data on unsterilized soil.

(e) Close Jar Tests

This experiment was conducted to determine whether the loss of Daconil 2787 in a field experiment in S. Dakota was due to leaching or to volatilization by wind or heat.

(f) Daconil 2787 Residue in Soil

Time	20 ppm fortification			40 ppm fortification		
	76°F	86°F	100°F	76°F	86°F	100°F
0 day	22.6	20.0	19.4	36.9	37.4	38.5
7 days	7.5	4.2	3.7	14.0	10.2	4.4
14 days	5.5	0.9	0.1	12.0	3.8	1.3
36 days	1.5	-	-	5.3	-	-

The moisture content of the Lismore silty loam soil was 11.3%.

Recovery of Daconil 2787 ranged from 68% to 90% with a mean of 86%.

These experiments show that Daconil 2787 cannot be recovered quantitatively from soil after seven possibly less days of storage under these conditions. It appears that the rapid loss of Daconil 2787 is not primarily due to leaching or volatility of the compound.

(g) Effects of Temperature on the Disappearance of Daconil 2787 from Soil

Average PPM Daconil 2787 found in Soil

Days Stored	Control	%Recovery	76°F	86°F	100°F
0	N.D.	116	23	29	20
6	N.D.	86	20	13	6.7
10	N.D.	116	15	10	6.1
14	N.D.	105	11	7.4	3.1
21	N.D.	92	5.8	2.2	1.5
38	N.D.	99	3.3	1.2	0.9

Lab Conditions

Sufficient Daconil 2787 in NP form was added to a 2 kg of Lismore silty clay loam soil to give a conc. of 20-30 ppm. The soil had a moisture content of 10% and a pH of 6.6. The compd. was blended with the soil by tumbling end-over-end in gallon paint cans for 24 hours to give the above results.

Temperature appears to increase the disappearance of Daconil 2787 from soil over a range of 70°F to 100°F.

(h) Biodegradation (Conclusions) (Report 4)

1. The studies submitted appear to be incomplete and meaningless because of the following reasons:

(a) Table 1 does not have enough information to evaluate data

(1) If it contains 2 different studies these 2 tables would be advised.

(2) Time Daconil remained in culture or soil is not given.

(b) A tracer study should be able to account for all C^{14} material. C1 balance chart is not given. See Section III.

(c) Efficiency of analysis is not given

(d) Experimental procedures are not clear.

Conclusion of these studies

1. Daconil cannot be quantitatively recovered from soil after a period of 1 plus days.

2. Recovery data appear to be quantitative only when extracted soon after fortification.

3. Analytical method would not determine degradation products.

4. It appears that an increase of soil moisture level inhibits extration efficiency.

5. The effect of H_2O , pH, temperature on Daconil cannot be determine because of the lack of degradation analysis and validation of good extraction procedures on sample that were left standing.

6. The same above conclusions are made with study on sterile soils.

7. The following type data are needed:

(a) Studies for degradation products in the same type studies submitted.

(b) A method that can determine whether residues and or residue on or in fortified soil standing over a period of days. This should be on the same type studies submitted.

9. See Biodegradation conclusions

3. Section IV

(a) Degradation Rate of Daconil 2787 in Soil - Field Test (Report 8)

Georgia

Eight applications of Daconil 2787 W-75 were made to Bermuda grass plots at the rates of 2 oz and 4 oz per 1000 sq ft. from August to October in 1965. Two months prior to the Daconil application this area was treated with milorganite and ground limestone (4.08 to 8.167 lbs/A/A) (8 app)

The result of this study indicated that the average half life for the lower rate was 38 days and 56 days for the higher rate. Residues of Daconil were found to be negligible after 10 months at the lower rate and 14 months at the higher rate.

PHI (days)	Rate per 1000 sq ft	Daconil 2787 Residue (PPM) Depth Inches		
		0-3	3-6	6-9
56	4 oz	37.2	5.7	1.1
97	4 oz	26.8	1.1	2.4
125	4 oz	24.2	1.5	1.0
217	4 oz	7.4	0.35	0.34
285	4 oz	2.1	-	-
362	4 oz	3.1	-	-

Degradation 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

The test procedures used in Mississippi were the same procedures used in Georgia with the exception of milorganite and ground limestone added to the soil. The bermuda grass in Miss. also received 3 to 6 pounds of nitrogen per 1000 sq ft per sec on and watered regularly. (4.08 to 8.167 lbs/A/A) (8 apps)

PHI	Rate	Daconil 2787 Residue PPM Depth In.		
		0-3	3-6	6-9
98	4 oz	0.79	0.03	0.05
130	4 oz	0.33	0.02	0.03
159	4 oz	N11	N11	N11

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

Ohio

Four steel drums with holes punched in the bottom to allow for drainage were placed into holes dug so that the tops of the drums were flushed with the surrounding sandy loam soil. Each of the 3 drums was treated with the equivalent of 10 applications of Daconil 2787-W 75 at the rate of 2 lbs per acre. The 4th drum was untreated and served as a control.

Drum No.	PHI (mo.)	Rate (lb/A)	Daconil 2787 Residue PPM Depth Inches		
			0-6	6-12	12-18
1	10	2.0	0.99	N11	0.52
2	10	2.0	6.25	0.06	0.16
3	10	2.0	1.81	0.03	0.03
1	13	2.0	N11	0.6	0.03
2	13	2.0	2.3	N11	N11
3	13	2.0	0.3	N11	N11

The half-life of Daconil 2787 between June and November was approximately 51 days.

South Dakota

A portion of a field of lismore silty clay loam was sprayed with Daconil 2787 at the rate of 14 lbs. active per acre.

PHI (mo)	Rate lb/A/A	Daconil 2787 Residue (PPM) Depth Inches				
		0-2	2-4	4-6	6-8	8-10
1	14	N.D.	N.D.	N.D.	N.D.	N.D.
2	14	0.20	0.05	0.07	0.02	0.13

The total amount of Daconil found in the 2 month soil sample (0-10 inches) was 2.1% of the amount applied. It is apparent that Daconil 2787 applied to soil of high organic content is almost quantitatively degraded within one month after application.

Conclusion of Section IV

1. Extraction efficiency not validated for samples left standing.
2. Analysis for Daconil only
3. Soil type and composition, pH and % organic matter needed.
4. Test for DAC 3701 was not reported.

4. Section III

1. Isolation of Daconil 2787 Degradation Products from Soil (Report 6)

A fifty gram sample of S. Dakota soil was fortified with 100 ppm of carbon-14 labeled DAC-2787, incubated at 36°C and sampled at intervals. The results indicated that two degradation products are formed during the period of seven to 35 days incubation and that degradation product "A" may be lost slowly after the supply of DAC 2787 in the soil has been depleted.

Incubation Time days	DAC 2787 %	Product "A" %	Product "B" %	% Unextractable C ¹⁴ Activity
7	26.6	8.5	43.5	21.5
35	3.8	13.0	64.3	18.9
46	Nil	8.7	69.4	21.9

Product B was identified as DAC-3701 (hydroxytrichloroisophthalonitrile).

Product A: Data are presented showing that this compound probably has the formula, C₈H₂Cl₃N₂, 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 Mass Spectroscopy. 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.

Note: That soil studies would not determine DAC-3701 or Bound (unextractable material)

Note: Extraction procedure was not the same as used in previous reports.

Volatilization

Soil treated with C¹⁴ Daconil 2787 was incubated at room temperature for 3 weeks under a slight flow of air. The results indicated that C¹⁴ Daconil 2787 was not easily volatilized from the soil and that no volatile degradation products were found during the experiment.

Section III Conclusion

1. Daconil does degrade rapidly while its degradation and bound products are building up.

5. Animal Metabolism (Section III, Report 9)

Animal feeding and metabolism studies evaluated Oct. 20, 1970, in PP No. 1F1024 showed that at 3% feeding levels 85-90% of the ingested Daconil 2787 is excreted unchanged in the feces of dogs and rats within 48 hrs. See also PP No. 7F0599

Rats: 88.45% in feces, 5.14% in urine and 0.851% in rest of rat including CO₂

6. Residues in Cow's Milk and Tissues (Section III, Reports 10, 11, and 12)

This data were also evaluated Oct. 20, 1970, in PP No. 1F1024. The results of the study showed that no significant DAC-2787 residues were detected in the tissues or milk after 30 days of feeding at a level of 25 to 250 ppm.

DAC-3701 residues were found in milk and tissues after 30 days of feeding at the level of 25 to 250 ppm. However, after a withdrawal period of 21 days no significant residues of DAC-3701 were detected.

Feeding of DAC 3701 at levels of 0.2, 0.6 and 2.0ppm for 30 days resulted in residues in milk and tissue.

Note: Control samples had high residues or background.

7. C¹⁴ Study in Plants

This C¹⁴ study evaluated Oct. 20, 1970, in PP No. 1F1024 showed that Isotopic DAC 2787 did not translocate from tropical applications on cucumber and tomato leaves and other plant parts. The C¹⁴ isotope was not translocated into aerial parts of corn or tomato when these plants were cultivated for 23 days in soil treated with C¹⁴ DAC 2787.

III. Analytical Methods (Soil)

1. For Daconil (Section IV, Report 5). Air dry soil. Extract with acetone, filter, evaporate and bring to volume with benzene for GC determination on Dohrmann Model G 100 equipped with T-100 cell.

Note: degradation products left in residue

Note: Extraction for 1 to 2 days samples may not be valid

2. For DAC 3701 (4-OH) (Section IV, Report 5, Part III)

4-hydroxy-2,5,6-trichloroisophthalonitrile.

Extract with acetone, filter, evaporate, dissolve the residue in NaOH and partition with methylene dichloride and discard.

Adjust to pH 2 with H_2SO_4 and extract with methylene dichloride and concentrate. Add Tri-Sil reagent and warm to 60°C then inject into GC. Tri-Sil is added to form the trimethylsilyl ether of DAC 3701

Note: NaOH extraction indicate bound residues may be present

3. DAC 3701 (Report 6)

Extract with acetone- H_2O - H_2SO_4 (48:1:1 by volume), evaporate acetone and extract in 2:1 ether-acid mixture. Add Tri-Sil and determine by GC. Retention time very close to Daconil.

Note: In method before this methylene dichloride was used. The study in this Section states that methylene dichloride will not extract 3701.

4. For Daconil (Section I) (A-4)

Extract with methylene chloride, filter, and evaporate to dryness, column chromatography may be needed for some soils. Aluminum oxide is used. Elute with acetone in methylene chloride. Evaporate and prepare for MGC.

IV. Conclusion

1. Laboratory Test

The petitioner showed that Daconil 2787 degrades rapidly in contact with soil to DAC 3701 and unextractables. However, in many instances the identity of the soils were not given or their composition. Therefore, the major factors that influence DAC 2787 dissipation could not be totally assessed. Although it was demonstrated that temperature, organic content and moisture content effect the rate of degradation of DAC 2787, no conclusive relationship could be established to show which had the greatest effect on degradation in different type soils. Also, analysis of DAC 3701 was not made. The soil pH had no apparent effect on the degradation of DAC 2787 in Lismore silty clay loam. Since this data is limited to one type soil, it would be difficult to justify an extrapolation of this conclusion to other type soils. Additional data are needed on other soil to establish conclusive or a reasonable relationship that pH does not effect the degradation of DAC-2787 in soil.

2. Field Test

The degradation rate of DAC 2787 was evaluated at 3 separate locations under field conditions. It was determined that DAC-2787 degrades rapidly in soil; leaches poorly and lack mobility through the soil tested. These tests did not include DAC 3701. The degradation rate of DAC 2787 in field test correlates well with laboratory test. However, inadequate soil descriptions in terms of physical and chemical characteristics and the lack of identification of soils preclude the establishment of meaningful relationships and interpretation of the results.

3. The soil sterilization study indicated that sterile soil prolong the persistence of DAC 2787 in soil.

4. The test on volatilization effectively demonstrated that DAC 2787 was not lost by volatilization.

5. Refer to this evaluation for additional conclusion on animal metabolism, plant metabolism, etc.

V. Recommendations

1. Additional data are needed to permit a complete evaluation and interpretation in support of a conclusion for soils normally used for agriculture purposes in relation to the degradation

of Daconil 2787. Other type soils and their physical and chemical characteristics should be given such as pH, percent moisture content, percent silt, clay, sand and organic content. These soil characteristics would more adequately permit the establishment of correlations between various soils and their components.

2. The persistence of the degradation product (B), hydroxy-trichloroisophthalonitrile and product (A) should be determined. Leaching and runoff data are also needed.

3. Conclusive identification of product (A) should be determined as soon as possible (17-15)

4. Rainfall and percent water applied to the soil are needed in regard to field test.

5. Degradation studies in water and photodecomposition studies are needed (70-15)

6. Data submitted on birds are inadequate, in that no residue data were submitted (70-15)

7. It should be noted that the parent compound Daconil may not be an environmental problem. The degradation product DAC 3701 4-hydroxy-2,5,6-trichloroisophthalonitrile would. DAC 3701 is persistent shows up in milk at feeding levels of 0.2 ppm for 30 days and in tissue at feeding levels of 0.2 ppm. Test also run at 0.6 and 2 ppm with residue found in milk and tissue

Registration
Questions

Recommendation for Registration

The following comments are for registration and should be objections.

1. The following information and discussion are needed to support Sections I and II

1. Can Daconil and/or its degradation products be quantitatively recovered from soil after a 1 to 5 day interval from fortification?

2. Can the analytical method used in these test determine degradation products? NO.

3. Does an increase in soil moisture inhibit extraction efficiency or binding of compounds to soil?
4. We agree that water, pH and temperature have an effect on the degradation of Daconil. What effect do they have on DAC 3701, unextractable material and other degradation products?
2. The following information are needed to support the bio-degradation study (Report 4)
 1. Time interval from treatment to sampling. *→ culture 100 hrs*
 2. It has been demonstrated that CO₂ is not given off. We would like to know what happen to the labeled material which was not recovered. A balance chart for Daconil and its degradation products should be submitted.
 3. The experimental procedure is not clearly stated.
 4. The results given in table 1 of this report are not clear.
 5. Does percent consumed mean disappearance from soil or material that cannot be recovered.
 6. Extraction efficiency should be determined for Daconil and its degradation products.
3. The studies indicating degradation or dissipation are incomplete in that data should have been submitted at zero time, 1 day, 3 days 7 days and 14 days. The other time intervals appear to be adequate. These data are needed to determine extraction efficiency and build up of the degradation products and unextractable materials.
4. The following information are needed to support report 5.
 1. Extraction efficiency.
 2. Analysis for degradation products.
 3. Soil composition, pH and percent organic matter.
 4. Rainfall data.

5. The following information or discussions are needed to support report 6

1. Data submitted indicates that degradation products and unextractables would be indifferently present in soil. Please give your opinion.

2. The extraction procedure for DAC 3701 indicates that a mixture of acetone-water-sulfuric acid are needed for good extractions. It also indicates that methylene dichloride extract of materials from TLC plates was poor. The same report states that extraction with acetone is incomplete. We refer to Section IV, Report 5, Part III, Page D-16 which use acetone extraction and methylene dichloride partition. Data from this method is questionable. Please explain why the difference in each method and the extraction and cleanup efficiency of each method.

6. Answer to questions in PR Notice 70-15 must be submitted.

DAC 3701
Does Leach.

Will it break down after it reaches
lower levels of soil 12" below

What is the significance if reaches water table

