

Meeting
9/23/76

EEE BRANCH REVIEW

DATE: IN _____ OUT _____ IN 3/10/76 OUT 4/27/76 IN _____ OUT _____
FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. _____

PETITION OR EXP. PERMIT NO. 6F1749

DATE DIV. RECEIVED _____

DATE OF SUBMISSION _____

DATE SUBMISSION ACCEPTED (3)(c)(1)(D) STATUS= 2A Yes

TYPE PRODUCT(S): I, D, H, (E), N, R, S

PRODUCT MGR. NO. 21 (Wilson)

PRODUCT NAME(S) Bravo 6F

COMPANY NAME Diamond Shamrock

SUBMISSION PURPOSE Registration on Peaches and cherries

CHEMICAL & FORMULATION chlorothalonil (tetrachloroisophthalonitrile)
(daconil)

1. Introduction

1.1 Applicant wishes to register a new use on peaches and cherries for this fungicide. This is a 2A submission consisting of previously reviewed data and new studies.

1.2 This product has EPA Reg #677-313

1.3 Other names for this product are BRAVO 6F, Daconil 2787, Forturf, CAS 1897-45-6, DAC-2787, BRAVO 475, and chlorothalonil.

1.4 The product contains 6 lbs active per gallon.

2. Directions for Use

2.1 For peaches: Apply 1 to 1 1/2 pints per 100 gallons of water, depending on the specific fungus and the severity of the problem. DO NOT apply within 7 days of harvest. DO NOT exceed 7 1/2 pints per acre per application. Apply by ground equipment only.

2.2 For cherries (sour and sweet): Apply 3/4 to 1 1/2 pint per 100 gallons of water depending on specific fungus and severity of the problem. DO NOT apply within 7 days of harvest. DO NOT exceed 15 pints per acre per application. Apply by ground equipment only.

2.3 DO NOT reuse empty container. Destroy by perforating, crushing, and burying or discarding in a safe place. This product is toxic to fish. Keep out of lakes, streams or ponds. DO NOT apply where runoff is likely to occur. DO NOT contaminate water by cleaning of equipment, or disposal of wastes.

3.0 Discussion

3.1 Hydrolysis studies

Hydrolysis of Daconil and its metabolite, 4-Hydroxy-2,5,6-trichloroisothalonitrile in the absence of light at pH levels of 5,7,9 (2/5/76)

Hydrolysis was studied in buffered solution as described also above with pesticide concentrations of .5 and 1.5 ppm. The study at .5 ppm was a cold study using GLC with an electron capture detector for analysis. At 1.5 ppm a ¹⁴C ring labeled preparation was used, detection was by TLC followed by radioassay. Results are tabulated:

Time Days	pH5			pH7		
	% DACONIL	% DACONIL Degraded to DS-19221 (3-cyano-2,4,5,6- tetra-chloro- benzamide)	% DACONIL Degraded to DAC-3701 (4-hydroxy-2,5,6- trichloro isophthalo- nitrile)	% DACONIL	% DACONIL Degraded to DS-19221	% DACONIL Degraded to DAC-3701
0	97.4	0.8	0.8	90.4	0.3	5.7
7	97.4	1.6	0.3	96.8	0.3	2.5
28	95.2	4.3	0.2	95.3	1.1	1.6
72	98.9	0.4	0.0	96.3	2.1	0.9

pH9		
% DACONIL	% DACONIL Degraded to DS-19221	% DACONIL Degraded to DAC-3701
94.6	0.3	2.8
84.0	11.9	3.1
56.4	34.1	7.9
36.4	48.9	11.3

The hydrolysis of DAC-3701 was studied at 1,000 ppm. No degradation was noted under any pH.

In all of these studies greater than 98.5% of the residues were ether soluble.

Conclusions

- 1) Daconil does not hydrolyze under acid or neutral conditions. In basic solution hydrolysis is to DAC-3701 or DS-19221 with a half-life of about 35 days
- 2) The metabolite, DS-3701, does not hydrolyze under the tested conditions.

3.2 Photodegradation Studies

3.2.1 Photodegradation of Daconil in Aqueous Systems (2/9/76)

Daconil was exposed to artificial sunlight in acid solution and in buffered solution at pH 5 and 7. No degradation was noted after 90 hrs in acid; however, in the buffer more than 90% was converted to polar water soluble that could not be partitioned on either or identified. It is postulated that this was due to reactions with the buffers; analysis indicated the presence of salts.

Ring labeled Daconil was used for these experimental run at 8°C. Buffered samples had a pesticide concentration of .5 ppm, the nonbuffered .2 ppm. Detection was by TLC followed by radio-assay.

Conclusion

- 1) Daconil was not decomposed in acid solution when exposed to artificial sunlight.
- 2) Applicant should submit an explanation for the stability of Daconil in buffered solution as shown in 3.1 and the reactivity in these same buffers in 3.2.1 In the meantime we must conclude that Daconil is stable with respect to aqueous photodegradation. This position is supported by the other photodegradation studies discussed in section 3.2 of this report.

3.2.2

Photodegradation of Daconil and its Metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile on Inert Surfaces (2/5/76).

¹⁴C Daconil and DAC 3701 were deposited on glass beads and then placed in petrie jars. The beads were exposed to artificial sunlight in the jars. The system was kept under negative pressure, and a NaOH trap was used to determine CO₂ eliminated. *PERIODICALLY THE BEADS WERE SAMPLED FOR RESIDUES.* After the equivalent of 14.6 days exposure, 77.3% of the radioactivity remained on the inert surface, at least 91.3% of this was the parent. Only 1.6% of the ¹⁴C vapor was trapped.

In the ¹⁴C DAC 3701 study, 49.2% of the radioactivity remained after the equivalent of 28.6 days; analysis showed this to be entirely DAC 3701. 20% was trapped and could have been CO₂.

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

Conclusion

- 1) The loss of DAC-3701 from inert surfaces was probably due to volatilization (cf. 3.2.3)
- 2) Neither Daconil nor DAC-3701 are rapidly photolyzed on inert surfaces.

3.2.3

Photodegradation of Daconil and 4-hydroxy-2,5,6-trichloroisophthalonitrile on Silica Gel Plates.

After exposure to 168 12 hour days of artificial sunlight on silica gel 54% of the Daconil and 46% of the DAC 3701 were volatilized.

The major photodegradation products of Daconil were DAC 3701 and its salts. The salts were also found to be the principle degradation products of DAC-3701. They are probably due to reactions with the TLC binders.

Conclusions

- 1) The principle photodegradation product of Daconil is DAC-3701; the photodegradation half life on Silica gel is long.
- 2) Triplet sensitizers *did NOT ALTER* ~~do~~ after the above conclusions.

3.2.4

Photodegradation and Mobility of Daconil and its Major Metabolite on Soil thin Films

The following soil types were used:

<u>Location</u>	<u>Soil Type</u>	<u>% Organic Carbon</u>	<u>% Total Sand</u>	<u>% Total Clay</u>	<u>% Total Silt</u>	<u>pH</u>
York, Nebraska	Silt loam	1.91	1.4	27.1	71.5	5.6
Blackburn, Missouri	Silt loam	1.93	1.2	24.7	74.1	6.0
Macombe, Illinois	Silty loam loam	2.31	0.6	25.8	73.6	5.1
Allsworth, Illinois	Silty clay loam	2.57	2.4	25.3	72.3	5.3
Rosemont, Minnesota	Silty clay loam	3.40	13.7	22.6	63.7	5.6

Exposure was for 168 12 hr days of artificial sunlight. Leaching and degradation were examined.

Average soil TLC thickness was 461 microns. Ring labeled pesticide was used.

Conclusions

- 1) Daconil does not leach; ^{DAC} 3701 leaches. The leaching of DAC 3701 is inversely proportional to ^{clay} content of the soil. Sunlight did not effect leaching.
- 2) Neither compound showed significant photodegradation under these conditions; 97% of the Daconil remained at the end of the test period.
- 3) Little volatility was observed.

3.3 Soil Metabolism

3.3.1 Degradation of Daconil and its metabolite, 4-Hydroxy-2,5,6-trichloroisophthalonitrile, in soil (2/5/76)

Ring labeled Daconil was put in soil at 15 ppm and stored in the greenhouse for 30 days. The soil was then analyzed for degradation products.

The following soils were used:

<u>Soil Type</u>	<u>Location</u>	<u>% Organic Matter</u>	<u>% Sand</u>	<u>% Clay</u>	<u>% Silt</u>	<u>pH</u>
Silty Clay Loam	Concord, Ohio (Lake County)	1.23	7.8	20.0	72.3	6.7
Sandy Loam	Painesville, Ohio (Lake County)	3.2	62.2	6.8	31.0	6.0
Silty Clay	Macomb, Illinois	2.31	0.6	25.8	73.6	5.1
Sandy Loam	Tulia, Texas (Swisher County)	1.6	54.0	19.5	25.0	8.0
Peat Loam	Iowa	7.16	29.7	20.3	50.0	7.0

Soil was maintained at 80% of the 1/3 bar moisture content throughout the text. Storage involved 12 hours a day of 92-95° F under Sun-
brella - build lights and 12 hours a day of 80-85° F in dark. Humidity was maintained between 80 and 90%.

Analysis was accomplished through the use of soil extraction by acidified acetone followed by radiotracer techniques. Extractables were characterized by TLC. Results of the Daconil ageing are tabulated below. Residues were considered bound if not extractable in acidified acetone.

Distribution and Characterization of ¹⁴C-DACONIL Residues Applied to Various Soils and "Aged" 30 Days Under Greenhouse Conditions

Soil Type	% Non-Extractables	% Water Solubles	% DACONIL	% DAC-3701	% DS-19221	% Polar Organic Extractables ¹	Half Life (Days)
Clay Loam (Concord, Ohio)	47.0	24.2	7.4	5.1	2.2	9.3	8.0
Sandy Loam (Painesville, Ohio)	44.5	19.2	10.2	10.8	4.7	4.6	9.1
Silty Clay Loam (Macomb, Illinois)	33.3	20.3	13.4	7.6	6.1	6.2	10.3
Sandy Loam (Texas)	44.2	23.5	2.7	20.3	1.4	4.1	5.8
Peat Loam (Iowa)	38.6	21.2	4.4	17.2	5.0	5.4	6.7

¹ These are the compound(s) remaining on the origin of the TLC plates.

Conclusions

- 1) Daconil degrades very quickly in soil. The half-life is about 8 days. Non-extractable residues comprise about 40% of the starting material after 30 days. Greater than 94% of the radioactivity was still in the soil after 30 days. The half-lives presented in 3.4.1 were determined in a study that followed over protocols more closely.
- 2) The metabolite DAC 3701 is very stable in soil: No degradation was noted in 30 days.
- 3) Observations were made only at T=0 and 30 days this is an insufficient number of data points to define a decline curve; consequently, the study is unacceptable.
- 4) The temperatures used to age the soil (85-95° F) are too high. Microbial process may have been affected; therefore, data from soil aged in this manner is unacceptable for metabolism studies.
- 5) We need to have data on the half life of the principle degradation product.

3.3.2

Aerobic and Anaerobic Soil Metabolism of Daconil (2/12/76)

Soil aged in 3.3.1 was used in these studies. Anaerobic conditions were generated by placing soil in test tubes, adding sufficient water to yield a 2-3 cm water surface layer, ^{SYSTEM} purging the atmosphere twice with N₂, and sealing the resulting Aerobic conditions were tested by placing soil in a test tube, sealing and then inserting a hypodermic needle to allow air entry.

Degradation was monitored at 45 and 60 days. No significant differences were noted between the aerobic and anaerobic results.

Conclusions

- 1) These studies are unacceptable
 - a) The ageing procedure is incorrect, and may have affected the microbial population prior to anaerobiosis.
 - b) The aerobic protocol does not allow sufficient airflow; in time the atmosphere will become saturated with CO₂,
 - c) larger containers should be used for soil samples.

3.3.3

Leaching of Degradation Products (9/18/76)

Soil incorrectly aged as documented in 3.3.1 was applied to the top of a soil column and treated with the equivalent of 1/2 acre inch of water a day for 45 days. The soil columns were packed by water saturation; bulk density was not reported.

Leaching of Daconil and DAC-3701 were examined. The Data is summarized below:

Distribution and Extraction of
¹⁴C-Daconil Residues on
Leached Soil Columns

<u>Soil Type</u>	<u>Column Fraction</u>	<u>Total Residues</u> % of applied ¹⁴ C Water	<u>Extracted Soil Residues</u> % of applied ¹⁴ C	<u>Non-Extracted Soil Residues</u> % of applied ¹⁴ C
Clay Loam (Concord, Ohio)	1	73.4	43.3	31.6
	2	3.9	2.3	.8
	3	1.9	1.5	0.
	4	1.3	0.	0.
	5	1.1	0.	0.
	6	1.0	0.	0.
		<u>12.4</u>	<u>82.6</u>	<u>47.1</u>
Sandy Loam (Painesville, Ohio)	1	64.1	26.0	31.5
	2	9.8	7.5	1.0
	3	2.4	3.1	0.
	4	1.6	1.6	0.
	5	1.0	3.1	0.
	6	0.6	.6	0.
		<u>9.8</u>	<u>79.5</u>	<u>40.1</u>
Silty Clay Loam (Illinois)	1	58.2	34.5	22.7
	2	4.7	5.2	1.3
	3	2.5	2.0	0.
	4	2.2	0.	0.
	5	1.2	0.	0.
	6	1.1	0.	0.
		<u>22.1</u>	<u>68.8</u>	<u>41.7</u>
Peat Loam (Iowa)	1	69.5	38.7	25.4
	2	2.9	1.3	.5
	3	3.2	2.3	0.
	4	1.8	0.	0.
	5	1.4	0.	0.
	6	1.9	0.	0.
		<u>11.0</u>	<u>80.7</u>	<u>42.3</u>

1 Each column fraction represents 5 cm of a 30 cm soil column, fraction #1 being the uppermost 5 cm and fraction #6 the lowest 5 cm.

Distribution and Extraction of "Aged" ^{14}C -DAC-3701
Soil on Leached Soil Columns

Soil Code and Type	Column Fraction ¹	Total Residues found % of applied ^{14}C Water Soil	Extracted Soil Residues % of applied
Clay Loam (Concord, Ohio)	1	53.5	41.4
	2	29.7	28.1
	3	1.7	----
	4	0.6	.7
	5	0.5	.4
	6	1.0	.7
		4.3	87.5
Sandy Loam (Painesville, Ohio)	1	40.5	47.2
	2	33.9	33.7
	3	6.3	4.0
	4	0.7	0.
	5	0.7	0.
	6	0.5	0.
		1.4	82.6
Silty Clay Loam (Illinois)	1	46.1	46.4
	2	17.2	14.2
	3	5.4	5.2
	4	6.4	3.1
	5	0.6	0.
	6	0.4	----
		2.3	76.1
- Sandy Loam (Texas)	1	9.7	12.3
	2	9.8	10.7
	3	15.4	13.9
	4	25.3	18.3
	5	10.9	8.0
	6	3.1	1.1
		5.3	74.2
Peat Loam (Iowa)	1	63.7	60.7
	2	6.5	6.8
	3	4.8	4.2
	4, 5, 6	3.5	0.
		2.1	78.5

Radioactivity was monitored by total combustion; analysis was by extraction followed by TLC.

Neither Daconil nor its metabolites were found in the leachate. Extractable residues in fraction 1 consisted of Daconil, DAC-3701, and DS-19221, in the second fraction primarily DAC-3701 and its salts were found. No additional analysis was attempted.

Conclusions

- 1) The parent fungicide does not leach; however, the principle degradation product does leach. Leaching appears to be related to % sand/pH.
- 2) Non extractable residues were 10% less at the end of the leaching study than at the end of the ageing period (cf. 3.3.1).
- 3) Half life of total ^{14}C from a Daconil application is quite long. After 75 days greater than 80% of the label can still be found in soil. However, the problem with this may be mediated as bound residues decrease with time.
- 4) Despite the incorrect ageing procedure, the leaching study is sufficient to access the hazard with regard to Daconil movement in soil (The incorrect ageing procedure effected the relative proportions of the metabolites found, not their identity; hence, it does not effect the conclusions which can be drawn regarding pesticide mobility).

3.3.4

Bound Residue Study - Appendix I (2/5/76)

Soil was aged 30 or 90 days (Report stated both) under unspecified conditions and then was analyzed for Bound residue distribution.

A fractionating scheme similar to the one presented in the Federal Register, June 25, 1975, page 26894 was used. Attempts were made to characterize the Fulvic acid residues. Of the quantity of radioactivity in the Fulvic acid fraction 26 to 56 percent could be partitioned in ether, 34 to 48 percent of this was DAC-3701 as determined by TLC. Results:

<u>Soil Type</u>	<u>% of Applied Radioactivity in Humin</u>	<u>% of Applied Radioactivity in Humus</u>	<u>% of Applied Radioactivity in Fulvic Acid</u>
Silty Clay Loam	11.2	3.8	10.2
Peat Loam	15.9	10.1	10.3
Sandy Loam	18.5	2.8	11.9
Sandy Loam	12.8	8.6	13.9

Conclusions

1) Soils were extracted with .3NHC1 and then acetone before the bound residue fractionating scheme was employed. This extraction technique, compared to the use of acidified acetone, cf. 3.4.1, removes about 2% more ¹⁴C from the soil. It may also effect the fractionation of bound Residues.

2) Further, details would be required in order to support the results of this study; however, the study is not germane to the EC assessment.

3) Part of the bound residue is in the form of DAC-3701. Bound residues are stored primarily in the Humin and Fulvic Acid fractions.

3.4 Microbiological Studies

3.4.1 Effect of Microorganisms upon the soil metabolism of Daconil and 4-Hydroxy-2,5,6-trichloroisophthalonitrile (2/5/76).

Ring labeled Daconil and DAC-3701 were used in these studies. Soil sterilization was achieved by autoclaving soil three times. Soil characteristics were:

<u>Soil Type</u>	<u>Soil Location</u>	<u>% Organic Matter</u>	<u>% Sand</u>	<u>% Clay</u>	<u>% Silt</u>	<u>pH</u>
Silty Clay Loam	Macomb, Illinois	2.31	0.6	25.8	73.6	5.1
Peat Loam	Iowa	7.16	29.7	20.3	50.0	7.0
Sandy Loam	Tulia, Texas (Swisher County)	1.6	54.0	19.3	25.0	8.0
Sandy Loam	Painesville, Ohio (Lake County)	3.2	62.2	6.8	31.0	6.0

In the first three soils Daconil was applied at 39 ppm, in the other 3.9 ppm. DAC-3701 was applied at 4.3 ppm. The study was conducted in the dark at 25°C. Soils were maintained at 80% of the 1/3 bar moisture content.

Soils were monitored for 90 days. It was stated that no degradation or dissipation of DAC-3701 was seen; no data was presented to support this position.

Daconil degradation proceeded faster in nonsterile than in sterile soil for at least 1 month. By the end of the three month sampling period, the differences in the degradation rate were not at all clear cut. It is speculated that this maybe due to contamination.

The formation of both DAC-3701 and DS-19221 proceeded faster under nonsterile conditions. It is interesting to note that dissipation of DAC-3701 was seen in this study (but in none of the others submitted). Typical data are presented below:

Time Days	Sandy Loam (Ohio) % Species Remaining							Half-life (days)
	0	7	16	22	31	60	90	
Daconil (s)	83.4	90.3	61.2	41.5	67.1	24.9	5.7	21.9
(ns)	97.2	44.8	32.1	21.0	11.2	10.7	4.7	10.3
Water Sol. (s)	1.1	2.6	14.3	11.9	9.0	11.0	18.6	
(ns)	1.1	19.7	22.4	22.7	26.5	17.2	24.4	
Dac 3701 (s)	0	5.1	6.2	6.3	4.7	7.6	4.1	
(ns)	0	12.4	15.0	11.2	7.2	11.6	6.2	
Ds-19221 (s)	0	.2	1.2	3.0	.6	1.4	2.3	
(ns)	0	3.1	7.4	5.0	6.1	2.6	3.1	

Since this data is applicable to a soil metabolism study, some additional results will be given.

Soil Type	Half-life	Extractable % ¹⁴ C Remaining			Daconil Remaining		
		31	60	90	31	60	90 (Days)
Peat Loam (s)	31.3	64.2	37.6	28.8	51.3	19.5	13.9
(n)	14.7	64.0	58.1	38.9	23.9	14.4	6.0
Sandy Loam (s)	18.0	54.0	30.9	18.2	41.7	21.0	8.1
(n)	12.8	59.4	50.8	29.3	26.0	12.8	4.6
Silty Clay Loam (s)	213.8	87.2	84.3	55.8	80.9	78.4	45.0
(n)	36.5	71.0	71.6	54.3	46.5	51.1	33.3

Study 3.3.4 was a bound residue study done on the soil from this study: it indicated that almost 100% of the radiolabel remained in soil for greater than 90 days.

Sample analysis was by extraction followed by TLC/Radioassay.

Conclusions

- 1) The half life of Daconil in soil under standard test conditions is between 10 and 40 days.
- 2) The half life of the principle metabolite DAC-3701 is extremely long.
- 3) Autoclaving does reduce the rate of pesticide degradation; however, it is not clear what the nature of its effect is.
- 4) Under all conditions the half life of total ^{14}C is long.
- 5) This constitutes an acceptable aerobic metabolism study on the parent pesticide.

3.5

The following submitted studies have been previously reviewed:

3.5.1

Fish studies

- a) Exposure of Fish to ^{14}C -labeled chlorothalonil (DAC 2787. Tech): Accumulation, Distribution and Elimination of Residues. Reviewed and accepted 5/29/75. ✓
- b) Exposure of fish to ^{14}C -labeled DAC 3701: Accumulation, Distribution and Elimination of Residues. Reviewed and accepted 5/29/75. ✓

3.5.2

Soil Metabolism Studies

- a) The Fate of 2,4,5,6-Tetrachloroisophthalonitrile (Daconil 2787) In Soil

Section I. Determination of DACONIL 2787 in Soil.

Section II: Degradation of DACONIL 2787 in Soil.

Section III: Isolation of DACONIL 2787 Degradation Products from Soil-Laboratory Test.

Section IV: Degradation Rate of DACONIL 2787 in Soil-Field test.

Reviewed but not entirely accepted due to poor analytical techniques in sufficient experimental details and incomplete analysis. (7/15/71).

b) The Fate of DAC-3701 (4-hydroxy-2,5,6-trichloroisophthalonitrile in Soil)

Reviewed and Accepted 8/7/68.

c) Daconil 2787 Degradation in Soil. Reviewed and Accepted 8/6/71.

3.5.3 Leaching Studies

Evaluation of the Leaching of Chlorothalonil Under Field Conditions and Its Potential to Contaminate Underground Water Supplies. Reviewed and accepted 5/29/75.

3.5.4 Microbiological Studies

Biodegradation of DACONIL 2787

(Bacteria isolated by soil column perfusion enrichment technique cometabolize DACONIL 2787 in shake flask culture) Reviewed and accepted 8/6/71.

3.5.5 Plant Metabolism Studies

a) Absence of ^{14}C Movement in Crop Plant Organs After Topical Application of Soil Amendment Treatments with Isotopic DACONIL 2787

b) Analysis of DACONIL 2787 W75 Treated Potato Tubers for Residual DAC-3701

c) The Disappearance of Chlorothalonil During Ensiling of Treated Forage

d) Hydrolysis of Chlorothalonil Treated Silage

e) Translocation of ^{14}C in Crop Plants by Exposure of Roots to Soil Substrate Amended With Isotopic 2,4,5-trichloro-6-hydroxyisophthalonitrile (DAC-3701)

f) Translocation of ^{14}C Employing Prolonged Radish Root Exposure in Soil Amended with Isotopic 2,4,5-trichloro-6-hydroxyisophthalonitrile (DAC-3701)

g) Movement of ^{14}C in or on Roots of Crop Species Grown in Soil Amended with Isotopic DACONIL 2787 (all Reviewed and accepted.)



3.5.6

Animal Metabolism Studies

- a) Metabolism of DACONIL and DACTHAL Pesticides in Lactating Cows.
- b) Residue in Milk from Cows Fed 2,4,5,6-tetrachloroisophthalonitrile (DACONIL 2787)
- c) Residue in Tissue of Dairy Cows Fed DACONIL 2787 and 2,5,6-trichloroisophthalonitrile
- d) Residues in Milk from Cows Fed 2,5,6-trichloro-4-hydroxy-isophthalonitrile
- e) Supplementary Milk and Meat Study
 - (1) Analytical Data
 - (2) Meat and Milk Residue Study with Technical DACONIL 2787 - 97% and Pure DAC 3701 in Dairy Cattle
- f) Reinvestigation of the Degradation of Chlorothalonil by Bovine Rumen Fluid
- g) Interim Report on DACONIL 2787 Metabolism Distribution of chlorothalonil in urine, feces, blood and tissue
- h) DACONIL 2787 Animal Metabolism Study
 - I Elimination and Distribution Study
 - (a) Single dose
 - (b) Dietary administration - chronic feeding
 - II. Analysis of Urine, Feces, Blood & Tissue for DACONIL 2787 and Metabolites
- i) Radiotracer Metabolism Study
- j) Elimination and Distribution of DAC 2020, DAC 3200 & DAC 3297 (analogues of DACONIL 2787)
- k) Analysis of Tissue and Organs For Storage of the DACONIL Metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile (animals from two chronic feeding studies) All reviewed and accepted *as applicable*

4. Conclusions

4.1 Daconil does not leach; it has a half life of less than 30 days. Therefore, no problems are anticipated with regard to the persistence of parent Daconil. However, the principle degradation product DAC-3701 is extremely persistent (no dissipation of this product was seen within 90 days). DAC-3701 leaches significantly in many types of soil. Both Daconil and DAC-3701 are stable to hydrolysis. Daconil is stable to photodegradation in solution and on surfaces. DAC-3701 is stable to photolysis on surfaces.

The half life of total ^{14}C in soil is quite long $\gg 90$ days. The limited studies submitted seem to show that the ^{14}C is in the form of extractable residues. Clearly, for other applications we will need rotational crop data to assess this apparent hazard.

4.2 No rotational crop data was submitted as it is not germane to orchard crop uses.

4.3 Daconil shows a plateau bioconcentration of 200 X edible and 3000 X in visceral tissue; 50% is eliminated after two weeks exposure to clean water. DAC-3701 showed fish mortality (18%) at .6 ppm; at lower concentrations bioconcentration plateaued at 50 X edible, 250 X nonedible.

5. Recommendation

5.1 We do not concur with the proposed new use.

5.2 The following environmental chemistry data requirement, as given in Section 3 of the Regulations has not been addressed:

5.2.1 Effect of pesticide on microorganisms.

To assess the impact of pesticides on soil microbes the following are needed

a. Population analyses using a variety of selective procedures including the use of restrictive growth media, the use of special isolation techniques (i.e. Anaerobic isolation, thermophilic isolation) and direct counting procedures are to be made to determine the effect of the chemical on normal soil microflora.

b. Effects on the enzyme activity of microbes that degrade the pesticide should be determined. Additionally, effects on general soil enzyme activities such as soil dehydrogenase and phosphatase may be determined.

Changes in population of common pesticide degraders such as Bacillus sp., actinomycetes, pseudomonads, coryneform bacteria, Trichoderma, Aspergillus etc. should be determined.

c. The effects on the transformations of nitrogen compounds should be determined.

Effects on carbohydrate transformations should be determined.

5.3 In addition, the following submitted studies are insufficient to assess the environmental chemistry hazard.

5.3.1 Photodegradation of Daconil in Aqueous solutions. Submit an explanation for the reactivity of Daconil in buffered solution suggested by this study, and the stability of Daconil in the identical buffers in the hydrolysis study.

5.3.2 Degradation of Daconil and its Metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile, in soil: in order to determine the rate of pesticide degradation, more than two data points are needed. Soil should be aged at 25°C. Data should be sufficient to estimate the half life of total ^{14}C and its composition in soil.

5.3.3 Aerobic and Anaerobic Soil Metabolism of Daconil: aerobic soil metabolism requires the use of an apparatus that can monitor volatilization products; however, the apparatus used must allow sufficient airflow so that the atmosphere doesn't become saturated with CO_2 . It is preferable that soil samples be aged in containers larger than test tubes.

5.3.4 Bound Residue Study - Appendix I: soils should not be extracted with .3N HCl prior to removal of the extractable residues (i.e. acidified acetone wash). This is not the procedure used elsewhere in this report.

5.4 At this time the Microbial study submitted will constitute an acceptable aerobic soil study for the proposed use.

5.5 Based on the studies submitted, we assume DAC-3701 is stable in soil. Therefore, rotational crop studies may be required for other use patterns.

5.6 An anaerobic soil metabolism study, using soil aged at 25°C, may be required for other use patterns.

5.7

Due to the information contained in the soil studies submitted for review, previously submitted soil studies were considered not germane. Hence, outstanding data in support of these studies need not be submitted for the proposed use.

R. E. Ney 5/4/76

Ronald E. Ney, Jr. 4/27/76

R. S. Terkowitz 5/5/76

Ralph S. Terkowitz
Efficacy and Ecological Effects Branch
Environmental Chemistry Review Section

RAM
7/31/76

5.6 An anaerobic soil metabolism study, using soil aged at 25°C, may be required for other use patterns.

5.7 Due to the information contained in the soil studies submitted for review, previously submitted ^{soil} studies were considered not germane. Hence, outstanding data in support of these studies need not be submitted for the proposed use.

Ronald E. Fry, Jr. 4/27/76
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