

6/3/75

9/29/75

EEE BRANCH REVIEW

DATE: IN _____ OUT _____ IN _____ OUT _____ IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. _____ Data Review

PETITION OR EXP. PERMIT NO. _____

DATE DIV. RECEIVED _____

DATE OF SUBMISSION _____

DATE SUBMISSION ACCEPTED _____

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

PRODUCT MGR. NO. _____ 21

PRODUCT NAME(S) _____ Bravo 6F

COMPANY NAME _____ Diamond Shamrock

SUBMISSION PURPOSE _____

CHEMICAL & FORMULATION Chlorothalonil
(tetrachloroisophthalonitrile)

Environmental Chemistry Evaluation for Chlorothalonil

Diamond Shamrock

I. INTRODUCTION

1. Daconil, Bravo W-75, Bravo 6-F.
2. See evaluation of 7-19-72 by S. Howard and R. Ney Jr. by F. Sanders of 7-15-71 and re-evaluations 1,2,3 by R. Ney Jr. 2-12-71, 7-27-72, 8-6-72.

II.

III. DISCUSSION OF DATA

A. Introduction

PP# 1F1024 proposed the use of the compound chlorothalonil under the trademark Daconil for various crops. This petition was objected to on various environmental grounds. The company then sent further supportive environmental data to EPA. According to reevaluation #3 of PP# 1F1024, the environmental criteria for the original objection to the petition were resolved satisfactorily with the exception of the following points.

- 1) 70-15 data on fish was not submitted.
- 2) The fate of the primary breakdown product, 4 hydroxy 2,5,6, trichloroisophthalonitrile, also known as DAC 3701, in soil.
- 3) A paucity of data existed on breakdown in various soil types.
- 4) Need for data on aqueous stability including temperature, pH and sunlight.

Since then the manufacturer has submitted further environmental data which will be reviewed at this time.

B. Exposure of fish to ^{14}C labeled Chlorothalonil:

Accumulation, Distribution and Elimination of Residues (by Bionomics Inc.)

1. Bluegill sunfish were exposed to ^{14}C -Chlorothalonil at a concentration of ~~0.97~~^{0.01} mg/l for 28 days in a dynamic flow system. Fish remaining were transferred to an uncontaminated system for 14 days. Tissue samples were eviscerated and analyzed radiometrically to determine ^{14}C residue content at 0, 7, 14, 28 days and 7 and 14 days after transfer to uncontaminated water. Relative distribution of residues in edible and non-edible portions were investigated after 28 days by radioassaying the visceral mass. Relative amounts of polar and non-polar residues were investigated by assaying solvent extracts of pooled samples.
2. Duplicate tissue samples were combusted and the resulting $^{14}\text{CO}_2$ was trapped as a carbonate.
3. Hexane and methanol extractions of tissue blended at 22,000rpm in a waring blender were used to determine relative amount of polar and non-polar residue.
4. Radiometric analysis of water samples indicated that the concentration of chlorothalonil declined rapidly in the first 24 hours and then levelled off to 30% of nominal exposure. This may have been due to adsorption of material on the system.
5. Fish reached a plateau level of residue between 3-7 days of exposure and maintained this level throughout the exposure period. Mean residue concentration was 0.56 mg/kg. There was 15 times as much residues in nonedible portions as compared to the edible portions. 16% of the residue was extractable with hexane and 18% was extractable with methanol.
6. After 7-10 days in fresh water, 50% of the residue was eliminated. Assuming a linear rate of elimination, residue concentration in fish would decline to a level equal to the water concentration after 8 weeks in uncontaminated water. Residue elimination on edible portions of the fish resulted in 50% elimination in 7 days and elimination to 33% of original tissue concentration after 14 days.

C. Exposure of Fish to ^{14}C -labelled DAC-3701:

Accumulation, Distribution and Elimination of Residues.

1. Bluegill sunfish were exposed to ^{14}C -labelled DAC-3701 at a concentration of .01 mg/l for 28 days and 1.0 mg/l for 49 days.

After 28 days some of the fish were transferred to uncontaminated water for 28 days. Water and fish were analyzed radiometrically at 7 day intervals starting with the first day. Edible portions were analyzed at each interval and relative distribution in edible and non-edible portions were investigated after 28 days (lower level) and 49 days (higher level).

2. Duplicate tissue samples were combusted and the resulting $^{14}\text{CO}_2$ was trapped as a carbonate.

3. Hexane and methanol extractions of tissue blended at 22,000 rpm in a waring blender were used to determine relative amount of polar and non-polar residue.

4. There was an 18% mortality and generally poor physical condition observed for fish exposed to 1.0 mg/l.

5. Radiometric analysis of water samples indicated an exposure level of .005 mg/l for the lower level and 0.61 mg/l for the higher level. The lower levels may have resulted from adsorption onto the surface of the system.

6. Fish exposed to .01 mg/l accumulated a maximum between first and third day of exposure. Mean maximum level observed in edible portion was 0.19 mg/kg, a bioconcentration of 40X. ^{check + out} The maximum level observed in fish exposed to 1.0 mg/l was 48.9 mg/l, a bioconcentration 50X, after which residue levels decreased over 28 days despite continued exposure.

7. At end of exposure period the relative distribution between viscero and carcass indicated there was 5 X the concentration of residues in the non-edible compared to the edible portion. Of the residue remaining in edible portion of fish exposed to 1.0 ~~1.0~~ mg/l for 49 days, approximately 1% was extractable with hexane and an additional 34% was extractable with methanol. Corresponding values for fish exposed to .01 mg/l for 28 days were 8% for hexane and 24% for methanol.

8. With both concentrations, transfer to uncontaminated water resulted in a decline in residue. More than 50% of the residue in the edible portion was eliminated within 1-3 days. Less than 15% of the total residue present in edible portions of fish exposed to .01 mg/l for 28 days remained after 14 days in uncontaminated water. Less than 4% of the residue present in fish exposed to 1.0 mg/l for 49 days remained after 28 days in uncontaminated water.

D. Evaluation of the Leaching of Chlorothalonil Under Field Conditions and Its Potential to Contaminate Underground Water Supplies.

1. Test plot had adequate runoff, had not been planted for one year, and was a sandy loam. Lab tests showed that the half life of Chlorothalonil in this soil was 5 days and that 90% degradation occurred after 15 days.

2. One section was subjected weekly applications of 3 lb a.i. per 400' x 327' plot for 5 weeks while an adjoining section served as a control.

3. Experimental Water Analysis

A well point was sunk to a level of 12 feet, 2 feet below the water table. Samples were taken prior to initial application and immediately after each weekly application for 5 weeks and then on a monthly basis for several months. Water samples were extracted with isopropyl ether, evaporated to dryness, dissolved in benzene and analyzed for chlorothalonil by gas chromatography using an electron capture detector. To analyze for DAC-3701, the benzene sample was evaporated re-dissolved in isopropyl ether and analyzed by g.l.c. using an electron capture detector.

4. Experimental Soil Analysis

Soil was air dried and dissolved in an acetone-dilute H_2SO_4 mixture. Acetone was evaporated and residue was extracted into isopropyl ether. A reagent was added to form the propyl ether of DAC-3701 which was analyzed by g.l.c. using an electron capture detector.

5. No detectable residues of chlorothalonil or DAC-3701 were found in well water or stream water samples. Recovery of residues from water was checked, and recovery of both compounds was 96%, with a sensitivity of 1 p.p.b.

6. Maximum soil residue was found after 2 weeks of application of 3 lbs a.i./acre. Additional weekly applications failed to increase level of chlorothalonil in soil. Over 8 months 26.2" rain fell, chlorothalonil remained in the top 3" of the soil.

7. Based on the data presented it could be expected that chlorothalonil and DAC-3701 do not pose a threat to water supplies nor will they build up in the soil.

E. The Effects of Ultra-Violet Radiation on DAC-3701 in aqueous solutions.

1. A stock solution of .02g pure DAC 3701 in 400 ml tap water was prepared. One sample was exposed to a 275 watt Sears sunlamp at 8", and 40°C and samples were taken after 0,1,2, and 3 hours. Another sample was exposed for 2 hours at a temperature of 18°C. In both experiments the pH was adjusted to pH 6,7, and 8.
2. The water was analyzed for DAC-3701 by g.l.c. using the method described in section D above.
3. The pH of the water had no effect on the degradation of DAC-3701.
4. One hour of exposure to a sunlamp at 8 inches was calculated to be equivalent to 41 hours of mid-summer sunlight.
5. The ultra-violet light produced produced at least 3 degradation products. These were separated by t.l.c., but they were not identified.
6. The half life of DAC-3701 under the ultra-violet light was 53 minutes at 18°C and 41 minutes at 40°C. By calculation this was considered to be equivalent to a half life of 36 hours and 18°C and 28 hours at 40°C under field conditions.
7. The use of artificial sources of light instead of sunlight is acceptable as long as provisions are made for removal of wavelengths below 290 nm. These provisions were not made in this study.
8. Fluorescent sunlamps are acceptable as long as composite radiation from two sources is used. Single sources peaking at 340-360 nm are not acceptable. A single source was used in this study and there is no indication as to where it peaked.

IV CONCLUSIONS

Data reviewed herein satisfies the requirements for environmental data requested in re-evaluation #3 of PP# 1F1024 by R. Ney Jr. except for a detail on choice of light source in the photodegradation study.


Ronald E. Ney, Jr. 5/29/75

Frank J. Schenck 5/29/75

Environmental Chemistry Section
Ecological Effects Branch

6/2/75

6