April 11, 1986

**DYNAMAC CORPORATION**

**PP 321 (KARATE)**

Final Report

# Task 1: Review and Evaluation of Individual Studies

# Task 2: Environmental Fate and Exposure Assessment

**Contract No. 68-01-6679**

**APRIL 11,1986**

**Submitted to:**
Environmental Protection Agency
Arlington, VA 22202

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# PP321 (Karate)

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## INTRODUCTION

This report is a scientific evaluation of environmental fate data submitted to EPA by ICI Americas Inc. in order to obtain an experimental use permit (EUP) for PP321 (Karate), a 1 lb/gallon EC broad spectrum pyrethroid contact insecticide developed for use on a variety of field and vegetable crops including alfalfa, corn, cotton, lettuce, sorghum, soybeans, sunflowers, and wheat. The company proposes to apply multiple treatments (≤30 applications per season) of PP321 as needed to 9400 acres of crops throughout the United States at 0.005-0.04 lb ai/A per application; the total application over a two-year period (1986 and 1987) would be 3488 lb ai. PP321 would be applied to the crops as a foliar spray.

Three studies using PP321 and two using cyhalothrin as the test substance are reviewed herein; the isomers that comprise PP321 are part of the mixture of isomers that comprise cyhalothrin. Also, four studies that use cypermethrin as the test substance that were originally reviewed by the EAB for the cypermethrin EUP are included. Because of the structural similarity between PP321 and cypermethrin (Figure 1, Study 4), these studies can be used to provide information on the alcohol half of the PP321 molecule in soil. The contribution of all studies that have been reviewed to date toward fulfillment of data requirements is considered under Recommendations.

## STUDY 1

Collis, W.M.D. and J.P. Leahey. 1984. PP321: Hydrolysis in water at pH 5, 7, and 9. RJ 03388. ICI Americas Inc., Wilmington, DE. Reference 1J.

### CONCLUSION:

### Degradation - Hydrolysis

This study is scientifically invalid because 6-78% of the applied PP321 was not in solution during the study. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the pesticide was not completely dissolved.

### MATERIALS AND METHODS:

Cyclopropane-labeled [$^{14}$C]PP321 (Karate, 95% pure, specific activity 1.93 GBq/mM, Figure 1) was added at 0.1 ppm to glass vials containing sterile buffered aqueous solutions (pH 5, 7, and 9). The vials were sealed and incubated in the dark at 25 ± 1 C. Duplicate vials were removed up to 30 days posttreatment and stored at -15 C until analysis.

A portion of each solution was analyzed before extraction for total radioactivity using LSC. Then, methylene chloride was added to each vial, the vial was shaken, and the contents of the vial were acidified to <pH 1. The methylene chloride layer was removed and the aqueous fraction was extracted twice more with methylene chloride. The combined extracts and the extracted aqueous solution were analyzed for radioactivity using LSC. The methylene chloride extracts were further analyzed using TLC on silica gel plates developed in hexane:diethyl ether (7:3) or cyclohexane saturated with formic acid:diethyl ether (3:2) and visualized using autoradiography and a TLC linear analyzer. The extracts were also dried, redissolved in hexane, and analyzed using a GC with an electron capture detector.

### REPORTED RESULTS:

Two processes, hydrolytic degradation and isomerization, occurred concurrently in the solutions. [$^{14}$C]PP321 and its isomers, at pH 9, degraded with a half-life of 3-7 days, producing (1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)2,2-dimethylcyclopropanecarboxylic acid (Figure 2, Table 1). Approximately 50% of the PP321 was immediately (time 0 analysis) isomerized in the pH 9 solution (Table 2). At pH 7, [$^{14}$C]PP321 was slowly hydrolyzed (~7% was degraded in 30 days) and isomerized (~50% after 30 days). [$^{14}$C]PP321 was stable to hydrolysis and isomerization at pH 5.

### DISCUSSION:

1. Only 22.0 to 93.7% of the applied was in solution at the time of analysis (Table 1).

2. Recovery from fortified samples and detection limits were not reported.

3. Studies in which cyclopropane-labeled [$^{14}$C]PP321 was used provide no information on the fate of the alcohol half of the PP321 molecule.

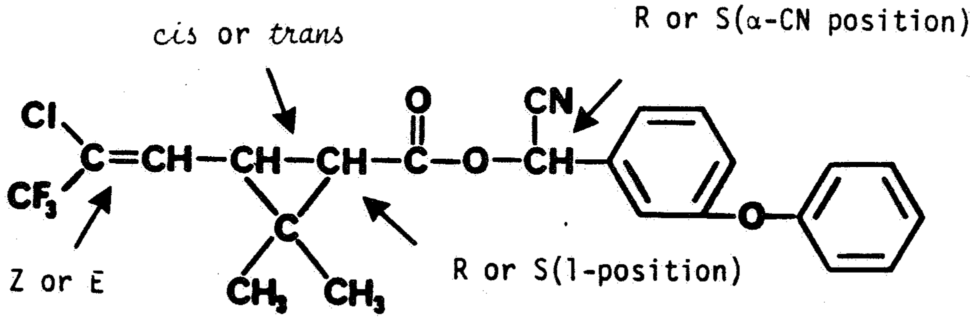


Figure 1. PP321 and its isomers. PP321 is a mixture of the enantiomers (S)-α-cyano-3-phenoxybenzyl-(1R)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (R)-α-cyano-3-phenoxybenzyl-(1S)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

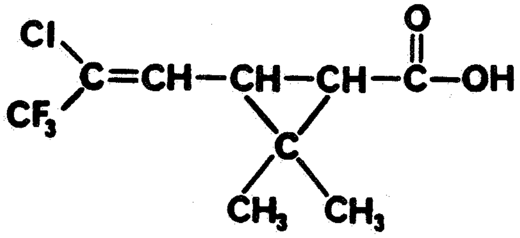


Figure 2. (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

Table 1. $[^{14}C]$PP321 and its degradates in sterile buffered aqueous solutions (pH 5, 7, and 9) treated with $[^{14}C]$PP321 (95% pure) at 0.1 ppm and incubated in the dark at 25 C.

| Sampling interval (days) | Total radioactivity (% applied) | PP321[a] | Degradate[b] | Origin | Distributed over remaining chromatogram |
|---|---|---|---|---|---|
| | | % recovered | | | |
| | | pH 5 | | | |
| 0 | 69.8 | 96 | ND[c] | ND | 3 |
| 3 | 22.0 | 97 | ND | ND | 3 |
| 7 | 45.6 | 96 | ND | ND | 4 |
| 14 | 70.5 | 98 | ND | ND | 2 |
| 30 | 65.8 | 98 | ND | ND | 1 |
| | | pH 7 | | | |
| 0 | 80.7 | 96 | ND | ND | 4 |
| 3 | 50.9 | 98 | ND | ND | 2 |
| 7 | 59.0 | 95 | ND | ND | 4 |
| 14 | 73.6 | 95 | 2 | 1 | 2 |
| 30 | 79.3 | 93 | 2 | 2 | 3 |
| | | pH 9 | | | |
| 0 | 78.4 | 93 | 4 | ND | 3 |
| 3 | 55.3 | 59 | 36 | 2 | 2 |
| 7 | 71.0 | 44 | 48 | 5 | 3 |
| 14 | 92.0 | 30 | 62 | 4 | 4 |
| 30 | 93.7 | 16 | 72 | 8 | 2 |

[a] PP321 and its isomers (see Table 2).

[b] (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[c] Not detected; detection limit was not specified.

Table 2. Isomerization (% of recovered) of PP321 (95% pure) in sterile aqueous buffered solutions.

| Sampling interval (days) | pH 5 | | pH 7 | | pH 9 | |
|---|---|---|---|---|---|---|
| | PP321 | Isomers | PP321 | Isomers | PP321 | Isomers |
| 0 | 96 | 4 | 89 | 11 | 52 | 48 |
| 3 | 96 | 4 | 82 | 18 | 49 | 51 |
| 7 | 96 | 4 | 72 | 28 | 47 | 53 |
| 14 | 98 | 2 | 59 | 41 | 44 | 56 |
| 30 | 95 | 5 | 54 | 46 | 47 | 53 |

STUDY 2

Bharti, H., D.W. Bewick, and R.D. White. 1985. PP563 and PP321: Degradation in soil. RJ 0382B. ICI Americas Inc., Wilmington, DE. Reference 4J.

## CONCLUSIONS:

### Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Cyclopropane-labeled [$^{14}$C]PP321 (97.7% isomeric purity), at 0.46 µg ai/g, degraded with a half-life of <30 days in sandy loam soil moistened to 40% of the moisture holding capacity at zero suction and incubated at 20 C. The major nonvolatile degradates were (1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (6.2% of applied on day 30) and (RS)-α-cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl])-2,2-dimethylcyclopropanecarboxylate (12.1% of applied on day 63); $^{14}CO_2$ accounted for ~36% of the applied radioactivity by day 92. [$^{14}$C]PP321 did not isomerize in the soil during the study.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the sampling intervals were too infrequent. However, this study may be used to support an EUP.

## MATERIALS AND METHODS:

Cyclopropane labeled [$^{14}$C]PP321 (Karate, 97.7% isomeric purity, specific activity 1.93 GBq/mM) was applied at 0.46 µg ai/g to pots (25 g soil, 3.8 cm diameter x 3 cm depth) of sandy loam soil (28% coarse sand, 33% fine sand, 17% silt, 22% clay, 4.0% organic matter, pH 6.7, CEC 16.8 meq/100 g) moistened to 40% of the water holding capacity at zero suction. The treated pots were placed in sealed glass columns through which moistened carbon dioxide-free air was drawn; air passing over the pots was drawn through one tube of 2-methoxyethanol and two tubes of ethanolamine. Soil samples were taken 0, 30, 63, and 92 days posttreatment; $^{14}CO_2$ evolved was determined 7, 14, 30, 63, and 92 days posttreatment. Soils were incubated aerobically at 20 C.

The trapping solutions were analyzed by LSC. The soils were extracted with acetonitrile (30 minutes at room temperature) followed with acetonitrile:water (70:30; 3 hours refluxing). Aliquots of the extracts and the extracted soil were analyzed by LSC. The extracts were also analyzed by TLC as described in Study 1, HPLC, and MS.

## REPORTED RESULTS:

[$^{14}$C]PP321 degraded with a half-life of <30 days in sandy loam soil (Table 1). (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (6.2% of applied on day 30;

Figure 2 in Study 1) and (RS)-α-cyano-3-(4-hydroxyphenoxy)benyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl-cyclopropanecarboxylate (12.1% of applied on day 63, Figure 1) were the major nonvolatile degradates; 35.6% of the applied was evolved as $^{14}CO_2$ by day 92. [$^{14}$C]PP321 did not isomerize in the soil during the study (~94% of compound remained as PP321).

## DISCUSSION:

1. The sampling intervals were too infrequent to precisely establish the half-life of PP321.

2. Studies in which cyclopropane-labeled [$^{14}$C]PP321 was used provide no information on the fate of the alcohol half of the PP321 molecule in soil.

3. The soil that was used was collected in Berkshire, England and was classified by a method other than the USDA textural classification system. The soil was not reclassified.

4. Recovery from fortified samples and detection limits were not reported.

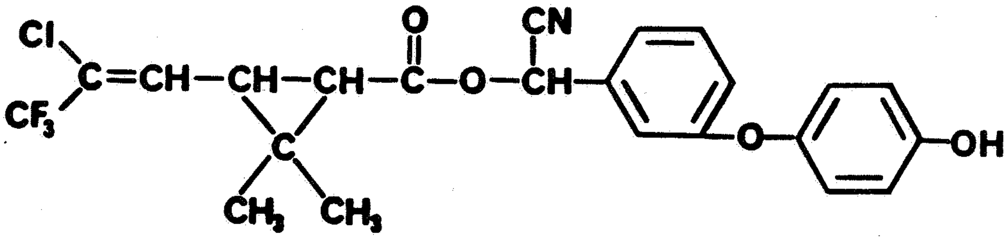


Figure 1. (RS)-α-Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

Table 1. PP321 and its degradates (% of applied) in sandy loam soil treated with [$^{14}$C]PP321 (98% pure) at 0.46 μg ai/g and incubated aerobically at 20 C and 40% of moisture holding capacity at zero suction.

| Sampling interval (days) | PP321 | Degradate A[a] | Degradate B[b] | Origin | Other | $^{14}CO_2$ | Unextractable compounds |
|---|---|---|---|---|---|---|---|
| 0 | 98.9 | <0.5[c] | <0.5 | <0.5 | <0.5 | -- | 0.2 |
| 30 | 45.8 | 6.2 | 2.5 | 12.0 | 2.1 | 16.1 | 9.6 |
| 63 | 30.1 | 5.1 | 12.5 | 3.4 | 0.6 | 31.8 | 14.5 |
| 92 | 24.4 | 6.0 | 4.2 | 2.2 | <0.5 | 35.6 | 16.8 |

[a] (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[b] (RS)-α-Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

[c] Detection limit was not specified.

## STUDY 3

Stevens, J.E.B. and D.W. Bewick. 1985. PP563 and PP321: Leaching of PP563 and PP321 and their degradation products in soil columns. RJ 04088. ICI Americas Inc., Wilmington, DE. Reference 8J.

## CONCLUSIONS:

### Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Aged (30 days) cyclopropane-labeled [$^{14}$C]PP563/321 residues (23-31% as PP321 after aging) were immobile in columns (30-cm height) of loamy sand and sandy loam soil treated at 0.04-0.05 kg PP563 eq/ha and leached with ~26 inches of a 0.01 M calcium chloride solution over a 9-week period.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of aged cyclopropane-labeled [$^{14}$C]PP321 residues.

## MATERIALS AND METHODS:

Cyclopropane-labeled [$^{14}$C]PP563/321 [98% (RS)-α-cyano-3-phenoxybenzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl-cyclopropanecarboxylate:cyhalothrin; 36.2% PP321:Karate; specific activity unspecified] was added at ~0.45 μg ai/g to sandy loam (25% coarse sand, 35% fine sand, 18% silt, 22% clay, 4.6% organic matter, pH 6.8, CEC 20 meq/100 g) and loamy sand (38% coarse sand, 40% fine sand, 12% silt, 10% clay, 2.0% organic matter, pH 5.3, CEC 7 meq/100 g) soils. The treated soils were incubated under aerobic conditions at 20 C and 40% of their moisture holding capacity at zero suction as described in Study 2. Radioactive residues in the soil were characterized after 30 days of incubation and the quantity of $^{14}CO_2$ evolved was determined as described in Study 2.

The incubated soils were transferred to the upper surface of columns of the appropriate soil (5.1 cm diameter, 30 cm height); the application rates in PP563 equivalents were 0.04 and 0.05 kg ai/ha for the sandy loam and loamy sand soils, respectively. The columns were maintained at 20 C in the dark and leached daily with 30 ml of a 0.01 M calcium chloride solution for 9 weeks; a total of ~26 inches of solution was added. The leachate was collected daily. After 9 weeks, the soil column was divided into 5-cm segments for analysis.

The leachate was analyzed for total radioactivity using LSC. The soil was dried, ground, and analyzed for total radioactivity using LSC following combustion. The detection limits (PP563 equivalents) were 0.000023 μg/ml in solution and 0.00047 μg/g in soil.

## REPORTED RESULTS:

Following aging, 23-31% of the [$^{14}$C]residues were PP321, 4-9% were

(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid, 1-17% were (RS)-$\alpha$-cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate, and 7-18% were unextractable compounds. The remaining residues were isomers of PP563 which did not also comprise PP321.

The aged residues of PP563/321 were immobile in the soil columns. No radioactivity was detected in either the leachate (<0.000023 μg/ml) or in the soil below the 0- to 5-cm depth (<0.00047 μg/g).

## DISCUSSION:

1. Although a mixture of isomers rather than pure PP321 was applied to the columns, this is a satisfactory mobility study for cyclopropane-labeled [$^{14}$C]PP321 because the presence of one isomer would not be expected to affect the mobility of another and all isomers and degradates were immobile.

2. Studies in which cyclopropane-labeled [$^{14}$C]PP321 was used provide no information on the fate of the alcohol half of the PP321 molecule in soil.

STUDY 4

Harvey, B.R., C.K.J. Zinner, R.D. White, and I.R. Hill. 1981. Cypermethrin: Degradation in soil in the laboratory. RJ 0162B. ICI Americas Inc., Wilmington, DE. Reference 5J.

This study was originally reviewed by EAB for the cypermethrin EUP and was found to be scientifically valid and fulfill data requirements. Because of the structural similarity between PP321 (Karate) and cypermethrin (Figure 1), this study can be used to provide information on the alcohol half of the PP321 molecule in soil.

## CONCLUSIONS:

### Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Benzene ring-labeled [$^{14}$C]cypermethrin (~95% pure), at 0.2-2.0 kg ai/ha, degraded with a half-life of <1 week in a clay loam, 1-3 weeks in a loamy coarse sand, and 1-3 weeks in a peat soil incubated aerobically at 25 C and 40-48% of the soil moisture holding capacity at zero suction. The major degradates were 3-phenoxybenzaldehyde (up to 6.4% of recovered), 3-phenoxybenzoic acid (up to 9% of recovered), and (RS)-α-cyano-4'-hydroxy-3-phenoxybenzyl-(1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (up to 4.5% of recovered). By 25 weeks posttreatment, 60-70% of the applied radioactivity had been evolved as $^{14}CO_2$.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the aerobic metabolism of the alcohol moiety of cypermethrin (which is identical to the alcohol moiety of PP321) in soil.

## MATERIALS AND METHODS:

Three soils obtained in the United Kingdom were used in this study (Table 1). Both nonsterile and sterile soils were studied; the soils used for the sterile treatments were irradiated with a 2.5 Mrad dose on each of two consecutive days. Soil moisture was adjusted to 40-48% of moisture holding capacity at zero suction. Prior to pesticide application the sieved soils were dispersed into glass pots (4 cm diameter x 3 cm high).

Benzene ring-labeled [$^{14}$C]cypermethrin (~95% pure, specific activity 52.8 mCi/mM) was applied to the surface of soil contained in the glass pots at application rates of 0.2 and 2.0 kg ai/ha. Application to sterile soils was carried out under aseptic conditions. Evaluation of radioactivity evolved from the soil was monitored throughout the period of incubation using sodium hydroxide and ethanolamine traps. All soils were incubated at 15, 25, or 35 C under either sterile or nonsterile conditions for up to 25 weeks.

Complete pots of soil were removed for analysis at 0, 1, 3, 10, and 25 weeks. At 0, 1, and 3 weeks the soils were extracted with hexane:

acetone (3:2, 18 hour reflux) followed by methanol (18 hour Soxhlet).

At week 10 the soils were extracted twice with hexane:acetone (18 hour reflux), then with methanol (18 hour Soxhlet) followed by distilled water (6 hour reflux). Radioactivity remaining in the soil after extraction was quantified by LSC following combustion.

At 0, 1, and 3 weeks, the soil extracts were dried with anhydrous sodium sulfate and concentrated by rotary evaporation under vacuum prior to chromatographic analysis. Duplicate samples of the concentrated extracts were applied to TLC plates (silica gel, 0.25 mm) mixed with authentic standards of cypermethrin and potential degradation products. Autoradiographs of the developed TLC's were prepared using Kodak Industrex 'C' x-ray film. The positions of the mixed cypermethrin and degradation standards were marked on the silica plates after visualization under UV. The amounts of [$^{14}$C]cypermethrin and degradation products on the TLC plates were determined by removing the appropriate areas of silica from the plate. The silica fractions were analyzed using LSC following combustion.

## REPORTED RESULTS:

The amounts of $^{14}CO_2$ evolved from all the nonsterile soils during the 25 weeks incubation period were very similar (60-70% of the recovered radioactivity). In sterile soils <8% of the recovered radioactivity was evolved as $CO_2$ by week 25.

The amount of unextractable radioactivity in the nonsterile soils increased from <1% at zero time to between 21 and 39% after 10 weeks. The amount of unextracted material did not increase appreciably between the 10 and 25 week period and in some cases fell. In the sterile soils, extractability remained high throughout the period of incubation. Over 85% of the radioactivity in the soil was extracted on all occasions. Amounts of extractable [$^{14}$C]cypermethrin decreased rapidly in all nonsterile soils; less than 50% of cypermethrin remained after 3 weeks incubation and 90% loss occurred in <25 weeks (Table 2). The rate of degradation was much slower under sterile conditions with 38 and 57% remaining in the two soils after 25 weeks incubation.

In nonsterile soils the amounts of extractable radioactivity other than cypermethrin increased up to week 3 then decreased (Tables 2 and 3). Three degradation products were present in all three soils: 3-phenoxybenzaldehyde, 3-phenoxybenzoic acid, and (RS)-α-cyano-4'-hydroxy-3-phenoxybenzyl-(1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Figure 2). 3-Phenoxybenzyl alcohol was not detected in any extract of soil. Of these compounds, 3-phenoxybenzoic acid was the major product, accounting for up to 15% of the recovered radioactivity by week 3. However, after 25 weeks of incubation <1% 3-phenoxybenzoic acid remained.

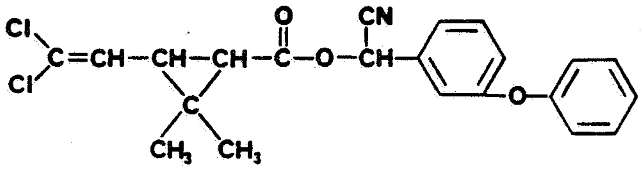
In sterile soils 3-phenoxybenzoic acid was the major identified product accounting for up to 41% of recovered radioactivity during the 25 weeks incubation.

Extractable radioactivity, not characterized, generally accounted for less than 10% of the recovered radioactivity (except in sterile soils, week 25).

DISCUSSION:

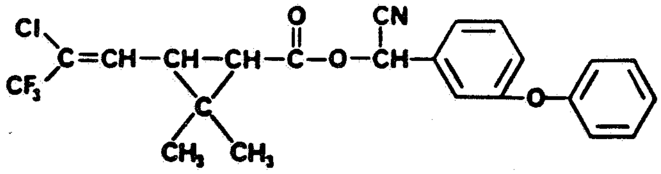
1. Studies in which benzene ring-labeled [$^{14}C$]cypermethrin was used provide no information on the fate of the cyclopropane half of the PP321 molecule in soil.

2. The soils that were used were collected in England and were classified by a method other than the USDA textural classification system. The soils were not reclassified.



± α Cyano-3-phenoxybenzyl (±) cis, trans, 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate

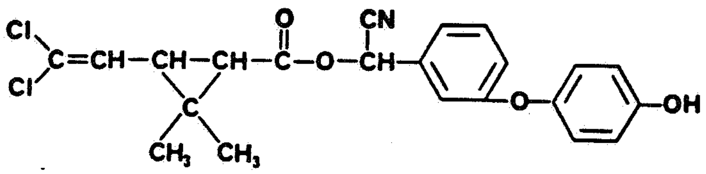
(Cypermethrin)



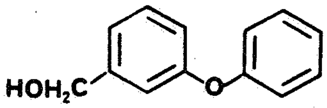
A 1:1 mixture of the enantiomers (S)-α-Cyano-3-phenoxy-benzyl (1R)-*cis*-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (R)-α-cyano-3-phenoxybenzyl (1S)-*cis*-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate

(Karate, PP321)

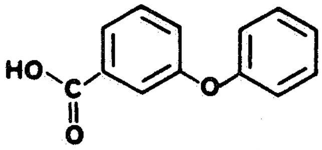
Figure 1. Cypermethrin and PP321 (Karate).



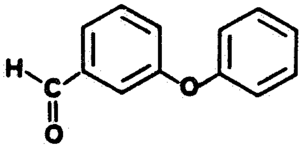
(RS)-α-Cyano-4'-hydroxy-3-phenoxybenzyl,*cis*, *trans*-3-(2, 2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate



3-Phenoxybenzyl alcohol



3-Phenoxybenzoic acid



3-Phenoxybenzaldehyde

Figure 2. Degradates of cypermethrin.

Table 1. Soil Characteristics.

| Soil type | Coarse sand | Fine sand | Silt | Clay | Organic matter | pH | CEC (meq/100 g) |
|---|---|---|---|---|---|---|---|
| | | | % | | | | |
| Clay loam | 4.6 | 31.2 | 19.6 | 44.6 | 12.2 | 7.5 | 47 |
| Loamy coarse sand | 45.0 | 35.6 | 9.6 | 9.8 | 1.8 | 6.1 | 7 |
| Fen peat | -- | -- | -- | -- | 72.7 | 7.4 | 55 |

Table 2. Rate of loss of extractable cypermethrin from soil.

| Soil type | Application rate (kg ai/ha) | Incubation temperature (C) | Time for loss of cypermethrin 50% (weeks) | Time for loss of cypermethrin 90% (weeks) |
|---|---|---|---|---|
| Clay loam | 0.2 | 25 | 1 | 5 |
| Loamy coarse sand | 0.2 | 25 | 2 | 20 |
| Fen peat | 0.2 | 25 | 3 | 20 |
| Clay loam | 0.2 | 15 | 2 | 15 |
| Clay loam | 0.2 | 35 | 1 | 8 |
| Clay loam | 2.0 | 25 | 3 | 15 |
| Clay loam (sterile) | 0.2 | 25 | 7 | >25 |
| Loamy coarse sand (sterile) | 0.2 | 25 | >25 | >25 |

## STUDY 5

Stevens, J.E.B. and I.R. Hill. 1980. Cypermethrin: Mobility of cypermethrin and its degradation products in soil columns. RJ 0166B. ICI Americas Inc., Wilmington, DE. Reference 9J.

This study was originally reviewed by EAB for the cypermethrin EUP and was found to be scientifically valid and fulfill data requirements. Because of the structural similarity between PP321 (Karate) and cypermethrin (Figure 1, Study 4), this study can be used to provide information on the behavior of the alcohol half of the PP321 molecule in soil.

### CONCLUSIONS:

### Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Aged (21 days) benzene ring-labeled [$^{14}$C]cypermethrin residues were immobile to slightly mobile in columns (30 cm height) of clay loam, loamy sand, coarse sand, and peat soils leached with ~26 inches of 0.01 M calcium chloride solution over a 9-week period.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of the alcohol moiety of aged cypermethrin residues (which is identical to the alcohol moiety of PP321).

### MATERIALS AND METHODS:

Benzene ring-labeled [$^{14}$C]cypermethrin (55:45, cis:trans; test substance not further characterized) was added at ~0.2 kg ai/ha to clay loam, loamy sand, coarse sand, and peat soils (Table 1). The treated soils were incubated under aerobic conditions at 25 C and 40% of their moisture holding capacity at zero suction as described in Study 4. Radioactive residues in the soil were characterized after 21 days of incubation and the quantity of $^{14}CO_2$ evolved was determined as described in Study 4.

Four soil leaching columns were prepared for each soil type. Each column consisted of seven 5-cm segments of aluminum tubing joined to form a hollow column 35 cm in length. Individual 5-cm segments were packed with a predetermined weight of soil until six segments were filled. To the seventh segment of 3 columns of each soil type was added the appropriate incubated soil containing [$^{14}$C]cypermethrin residues. To the fourth column was added untreated soil. Leaching columns were kept at 20 ± 2 C with 30 ml portions of 0.01 M calcium chloride solution added to each column daily for a total volume of 1380 ml applied to each column over a period of 9 weeks (~26 inches).

Radioactivity in the column leachate was determined using LSC. After leaching the columns were sectioned into six 5 cm segments, the soil segments were dried and combusted, and $^{14}CO_2$ was trapped and subjected to LSC.

## REPORTED RESULTS:

Following aging, 26-60% of the [$^{14}$C]residues were cypermethrin, <0.5% were 3-phenoxybenzaldehyde, 3-10.5% were 3-phenoxybenzoic acid, and 2.6-4.3% were (RS)-α-cyano-4'-hydroxy-3-phenoxybenzyl-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate. Unextractable residues accounted for 17-55% of the soil radioactivity, and 8-12% of the extractable residues were not identified.

The aged residues of cypermethrin were only slightly mobile in the soil columns. No radioactivity was detected (<0.0002 μg/ml) in the leachate of any column. No radioactivity was detected (<0.0004 μg/g) in the clay loam or loamy sand soil below the 0- to 5-cm depth. In the coarse sand and peat soils, ~0.001 μg cypermethrin eq/g (~0.4% of applied) was detected in the 5- to 10-cm depth but none in the 10- to 15-cm depth.

## DISCUSSION

1. Studies in which benzene ring-labeled [$^{14}$C]cypermethrin was used provide no information on the fate of the cyclopropane half of the PP321 molecule in soil.

2. The soils that were used were collected in England and were classified by a method other than the USDA textural classification system. The soils were not reclassified.

Table 1. Soil Characteristics.

| Soil type | Coarse sand | Fine sand | Silt | Clay | Organic matter | pH | CEC (meq/100 g) |
|---|---|---|---|---|---|---|---|
|  |  |  | % |  |  |  |  |
| Clay loam | 4.2 | 34.6 | 24.2 | 37.0 | 13.9 | 7.8 | 47.5 |
| Loam sand | 37.7 | 44.8 | 8.2 | 9.3 | 1.9 | 6.3 | 7.1 |
| Coarse sand | 61.6 | 31.2 | 2.6 | 4.6 | 1.0 | 5.9 | 2.8 |
| Fen peat | -- | -- | -- | -- | 72.7 | 7.4 | 55.0 |

## STUDY 6

Lloyd, S.J., E.A. Curl, and J.P. Leahey. 1984. Measurement of radioactive residues transferring into rotational crops grown in soil treated with $^{14}$C-PP321. RJ 0381B. ICI Americas Inc., Wilmington, DE. Acc. No. 073990. Reference 11J.

## CONCLUSION:

### Confined Accumulation - Rotational Crops

This study cannot be validated because no soil data were provided to confirm the application of PP321 to the soil at the rate specified. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because radioactive residues in the plant tissue were not characterized.

## MATERIALS AND METHODS:

Cyclopropane-labeled [$^{14}$C]PP321 (Karate, 95% isomerically pure, specific activity 2.59 MBq/mg) was applied at 0.31 ppm (110 g ai/ha) to pots (1.5 kg) of silty clay loam soil (59% sand, 17% silt, 23% clay, 4.3% organic matter, pH 6.6, CEC 18 meq/100 g). The soil was kept moist and weed-free in a greenhouse at >20 C. Thirty days after the application of PP321, half the treated pots were planted with lettuce, carrots, and wheat. The remaining pots were planted 120 days after the application of PP321 with the same crops. Untreated control pots were studied adjacent to the treated pots. Plant samples were taken twice during the immature stage and once at maturity (planting-to-harvest intervals unspecified).

Samples of the lettuce (leaves), wheat (grain, chaff, and straw), and carrots (roots and shoots) were analyzed by LSC following combustion.

## REPORTED RESULTS:

[$^{14}$C]PP321 residues were <0.003 mg PP321 eq/kg in mature lettuce leaves, <0.021 mg/kg in mature wheat (grain, chaff, and straw), and <0.004 mg/kg in mature carrots (roots and shoots) planted 30 and 120 days posttreatment (Tables 1 and 2). [$^{14}$C]Residues were higher (<0.041 mg/kg) in immature plant tissue.

## DISCUSSION:

1. No soil data were provided with the study. Instead, results from an aerobic soil metabolism study were presented to indicate possible concentrations of [$^{14}$C]residues at various intervals during the study.

2. Planting-to-harvest intervals were not specified.

3. Control plants probably contained radioactive residues because of adsorption of $^{14}$CO$_2$. This hypothesis was not confirmed with analysis of the radioactive residues in the plant tissue.

Table 1. [$^{14}$C]Residues (mg PP321 equivalent/kg) in lettuce, wheat, and carrots planted 30 days posttreatment in soil treated with PP321 (95% isomerically pure) at 0.3 ppm.

| Crop | Stage of harvest | | Treated soil | Control soil |
|---|---|---|---|---|
| Lettuce | Immature (1) | | 0.011 | -- |
| | Immature (2) | | 0.007 | 0.003 |
| | Mature | | 0.003 | 0.001 |
| Wheat | Immature (1) | | 0.010 | 0.002 |
| | Immature (2) | | 0.012 | 0.006 |
| | Mature: | grain | 0.003 | 0.003 |
| | | chaff | 0.005 | 0.004 |
| | | straw | 0.021 | 0.023 |
| Carrots | Immature (1) | | 0.041 | 0.004 |
| | Immature (2) | | 0.011 | 0.003 |
| | Mature: | roots | <0.001[a] | <0.001 |
| | | shoot | 0.004 | 0.002 |

[a] Detection limit not specified.

Table 2. [$^{14}C$]Residues (mg PP321 equivalent/kg) in lettuce, wheat, and carrots planted 120 days posttreatment in soil treated with PP321 (95% isomerically pure) at 0.3 ppm.

| Crop | Stage of harvest | | Treated soil | Control soil |
|---|---|---|---|---|
| Lettuce | Immature (1) | | 0.002 | <0.001[a] |
| | Immature (2) | | 0.002 | <0.001 |
| | Mature | | 0.001 | <0.001 |
| Wheat | Immature (1) | | 0.001 | <0.001 |
| | Immature (2) | | <0.001 | <0.001 |
| | Mature: | grain | 0.016 | 0.016 |
| | | chaff | 0.019 | 0.019 |
| | | straw | 0.010 | 0.009 |
| Carrots | Immature (1) | | 0.003 | <0.001 |
| | Immature (2) | | 0.002 | <0.001 |
| | Mature: | roots | 0.003 | 0.003 |
| | | shoot | 0.003 | 0.004 |

[a] Detection limit not specified.

## STUDY 7

Stevens, J.E.B. and N.J. Poole. 1981. Cyhalothrin: leaching on soil thick-layer chromatograms. RJ 0206B. ICI Americas Inc., Wilmington, DE. Acc. No. 073990. Reference 21J.

## CONCLUSIONS:

### Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Cyclopropane-labeled [$^{14}$C]cyhalothrin (99.5% pure) was immobile on loamy sand, clay loam, and sandy loam soil TLC plates; 66-90% of the recovered remained within 1-cm of the treated area.
3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of cyclopropane-labeled [$^{14}$C]cyhalothrin (of which PP321 is a constituent).

## MATERIALS AND METHODS:

Aluminum plates (5 x 30 cm) were covered with a 0.5-cm thick layer of loamy sand, clay loam, or sandy loam soil (Table 1). A cotton wick (5 x 6 cm) was attached to one end of each plate and the wicked end was elevated 5° to the horizontal; the lower end was attached to leachate collection flasks. A 1-cm wide band of soil was removed from the wick end of each plate, and the soil was mixed with cyclopropane-labeled [$^{14}$C]cyhalothrin (99.5% pure, specific activity 0.27 mCi/mM) at ~10 kg ai/ha or ethyl-1-[$^{14}$C]atrazine (93.6% pure, specific activity 2.3 mCi/mM) at ~0.4 kg ai/ha before being returned to its original position on the plate. There were three replicate plates per treatment. The cotton wicks were then placed in a 0.01 M calcium chloride solution and the plates were developed over a 3-day period with 80 ml of solution; 20-41 ml of leachate were collected from each plate. The plates were stored at -18 C until analysis.

Leachate was analyzed for total radioactivity by LSC. The plates were analyzed using radiochromatogram scanning to locate radioactive regions.

## REPORTED RESULTS:

[$^{14}$C]Cyhalothrin was immobile in the loamy sand, clay loam, and sandy loam soils; 66-90% of the recovered radioactivity remained within 1 cm of the treated area (Table 2). In contrast, [$^{14}$C]atrazine was detected throughout the soil and in the leachate, with the peak concentration occurring 6-13 cm from the treated area.

## DISCUSSION:

1. Although a mixture of isomers (cyhalothrin) rather than pure PP321 isomers was applied to the soil, this is a satisfactory mobility

study for PP321 because the presence of non-PP321 isomers would not be expected to affect the mobility of PP321 isomers and all isomers were immobile.

2. The soils that were used were collected in England and were classified by a method other than the USDA textural classification system. The soils were not reclassified.

3. Studies in which cyclopropane-labeled [$^{14}C$]cyhalothrin was used provide no information on the fate of the alcohol half of the PP321 molecule in soil.

Table 1. Soil characteristics.

| Soil type | Coarse sand | Fine sand | silt | Clay | Organic matter | pH | CEC (meq/100 g) |
|---|---|---|---|---|---|---|---|
| | | | % | | | | |
| Loamy sand | 40.1 | 42.0 | 9.6 | 8.3 | 2.2 | 6.2 | 7.1 |
| Clay loam | 4.2 | 34.6 | 24.2 | 37.0 | 13.9 | 7.8 | 47.5 |
| Sandy loam | 27.7 | 34.3 | 34.3 | 21.4 | 5.2 | 6.5 | 20.4 |

Table 2. $[^{14}C]$Cyhalothrin and $[^{14}C]$atrazine (% of applied) on soil TLC plates treated at 10 and 0.4 kg ai/ha, respectively, and leached with a 0.01 M calcium chloride solution.[a]

| Distance from top of plate (cm)[b] | Loamy sand | | Clay loam | | Sandy loam | |
|---|---|---|---|---|---|---|
| | Cyhalothrin | Atrazine | Cyhalothrin | Atrazine | Cyhalothrin | Atrazine |
| 1 | 0.02 | 1.09 | 0.18 | 0.78 | 0.48 | 0.36 |
| 2 | 4.03 | 1.96 | 3.46 | 1.09 | 7.27 | 0.64 |
| 3 | 31.52 | 5.86 | 44.64 | 3.35 | 55.81 | 1.09 |
| 4 | 30.88 | 13.59 | 39.28 | 3.83 | 26.31 | 2.27 |
| 5 | 7.06 | 5.78 | 3.79 | 2.45 | 1.84 | 1.53 |
| 6 | 2.85 | 3.40 | 0.46 | 2.40 | 0.33 | 1.60 |
| 7 | 3.14 | 4.40 | 0.41 | 3.00 | 0.81 | 1.60 |
| 8 | 2.62 | 5.90 | 0.07 | 4.05 | 0.36 | 2.21 |
| 9 | 2.62 | 5.66 | 0.48 | 5.74 | 0.61 | 3.04 |
| 10 | 2.41 | 5.90 | 0.41 | 5.70 | 0.56 | 4.17 |
| 11 | 1.93 | 4.49 | 0.57 | 6.44 | 0.27 | 4.99 |
| 12 | 1.88 | 4.50 | 0.19 | 7.01 | 0.40 | 6.08 |
| 13 | 2.33 | 4.48 | 0.28 | 6.66 | 0.46 | 7.40 |
| 14 | 1.69 | 3.95 | 0.37 | 7.04 | 0.39 | 7.92 |
| 15 | 0.58 | 3.33 | 0.47 | 7.02 | 0.12 | 7.67 |
| 16-20 | 3.11 | 12.68 | 1.42 | 20.01 | 1.18 | 30.59 |
| 21-25 | 1.30 | 8.87 | 2.98 | 8.45 | 1.62 | 12.78 |
| 25-30 | 0.02 | 4.17 | 0.64 | 5.01 | 1.20 | 4.04 |
| Leachate | 0.03 | 1.34 | 0.04 | 1.61 | 0.08 | 1.86 |

[a] Average of three TLC plates.

[b] Pesticide was applied ~2-3 cm from the top of the soil TLC plate.

STUDY 8

Askew, P.D. and I.R. Hill. 1985. A comparison of the microflora and physicochemical properties of soils used in UK laboratory studies with those of USA soils. ICI America Inc., Wilmington, DE. RJ 0429B. Acc. No. 073990. Reference 22J.

A number of studies in this report were conducted using foreign soils. The registrant has provided the results of soil analyses comparing eight soils from typical soybean growing areas in the US with two UK soils used in the laboratory studies of PP321 (Tables 1 and 2). Based on this information, all laboratory studies for karate using these UK soils are considered acceptable.

Table 1. Physiochemical properties of US vs. UK soils.

| Soil type | Soil source | Sand | Silt | Clay | Organic matter | pH | CEC (meq/100 g) |
|---|---|---|---|---|---|---|---|
| | | | | % | | | |
| Clay loam[a] | Champaign, IL | 27 | 38 | 35 | 5.9 | 7.0 | 31 |
| Loam | White Heath, IL | 48 | 33 | 19 | 1.7 | 6.8 | 11 |
| Sandy loam | Yanceyville, NC | 66 | 20 | 14 | 1.2 | 5.6 | 3.3 |
| Clay loam | Proctor, AR | 31 | 39 | 30 | 1.8 | 6.8 | 21 |
| Silty clay | Tallulah, LA | 12 | 40 | 48 | 3.0 | 6.1 | 26 |
| Clay | Thomastown, LA | 6 | 33 | 61 | 3.0 | 6.4 | 32 |
| Sandy loam[b] | Lebeau, LA | 77 | 15 | 8 | 0.9 | 6.6 | 4.5 |
| Sandy loam | Dothan, AL | 79 | 10 | 11 | 1.0 | 6.4 | 2.7 |
| Loamy sand | Frensham, Surrey, UK | 81 | 10 | 9 | 2.2 | 5.8 | 6.4 |
| Sandy clay loam | 18 Acres, Berkshire, UK | 59 | 17 | 23 | 4.3 | 6.6 | 18 |

[a] Reported as a silty clay loam.

[b] Reported as a loam.

Table 2. Microbiological properties of US vs. UK soils.

| Soil | Total microbes (x $10^9$/g dry wt soil) | Dilution plate counts (x $10^6$/g dry wt soil) | | | Ratio of Bacteria:Actinomyces:Fungi | | |
|---|---|---|---|---|---|---|---|
| | | Bacteria | Actinomyces | Fungi | | | |
| Champaign | 1.5 | 15 | 0.99 | 0.12 | 125 : | 8.3 | 1 |
| White Heath | 0.8 | 12 | 0.94 | 0.05 | 240 : | 18.8 | 1 |
| Yancyville | 0.7 | 20 | 0.92 | 0.15 | 133 : | 6.1 | 1 |
| Proctor | -- | 43 | 0.50 | 0.11 | 390 : | 4.6 | 1 |
| Tallulah | 1.4 | 16 | 0.63 | 0.10 | 160 : | 6.3 | 1 |
| Thomastown | 1.7 | 22 | 0.32 | 0.05 | 440 : | 6.4 | 1 |
| Lebeau | 1.1 | 30 | 0.52 | 0.15 | 200 : | 3.5 | 1 |
| Dothan | -- | 15 | 0.74 | 0.09 | 167 : | 8.2 | 1 |
| Frensham | 0.8 | 23 | 4.3 | 0.17 | 158 : | 19 | 1 |
| 18 Acres | 1.7 | 33 | 9.7 | 0.13 | 240 : | 49 | 1 |

STUDY 9

Woods, T.M., D.W. Bewick, and J.P. Leahey. 1980. Cypermethrin: Rotational crop study. RJ 0161B. ICI Americas Inc., Wilmington, DE.

This study was originally reviewed by EAB for the cypermethrin EUP. Because of the structural similarity between PP321 (Karate) and cypermethrin (Figure 1, Study 4), this study can be used to provide information on the behavior of the alcohol half of the PP321 molecule.

## CONCLUSIONS:

### Confined Accumulation - Rotational Crops

1. This study is scientifically valid.

2. [$^{14}$C]Cypermethrin residues were <0.07 ppm cypermethrin equivalents in mature wheat, <0.05 ppm in mature cotton, <0.01 ppm in mature lettuce and <0.06 ppm in mature sugar beets planted 29-120 days after the soil was treated with benzene ring-labeled [$^{14}$C]cypermethrin at ~1.8 ppm.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because radioactive residues were not characterized. Also, because of variability, the "background radioactivity" in the controls was not subtracted from the concentration measured in the treated plants.

## MATERIALS AND METHODS:

Greenhouse pots (27) of 23-cm diameter were filled with a sandy loam soil (coarse sand 25.4%, fine sand 26.5%, silt 20.1%, clay 28.0%, pH 6.8, 5.08% organic matter, CEC 21 meq/100 g ). The top 7.5 cm of the soil in the greenhouse pots was treated with benzene ring labeled [$^{14}$C]cypermethrin at 1.0 kg ai/ha rate which is about one-half of the maximum recommended rate of 1.875 lb/acre/season. The treated soil pots including 12 control pots were maintained in the greenhouse during aging and during the plant growth stages of the experiment.

Four rotational crops were used in this experiment: sugar beets, wheat, lettuce, and cotton. Fifteen seeds of cotton, sugar beet, wheat, and lettuce were sown to each pot at intervals of 29, 60, and 120 days after the application of [$^{14}$C]cypermethrin. Each crop was thinned several times during the study and the thinnings were analyzed for total [$^{14}$C]residues. At maturity, wheat (grain, chaff, and straw), sugar beets (foliage and root), cotton (lint, seed, boll husks, and foliage), and lettuce were analyzed for total $^{14}$C activity.

Soil cores from the top 7.5 cm of each pot were taken for analysis at the respective sowing intervals of 29, 60, and 120 days after treatment. When the crops were harvested soil cores were taken to the bottom of each pot.

The radioactive residues in the soil and crop samples were measured using LSC following combustion.

## REPORTED RESULTS:

Benzene ring-labeled [$^{14}C$]cypermethrin residues decreased from 1.77 ppm in the upper 7.5 cm of soil at the time of treatment to 0.81 ppm 120 days posttreatment and 0.57 ppm 252 days posttreatment.

[$^{14}C$]Residues were <0.07 ppm cypermethrin equivalents in mature wheat, cotton, lettuce and sugar beets planted 29, 60, and 120 days after the soil was treated with [$^{14}C$]cypermethrin (Table 1). Radioactive residues in the control samples were quite variable, ranging from <0.01 to 0.06 ppm.

## DISCUSSION:

1. Presumably, the control plants contained radioactive residues because of adsorption of $^{14}CO_2$. This hypothesis was not confirmed with analysis of the residues in the plant tissue.

2. [$^{14}C$]Residues in the soil and crops were not characterized.

3. Studies in which benzene ring-labeled [$^{14}C$]cypermethrin was used provide no information on the fate of the cyclopropane half of the PP321 molecule in soil.

Table 1. $[^{14}C]$Cypermethrin residues (ppm) in plants grown in soil treated with benzene ring-labeled $[^{14}C]$cypermethrin at ~1.8 ppm.

| Crop | Treatment-to-planting interval | Plant part | $[^{14}C]$Residue |
|---|---|---|---|
| Wheat | 29 | Thinnings | 0.04 |
| | | Thinnings | 0.04 |
| | | Grain | 0.06[a] |
| | | Chaff | 0.07[a] |
| | | Straw | 0.06[a] |
| | 60 | Thinnings | 0.01 |
| | | Thinnings | 0.02 |
| | | Grain | 0.06[a] |
| | | Chaff | 0.06[a] |
| | | Straw | 0.04[a] |
| | 120 | Thinnings | <0.01 |
| | | Thinnings | 0.01 |
| | | Grain | 0.04[a] |
| | | Chaff | 0.03[a] |
| | | Straw | 0.02[a] |
| Cotton | 29 | Thinnings | 0.02 |
| | | Thinnings | 0.04 |
| | | Lint | 0.02 |
| | | Seed | 0.03 |
| | | Boll husk | 0.02 |
| | | Foliage | 0.01 |
| | 60 | Thinnings | 0.01 |
| | | Thinnings | 0.04 |
| | | Lint | <0.01 |
| | | Seed | 0.05 |
| | | Boll husk | 0.03 |
| | | Foliage | <0.01 |
| | 120 | Thinnings | <0.01 |
| | | Thinnings | 0.01 |
| | | Lint | 0.02[a] |
| | | Seed | 0.03[a] |
| | | Boll husk | 0.02[a] |
| | | Foliage | <0.01[a] |
| Lettuce | 29 | Thinnings | 0.06 |
| | | Thinnings | 0.04 |
| | | Mature | <0.01 |
| | 60 | Thinnings | 0.05 |
| | | Thinnings | 0.03 |
| | | Mature | <0.01 |
| | 120 | Thinnings | 0.02 |
| | | Thinnings | 0.01 |
| | | Mature | <0.01 |
| Sugar beet | 29 | Thinnings | -- |
| | | Foliage | 0.01 |
| | | Root | 0.02 |
| | | Foliage | 0.01 |
| | | Root | 0.01 |
| | 60 | Thinnings | 0.02 |
| | | Foliage | 0.02 |
| | | Root | 0.06 |
| | | Foliage | <0.01 |
| | | Root | <0.01 |
| | 120 | Thinnings | <0.01 |
| | | Foliage | 0.01 |
| | | Root | 0.02 |
| | | Foliage | <0.01 |
| | | Root | <0.01 |

[a] Control values as high as samples.

STUDY 10

Hammer, M.J. and I.R. Hill. 1980. Cypermethrin: The accumulation of cypermethrin and its degradation products by channel catfish in a model soil/water system. RJ 0153B. ICI Americas Inc., Wilmington, DE.

This study was orginally reviewed by EAB for the cypermethrin EUP. Because of the structural similarity between PP321 (Karate) and cypermethrin (Figure 1, Study 4), this study can be used to provide information on the behavior of the alcohol half of the PP321 molecule.

EPA Reviewers Note: A "catfish" or soil/water ecosystem accumulation study is not now required by the current Environmental Fate Guidelines. The results of this study are briefly summarized and not reviewed in detail.

Channel catfish (Ictalurus punctatus) were exposed to benzene ring labeled [$^{14}$C]cypermethrin and its soil degradation products in a soil/water ecosystem for 23 days after which the fish were transferred to flowing, uncontaminated water for a 14 day depuration phase. Soil, water and fish (muscle, viscera, and whole fish) were analyzed for [$^{14}$C]residues at regular intervals.

During the initial 21 day aerobic incubation with soil, [$^{14}$C]residues decreased from 500 μg cypermethrin equivalents/kg dry wt soil to 300 μg/kg. Cypermethrin accounted for at least 90% of the applied radioactivity after application to the soil; by day 21 only 15% of the applied radioactivity remained as extractable cypermethrin. Following flooding of the soil there was little change in the total radioactivity in the soil. The [$^{14}$C]-residues in the water increased to a plateau of 1.9 μg cypermethrin equivalents/l, ~4% of the applied radioactivity. In the whole fish an apparent plateau concentration of 30 μg cypermethrin equivalents/kg wet wt fish was reached during the exposure phase, equivalent to approximately 0.023% of the radioactivity remaining in the ecosystem. At the end of exposure, muscle tissues contained 20 μg cypermethrin equivalents/kg. The mean maximum bioconcentration factors (concentration of [$^{14}$C]residues in fish/concentration of [$^{14}$C]residues in water) in whole fish and muscle were approximately 14x and 9x, respectively.

The concentration of [$^{14}$C]residues in the fish fell rapidly during depuration. Approximately 70% and 80% of the residues in the muscle and whole fish, respectively, were eliminated during the 14 day period.

In conclusion, the data presented in this report show that bioconcentration of residues of the [$^{14}$C]benzyl moiety of cypermethrin from a sediment/water ecosystem by channel catfish is relatively minor. Rapid loss of these same residues on depuration also shows that they are unlikely to possess the potential to accumulate through a food chain involving fish.

## EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed to date but do not fulfill data requirements unless noted in the Recommendations section of this report.

Cyclopropane labeled [$^{14}$C]PP321 (97.7% isomeric purity), at 0.46 µg ai/g, degraded with a half-life of <30 days in sandy loam soil moistened to 40% of the moisture holding capacity at zero suction and incubated at 20 C (Bharti et al., 1985). The major nonvolatile degradates were (1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (6.2% of applied on day 30) and (RS)-α-cyano-3-(4-hydroxyphenoxy)-benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (12.1% of applied on day 63); $^{14}CO_2$ accounted for ~36% of the applied radioactivity by day 92. [$^{14}$C]PP321 did not isomerize in the soil during the study.

Benzene ring-labeled [$^{14}$C]cypermethrin (~95% pure), at 0.2-2.0 kg ai/ha, degraded with a half-life of <1 week in a clay loam, 1-3 weeks in a loamy coarse sand, and 1-3 weeks in a peat soil incubated aerobically at 25 C and 40-48% of the soil moisture holding capacity at zero suction (Harvey et al., 1981). The major degradates were 3-phenoxybenzaldehyde (up to 6.4% of recovered), 3-phenoxybenzoic acid (up to 9% of recovered), and (RS)-α-cyano-4'-hydroxy-3-phenoxybenzyl-(1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (up to 4.5% of recovered). By 25 weeks posttreatment, 60-70% of the applied radioactivity had been evolved as $^{14}CO_2$.

Aged (30 days) cyclopropane-labeled [$^{14}$C]PP563/321 residues (23-31% as PP321 after aging) were immobile in columns (30-cm height) of loamy sand and sandy loam soil treated at 0.04-0.05 kg PP563 eq/ha and leached with ~26 inches of a 0.01 M calcium chloride solution over a 9-week period (Stevens and Bewick, 1985).

Aged (21 days) benzene ring-labeled [$^{14}$C] cypermethrin residues were immobile to slightly mobile in columns (30 cm height) of clay loam, loamy sand, coarse sand, and peat soils leached with ~26 inches of 0.01 M calcium chloride solution over a 9-week period (Stevens and Hill, 1980).

Cyclopropane-labeled [$^{14}$C]cyhalothrin (99.5% pure), of which PP321 is a constituent was immobile on loamy sand, clay loam, and sandy loam soil TLC plates; 66-90% of the recovered remained within 1-cm of the treated area (Stevens and Poole, 1981).

### Recommendations

Available data are insufficient to fully assess the environmental fate of, and the exposure of humans and nontarget organisms to PP321 (Karate). The submission of data relative to EUP requirements (Subdivision N) is summarized below.

Hydrolysis studies: One study (Collis and Leahey, 1984) was reviewed and is scientifically invalid because 6-78% of the applied PP321 was not in solution during the study. In addition, this study would not fulfill data requirements because the pesticide was not completely dissolved. All data (both cyclopropane and alcohol moieties) are required for an EUP.

Aerobic soil metabolism studies: One study (Bharti et al., 1985) was reviewed and is scientifically valid. This study does not fulfill data requirements because the sampling intervals were too infrequent. This study will support and EUP but will not satisfy requirements for full registration. Additional data are needed to define the decline of PP321 from 0 to 15 days. A valid study using benzene-labeled cypermethrin that provides information on the alcohol moiety has been provided.

Leaching and adsorption/desorption studies: Two studies were reviewed; in both, cyhalothrin rather than PP321 was the test substance. One study (Stevens and Bewick, 1985) was scientifically valid and partially fulfills data requirements by providing information on the mobility of aged cyclopropane-labeled PP321 residues. A second study (Stevens and Poole, 1981) is scientifically valid and partially fulfills data requirements by providing information on the mobility of unaged cyclopropane-labeled cyhalothrin in three soils. A valid aged benzene ring-labeled [$^{14}$C]cypermethrin study that provided information on the fate of the alcohol moiety was also provided. A study is needed showing the mobility of unaged PP321 in a fourth soil; this study should be conducted using a method other than the horizontal soil TLC plate procedure, since this procedure is atypical of standard Helling TLC.

Confined accumulation studies on rotational crops: One study (Lloyd et al., 1984) was reviewed and cannot be validated because no soil data were provided to confirm the application of PP321 to the soil at the rate specified. In addition, this study would not fulfill data requirements because residues in the soil were not analyzed and radioactive residues in the plant tissue were not characterized. A valid benzene ring-labeled [$^{14}$C]cypermethrin study was provided, but this study did not fulfill data requirements. All data (both cyclopropane and alcohol moieties) are required.

Laboratory studies of pesticide accumulation in fish: No PP321 data were provided. A benzene ring-labeled [$^{14}$C]cypermethrin study that was provided did not fulfill data requirements. All data (both cyclopropane and alcohol moieties) are required.

Studies in which cyhalothrin rather than PP321 was the active ingredient were submitted to satisfy several data requirements for the PP321 EUP with the explanation by the registrant that PP321 is a constituent of cyhalothrin, that the two pesticides are various isomers of a single molecule and should be interchangable. However, EPA Data Requirements for Registering Pesticides specify that studies must be done with the active ingredient in the product. Since the registrant differentiates between cyhalothrin and PP321, EPA cannot regard the pesticides as interchangable in fulfilling data requirements unless the registrant provides acceptable data showing that the configuration of the molecule has no effect on its behavior. All studies for the PP321 EUP must be done with PP321 rather than cyhalothrin. A one-time exception has been made in the case of mobility studies submitted for the EUP because all radiolabeled material applied to the soil was immobile; it is logical to assume that non-PP321 isomers would not cause PP321 isomers to be immobile in soil.

Studies which were submitted for the EUP but are not required (photodegradation in water and on soil, anaerobic aquatic metabolism, and field dissipation) should be resubmitted for review when full registration of the pesticide is requested.

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