Shaughnessy No. 128897

Date Out of EAB: SEP 17 1987

To: George La Rocca
Product Manager #15
Registration Division (TS-767C)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of...

Reg./File # : 10182-OA

Chemical Name: PP 321

Type Product : Insecticide

Product Name : Karate 1 EC

Company Name : ICI Americas Inc.

Purpose : Response to comments made on request for registration for use on cotton and review of additional data.

Date Received: 1/30/87

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Monitoring study requested: _____

Monitoring study voluntarily: _____

Deferrals to: _____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

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KARATE
10182-0A
87-132

DYNAMAC CORPORATION

COPY 4

PP 321 (KARATE)

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate and Exposure Assessment

Contract No. 68-02-4250

AUGUST 26, 1986

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
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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 full registration for PP321 (Karate), a 1 lb/gallon EC broad spectrum pyrethroid contact insecticide for use on cotton.

Six 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, five studies that use cypermethrin as the test substance are included. Because of the structural similarity between PP321 and cypermethrin, 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. All structures are illustrated in the appendix.

CASE GS -- PP321 STUDY 1 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

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.

SUBST. CLASS = S.

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

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SIGNATURE: DATE:

This study was previously reviewed for the EUP. The review is reproduced in its entirety.

CONCLUSION:

Degradation - Hydrolysis

This study is scientifically invalid because the test material was applied at a rate greatly exceeding its water solubility. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because no information was provided on the alcohol moiety of the parent compound.

MATERIALS AND METHODS:

Cyclopropane-labeled [^{14}C]PP321 (Karate, 95% pure, specific activity 1.93 GBq/mM) 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 post-treatment 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-dimethylcyclopropane-carboxylic 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. The test material was applied at a rate greatly exceeding its water solubility.

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.

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-dimethylcyclopropane-carboxylic 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

CASE GS -- PP321 STUDY 2 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

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

SUBST. CLASS = S.

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

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SIGNATURE: DATE:

This study was previously reviewed for the EUP.

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-dimethylcyclopropane-carboxylate (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 partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the aerobic metabolism of the acid moiety of PP321 in a sandy loam soil.

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) and (RS)-α-cyano-3-(4-hydroxyphenoxy)benyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (12.1% of applied on day 63) 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. 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.

2. 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.

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

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				$^{14}CO_2$	Unextractable compounds
		A[a]	B[b]	Origin	Other		
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-dimethylcyclopropane-carboxylic 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.

CASE GS -- PP321 STUDY 3 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Stevens, J.E.B. and D.W. Rewick. 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.

SUBST. CLASS = S.

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

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This study was previously reviewed for the EUP. The review is reproduced in its entirety.

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-dimethylcyclopropanecarboxylate:cyhalothrin; 36.2% PP321:Karate; specific activity unspec-

ified] 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)-α-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.

CASE GS -- PP321 STUDY 4 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Harvey, R.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.

SURST. CLASS = S.

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

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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, 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 post-treatment, 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-week 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. 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.

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)	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

CASE GS -- PP321 STUDY 5 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

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.

SUBST. CLASS = S.

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

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SIGNATURE: DATE:

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, 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

CASE GS -- PP321 STUDY 6 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Lloyd, S.J., F.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 12J.

SUBST. CLASS = S.

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

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This study was previously reviewed for the EUP. The review is reproduced in its entirety.

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.

CASE GS -- PP321 STUDY 7 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

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

SUBST. CLASS = S.

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

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This study was previously reviewed for the EUP. The review is reproduced in its entirety.

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.

CASE GS -- PP321 STUDY 8 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

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

SUBST. CLASS = S.

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

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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 PP321 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 ($\times 10^9$/g dry wt soil)	Dilution plate counts ($\times 10^6$/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

CASE GS -- PP321 STUDY 9 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Woods, T.M., D.W. Bewick, and J.P. Leahey. 1980. Cypermethrin: Rotational crop study. RJ 0161B. ICI Americas Inc., Wilmington, DE. Reference 13J.

SUBST. CLASS = S.

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

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This study was originally reviewed by EAB for the cypermethrin FUP. Because of the structural similarity between PP321 (Karate) and cypermethrin, 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 (days)	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.

CASE GS -- PP321 STUDY 10 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

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.

SUBST. CLASS = S.

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

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This study was orginally reviewed by EAB for the cypermethrin EUP. Because of the structural similarity between PP321 (Karate) and cypermethrin, 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 radioacti-

vity. 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.

CASE GS -- PP321 STUDY 11 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Curl, E.A., J.P. Leahey, and S.J. Lloyd. 1984. PP321: Aqueous photolysis at pH 5. RJ 0362B. ICI Americas Inc., Wilmington, DE. Reference 2J.

SUBST. CLASS = S.

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

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CONCLUSIONS:

Degradation - Photodegradation in Water

This study is scientifically invalid because the sampling protocol (one sample) was inadequate and the test material was used at a rate exceeding its water solubility. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because no material balance was provided for the dark control, a half-life could not be estimated, and the solutions may not have been sterile throughout the study.

MATERIALS AND METHODS:

Cyclopropane-labeled [^{14}C]PP321 (radiochemical purity 98%, isomeric purity 95%, specific activity 1.93 GBq/mM) was added at 0.105 µg ai/ml to three quartz flasks containing 25 ml of sterile buffered aqueous solutions. One flask was covered with aluminum foil to act as a dark control. The flasks were stoppered and placed outside in sunlight for 30 days (Tables 1 and 2). On day 30, the flasks were stored frozen at -15 ± 5°C until analysis.

Methylene chloride was added to the solutions; the mixture was shaken in the sample flasks, acidified to pH 1, and shaken again. Then, the phases were removed from the flasks and separated. The aqueous phase was extracted with methylene chloride two more times. The methylene chloride layers were combined and concentrated by evaporation. Aliquots of both

the methylene chloride and aqueous solutions were analyzed using TLC on silica gel plates developed in either hexane:diethyl ether (7:3), cyclohexane saturated with formic acid:diethyl ether (3:2), hexane:acetone:formic acid (70:30:0.5), or toluene:carbon tetrachloride (1:1). The plates were analyzed with an automatic TLC linear analyzer and autoradiography; radioactive compounds isolated on the plates were compared to standards. An aliquot of the methylene chloride extracts was analyzed using HPLC to determine the isomeric composition of the PP321.

REPORTED RESULTS:

[^{14}C]PP321 comprised 43.5% of the applied in a nonsterile solution and 66.7% of the applied in an apparently sterile solution irradiated with natural sunlight for 30 days (Table 3). Three major degradates, (1RS)-cis- and (1RS)-trans-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (degradates Ia and Ib) and (RS)-α-amido-3-phenoxybenzyl-(IRS)-cis,trans-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl-2,2-dimethylcyclopropanecarboxylate (degradate II), were each <10% of the applied; ~5 minor degradates were each <5% of the applied. No degradation occurred in the dark control.

Both optical and geometrical isomerization occurred in the irradiated flasks; only 21-27% of the radioactivity remained as unisomerized PP321. No isomerization occurred in the dark control.

DISCUSSION:

1. The solutions were analyzed only on day 30 of the experiment.

2. The test material was applied at a rate which exceeds its water solubility of 3-4 x 10^{-3} ppm.

3. No material balance was provided for the dark control.

4. One flask was not sterile at the termination of the study, as evidenced by algal growth. The second flask was not analyzed to insure that sterile conditions remained throughout the study.

Table 1. Meteorological data.[a]

Date (1983)	Hours of sun	Maximum temperature °C	Minimum temperature °C
20th July	4.5	21.8	15.6
21st	13.8	23.8	6.6
22nd	6.8	28.1	14.0
23rd	6.0	23.3	15.5
24th	3.9	20.7	15.1
25th	3.6	24.8	15.0
26th	7.4	27.3	13.0
27th	6.9	26.5	14.2
28th	9.1	25.8	15.7
29th	13.0	30.1	12.0
30th	10.9	28.9	14.2
31st	0.9	26.1	13.8
1st August	4.4	19.0	13.2
2nd	6.1	17.4	6.8
3rd	13.5	21.5	3.3
4th	5.0	22.9	6.6
5th	11.7	23.5	9.6
6th	6.2	20.7	14.2
7th	6.5	21.9	8.0
8th	9.6	25.1	13.1
9th	7.9	27.1	14.6
10th	10.1	24.6	14.8
11th	6.5	21.7	10.1
12th	9.7	24.7	9.0
13th	12.0	23.1	7.7
14th	12.1	27.9	9.8
15th	11.8	26.6	14.3
16th	7.2	23.9	12.8
17th	3.6	24.9	17.2
18th	12.0	25.9	8.9
19th	10.6	29.6	13.0

[a] Site located at Jealott's Hill, Berkshire, England: latitude 51°23'N and longitude 0°47'W.

Table 2. Intensity (mW-hr/cm^2) of incident sunlight during the study.[a]

Date	Hourly Totals															
	04-05	05-06	06-07	07-08	08-09	09-10	10-11	11-12	12-13	13-14	14-15	15-16	16-17	17-18	18-19	19-20
20th July 1983	1.8	8.8	16.0	23.3	45.4	52.8	62.7	66.8	64.5	45.8	28.6	61.5	18.3	9.8	6.5	2.5
21st	2.7	12.6	28.1	42.4	51.8	68.8	79.8	86.1	86.3	79.9	71.8	58.9	44.8	29.1	13.9	2.9
22nd	1.4	6.7	20.1	40.8	42.5	55.8	67.7	76.3	66.8	48.5	23.8	28.8	26.7	9.7	3.7	0.5
23rd	0.1	1.3	6.8	17.8	18.4	28.8	33.8	38.3	57.6	54.7	36.2	51.5	35.2	21.3	10.8	2.5
24th	1.8	7.6	12.6	17.5	22.2	48.1	32.8	42.4	35.8	39.5	43.6	44.8	27.1	28.9	4.8	1.2
25th	0.7	4.8	5.3	8.8	12.4	19.4	21.8	65.3	53.8	35.8	28.7	24.9	23.4	18.9	6.1	0.9
26th	1.6	6.9	12.4	24.1	35.7	57.5	65.4	44.9	54.9	52.6	52.8	34.5	23.2	12.7	7.7	1.3
27th	1.2	6.7	18.3	22.8	45.7	41.4	51.8	63.5	58.6	42.8	48.8	48.6	30.6	19.4	7.8	1.5
28th	0.8	4.7	8.8	13.9	25.4	38.6	79.4	83.9	82.2	74.8	69.7	54.8	38.5	14.3	8.5	1.3
29th	1.6	8.8	25.3	38.9	52.6	64.4	76.9	77.9	81.1	76.2	67.6	54.7	36.5	21.8	9.1	1.4
30th	1.8	8.4	25.5	36.9	46.6	67.3	72.1	79.5	79.7	75.1	64.4	51.4	36.2	21.8	6.4	0.9
31st	1.7	6.3	11.7	14.8	24.3	17.8	36.2	37.5	21.8	8.5	18.5	4.8	18.8	17.9	8.4	0.9
1st August 1983	0.1	0.9	4.2	8.2	25.6	56.4	48.3	68.8	18.8	32.8	61.7	27.3	13.6	9.9	3.6	0.1
2nd	0.8	5.3	10.8	16.4	26.4	47.5	57.8	48.7	45.3	34.8	44.5	51.6	38.2	14.6	11.4	1.6
3rd	1.5	10.2	25.4	48.3	54.9	67.2	78.1	84.3	83.3	66.6	66.1	46.8	36.4	21.7	8.1	1.8
4th	0.8	5.2	21.8	38.8	48.5	33.6	51.2	58.5	56.6	42.2	41.8	38.4	31.6	18.8	9.3	1.3
5th	1.1	9.3	23.8	38.7	48.6	38.5	47.8	63.4	64.8	78.5	61.8	52.5	37.7	22.5	7.1	0.8
6th	0.6	9.3	21.9	36.3	48.9	28.8	41.8	42.8	57.2	37.5	19.1	13.2	14.7	13.4	6.7	0.8
7th	0.9	5.4	18.4	31.9	31.7	33.3	43.4	63.1	78.1	67.4	42.8	32.5	28.8	16.8	5.9	0.9
8th	0.6	3.6	7.3	13.1	37.6	55.4	62.2	61.9	63.9	61.3	48.7	45.7	31.5	18.8	6.5	0.6
9th	0.6	5.5	9.1	18.3	15.8	25.5	52.3	71.2	68.3	64.2	54.2	37.4	28.8	17.8	6.2	0.6
10th	0.5	3.1	8.9	19.8	35.3	57.6	68.8	73.8	73.4	68.9	60.5	47.8	33.1	18.6	6.8	0.5
11th	0.4	3.8	8.6	14.4	19.8	24.8	38.6	35.2	77.8	68.7	63.1	48.7	34.5	20.1	6.8	0.4
12th	0.6	5.8	14.5	38.6	43.3	55.8	63.8	65.4	76.1	57.8	42.7	34.9	38.3	18.3	7.8	0.5
13th	0.5	6.6	28.8	35.8	48.4	52.8	73.7	63.9	72.1	61.9	68.7	47.6	32.4	18.1	5.3	0.4
14th	0.5	5.9	18.8	31.5	48.9	61.7	78.8	74.1	69.3	58.9	45.4	33.3	33.4	17.1	5.2	0.3
15th	0.4	5.9	18.1	32.4	47.8	61.3	78.8	68.7	56.8	47.7	38.8	33.9	28.3	14.3	4.6	0.3
16th	0.3	5.8	18.1	32.8	39.3	35.8	56.2	55.8	48.6	33.7	36.6	25.5	18.7	6.2	2.7	0.2
17th	0.2	2.3	8.8	14.9	22.9	24.9	34.2	37.4	25.9	44.3	48.2	35.5	22.7	8.7	2.7	0.1
18th	0.3	5.2	18.4	33.4	48.6	61.8	62.5	74.8	84.4	71.8	38.2	41.3	28.6	15.8	3.2	0.1
19th	0.3	4.8	13.9	28.5	42.8	55.1	63.6	68.8	68.8	63.1	53.8	48.5	27.2	12.6	2.9	0.1

[a] Chart copied directly from report.

Table 3. [^{14}C]PP321 and its degradates (% of applied) in aqueous solutions (pH 5) treated with [^{14}C]PP321 at 0.105 µg ai/ml and irradiated with natural sunlight for thirty days.

Sample	PP321 and its isomers	Ia[a]	Ib[b]	II[c]	Unidentified soluble degradates
A[d]	66.7	5.2	3.0	1.8	9.2[e]
B[d]	43.5	8.6	9.8	5.7	16.5[f]
Dark control	100[g]	ND[h]	ND	ND	ND

[a] Ia: (1RS)-cis-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[b] Ib: (1RS)-trans-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[c] II: (RS)-α-amido-3-phenoxybenzyl-(1RS)-cis,trans-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

[d] At day 30, flask B was obviously contaminated.

[e] At least 5 degradates, each <2.1% of the applied.

[f] At least 4 degradates, each <4.2% of the applied.

[g] Percent of recovered; % of applied was not reported.

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

CASE GS -- PP321 STUDY 12 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Curl, E.A., J.P. Leahey, and S. Lloyd. 1984. PP321: Photodegradation on a soil surface. RJ 0358B. ICI Americas Inc., Wilmington, DE. Reference 3J.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Photodegradation on Soil

This study is scientifically invalid because the sampling protocol was inadequate, the material balance was inadequate, and the data were too variable (artificial light only) to accurately assess the decline of PP321 in soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the temperature was outside the range of normal conditions (artificial light-irradiated soil), no precautions were taken to minimize loss of the test substance by volatilization, and differences in photolysis rates between artificial light and sunlight irradiated samples were not adequately explained. A photolysis half-life could not be estimated.

MATERIALS AND METHODS:

Cyclopropane-labeled [^{14}C]PP321 (radiochemical purity 98%, specific activity 1.93 GBq/mM) was applied at ~22 g ai/ha to the surface of sandy loam soil (17.1% coarse sand, 41.4% fine sand, 14.0% silt, 27.5% clay, 4.39% organic matter, pH 6.4, CEC 16.2 meq/100 g) TLC plates (0.5 mm thickness). Several of the plates were wrapped in foil to serve as dark controls. Sixteen plates (8 uncovered and 8 dark controls) were irradiated with a xenon arc lamp (Ushio UXL-1600, Figure 1) filtered through borosilicate glass. The plates were sampled after 2, 5, 7, and 10 days

of irradiation. An additional four plates (2 uncovered and 2 dark control) were placed outdoors in sunlight for 30 days (Tables 1 and 2). All plates were stored at -15 ± 5°C until analysis.

The soil was scraped from the plates and shaken with acetonitrile for 10 minutes. The supernatant was removed and the soil extracted with acetonitrile two additional times; all three extracts were combined. The soil (except for the time 0 sample) was then extracted three times with aqueous acetonitrile (1:1). The extracted soil was analyzed for nonextractable radioactivity using LSC following combustion. The acetonitrile and aqueous acetonitrile extracts were analyzed for [^{14}C]residues using TLC and HPLC. The TLC was conducted on silica gel plates developed in either hexane:diethyl ether (7:3) or cyclohexane saturated with formic acid:diethyl ether (3:2); radioactive areas were located and quantified using a TLC Linear Analyzer. Autoradiograms of the plates were also prepared.

Also, aliquots of the acetonitrile and aqueous acetonitrile extracts were extracted four times with hexane. The hexane extracts were concentrated and analyzed using normal and reverse phase HPLC to separate isomeric forms.

REPORTED RESULTS:

[^{14}C]PP321 degraded with a half-life of <2 days when irradiated with xenon arc light at 38°C and <30 days when irradiated with natural sunlight at <30°C (Table 3). The [^{14}C]PP321 in the dark controls for the artificial and sunlight irradiated samples degraded with half-lives of 5-10 and ~30 days, respectively. Two major degradates, (1RS)-cis-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (Ia) and (RS)-α-amido-3-phenoxybenzyl-(1RS)-cis,trans-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (II), were isolated from irradiated and dark control soils; up to six minor degradates, each <9% of the applied radioactivity, were isolated but not identified. Isomerization was minor during irradiation.

DISCUSSION:

1. The sunlight-irradiated soil was sampled only on day 30; one sample does not accurately establish a pattern of decline.

2. The material balance for the sunlight-irradiated soil failed to account for ~21% of the applied radioactivity; the material balance for the artificial light-irradiated soil failed to account for 10-28% of the applied.

3. The xenon arc light-irradiated soil was kept at 38°C, which is outside the range of normal environmental temperatures.

4. The data for the xenon arc light-irradiated soil is too variable to draw conclusions, except that the half-life appears to be less than 2 days. A pattern of decline was not established.

5. Volatilization was not measured or controlled; the forced air cooling system would probably have increased volatilization.

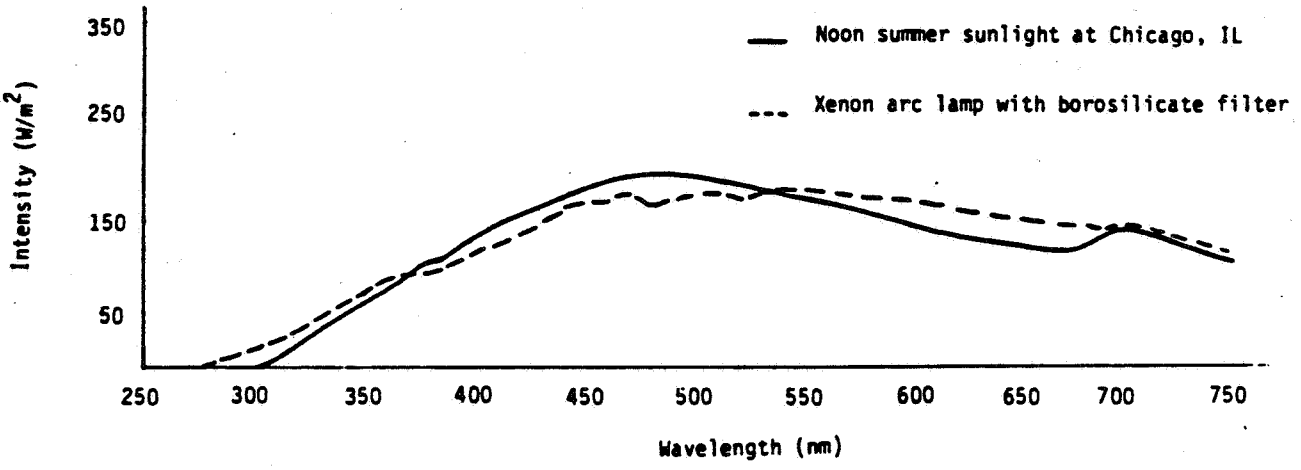

Figure 1. Spectral distribution of the xenon arc lamp light and sunlight (graph adapted from registrant-supplied data).

Table 1. Meteorological data.[a]

Date (1983)	Hours of sun	Maximum temperature °C	Minimum temperature °C
27th July	6.9	26.5	14.2
28st	9.1	25.8	15.7
29nd	13.0	30.1	12.0
30th	10.9	28.9	14.2
31th	0.9	26.1	13.8
1st August	4.4	19.0	13.2
2nd	6.1	17.4	6.8
3rd	13.5	21.5	3.3
4th	5.0	22.9	6.6
5th	11.7	23.5	9.6
6th	6.2	20.7	14.2
7th	6.5	21.9	8.0
8th	9.6	25.1	13.1
9th	7.9	27.1	14.6
10th	10.1	24.6	14.8
11th	6.5	21.7	10.1
12th	9.7	24.7	9.0
13th	12.0	23.1	7.7
14th	12.1	27.9	9.8
15th	11.8	26.6	14.3
16th	7.2	23.9	12.8
17th	3.6	24.9	17.2
18th	12.0	25.9	8.9
19th	10.6	29.6	13.0
20th	4.5	23.1	17.3
21st	5.4	22.0	13.7
22nd	3.6	24.1	16.3
23rd	6.3	25.1	12.5
24th	0.1	21.0	13.8
25th	reading missing	reading missing	9.1
26th	8.7	25.4	14.2

[a] Site located at Jealott's Hill, Berkshire, England: latitude 51°23'N and longitude 0°47'W.

Table 2. Intensity (mW-hr/cm^2) of incident sunlight during the study.[a]

Date	Hourly Totals															
	04-05	05-06	06-07	07-08	08-09	09-10	10-11	11-12	12-13	13-14	14-15	15-16	16-17	17-18	18-19	19-20
27th July 1983	1.2	6.7	18.3	32.0	45.7	61.4	51.8	63.5	59.6	62.8	68.8	60.6	39.6	19.4	7.8	1.5
28th	0.8	4.7	8.0	13.9	35.4	55.6	79.4	83.9	82.2	74.8	69.7	54.8	38.5	14.3	8.5	1.3
29th	1.6	8.8	26.3	38.9	52.6	64.4	76.9	77.9	81.1	76.2	67.6	54.7	36.5	21.8	9.1	1.4
30th	1.8	8.4	25.5	36.9	46.6	67.3	72.1	79.5	79.7	75.1	64.4	51.4	36.2	21.8	8.4	0.9
31st	1.7	6.3	11.7	14.8	24.3	17.8	35.2	37.5	21.8	8.5	10.5	4.8	18.8	17.9	8.4	0.9
1st August 1983	0.1	0.9	4.2	8.2	26.6	26.4	48.3	68.8	18.8	32.8	41.7	27.3	13.6	9.9	3.6	0.1
2nd	0.8	5.3	10.8	16.4	26.4	47.5	57.8	48.7	45.3	34.8	44.5	31.6	28.2	14.6	11.4	1.6
3rd	1.5	10.2	25.4	40.3	54.9	67.2	78.1	84.3	83.3	66.6	66.1	46.8	36.4	21.7	8.1	1.8
4th	0.8	5.2	21.8	38.8	48.5	33.6	51.2	38.5	36.6	42.2	41.8	38.4	31.6	18.8	9.3	1.3
5th	1.1	9.3	23.8	38.7	48.6	38.5	47.8	63.4	64.8	78.5	61.8	52.5	37.7	22.5	7.1	0.8
6th	0.6	9.3	21.9	36.3	48.9	28.8	41.8	42.8	57.2	37.5	19.1	13.2	14.7	13.4	6.7	0.8
7th	0.9	5.4	18.4	31.9	31.7	33.3	43.4	63.1	78.1	67.4	42.8	32.5	28.8	16.8	5.9	0.9
8th	0.6	3.6	7.3	13.1	37.6	35.4	62.2	61.9	63.9	61.3	48.7	45.7	31.5	18.8	6.5	0.6
9th	0.6	5.5	9.1	18.3	15.8	25.5	32.3	71.2	68.3	64.2	54.2	37.4	28.8	17.8	6.2	0.6
10th	0.5	3.1	8.9	19.8	35.3	57.6	68.8	73.8	73.4	68.9	60.5	47.8	33.1	18.6	6.8	0.5
11th	0.4	3.8	8.6	14.4	19.8	24.8	38.6	35.2	77.8	68.7	63.1	48.7	34.5	20.1	6.8	0.4
12th	0.6	5.8	14.5	38.6	43.3	35.8	63.8	65.4	76.1	57.8	42.7	34.9	38.3	18.3	7.8	0.5
13th	0.5	6.6	28.8	35.8	48.4	32.8	73.7	63.9	72.1	61.9	68.7	47.6	32.4	18.1	5.3	0.4
14th	0.5	5.9	18.8	31.5	48.9	61.7	78.8	74.1	68.3	38.9	45.4	33.3	33.4	17.1	5.2	0.3
15th	0.4	5.9	18.1	32.4	47.8	61.3	78.8	68.7	56.8	47.7	38.8	33.9	28.3	14.3	4.6	0.3
16th	0.3	5.8	18.1	32.8	39.3	35.8	36.2	35.8	48.6	53.7	36.6	25.5	18.7	6.2	2.7	0.2
17th	0.2	2.3	8.8	14.9	22.9	24.9	34.2	37.4	25.9	44.3	48.2	35.5	22.7	8.7	2.7	0.1
18th	0.3	5.2	18.4	33.4	48.6	61.8	62.5	74.8	84.4	71.8	58.2	41.3	28.6	15.8	3.2	0.1
19th	0.3	4.8	13.9	28.5	42.8	38.1	63.6	68.8	68.8	63.1	53.8	40.5	27.2	12.6	2.9	0.1
20th	0.3	2.9	13.8	16.7	24.1	12.6	18.3	31.8	21.3	28.2	32.3	28.9	26.4	17.8	5.9	0.2
21st	0.1	4.4	16.5	31.8	28.8	58.2	54.8	26.8	27.7	28.8	28.8	27.5	14.9	18.1	2.7	0.1
22nd	0.1	1.9	7.5	18.1	25.1	22.3	29.8	48.2	46.8	32.5	14.7	13.6	12.6	2.4	1.5	0.8
23rd	0.1	2.6	9.7	11.3	28.7	28.1	45.4	48.8	68.6	57.8	61.5	46.4	38.5	9.7	0.9	0.8
24th	0.1	1.7	4.8	18.7	11.8	11.7	18.8	16.8	18.6	28.1	27.6	26.3	16.4	7.8	1.8	0.8
25th	0.1	4.6	11.5	13.8	•	•	•	•	•	•	•	•	•	•	•	•
26th		8.8	3.3	8.7	29.3	47.1	68.7	66.8	67.8	61.8	48.7	28.8	28.9	18.4	2.1	

[a] Legibility of original chart is, poor, so July 27 - August 19th data are copied from the photodegradation in water study conducted at the same site on approximately the same dates.

Table 3. [^{14}C]PP321 and its degradates (% of applied) on sandy loam soil TLC plates irradiated with xenon arc light at 38°C or natural sunlight at <30°C.

Sample	Sampling interval (days)	PP321 and its isomers	Ia[a]	II[b]	Unidentified soluble degradates[c]	Un-extractable	Total [^{14}C][d]
Pre-exposure	0	93.0	1.0	--	--	0.4	97.8
			Xenon arc light				
Irradiated	2	21.3	10.9	16.5	26.9	9.0	90.5
	5	9.6	9.7	--	--	6.0	72.1
	7	15.2	6.9	--	--	12.2	89.2
	10	9.3	9.1	12.2	28.7	12.2	73.3
Dark control	2	78.3	3.3	14.6	7.3	1.1	104.9
	5	42.0	5.5	--	--	5.1	94.6
	7	62.8	6.8	--	--	2.9	107.4
	10	48.4	8.7	23.9	ND[e]	4.6	100.3
			Sunlight				
Irradiated	30	36.6	7.2	18.8	12.1	7.8	79.2
Dark control	30	53.8	2.4	30.2	10.5	1.6	89.1

[a] Ia: (1RS)-cis-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[b] II: (RS)-α-amido-3-phenoxybenzyl-(1RS)-cis,trans-3-(ZE-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

[c] Up to six degradates, each comprising <9% of the applied radioactivity.

[d] From LSC of soil before extraction.

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

CASE GS -- PP321 STUDY 13 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC)

FICHE/MASTER ID None CONTENT CAT 01

Ussary, J.P. 1985. PP321 Dissipation in U.S. soils-1983. TMU 1809. ICI Americas Inc., Wilmington, DE. Reference 11J.

SUBST. CLASS = S.

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

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TITLE: Chemist
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SIGNATURE: DATE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid.

2. PP321 (1 lb/gal EC) dissipated with a half-life of 14-28 days in sandy loam soils in North Carolina and California and 28-60 days in silt loam soil in Mississippi and silty clay loam soil in Illinois. PP321 was <0.01 ppm in the 6- to 12-inch soil depth at all sites at all sampling intervals. R157836, the opposite enantiomer pair formed by epimerization, was <0.03 ppm in the 0- to 6-inch soil depth and was not detected (<0.01 ppm) in the 6- to 12-inch depth at all sites.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because no analyses were made for degradation products.

MATERIALS AND METHODS:

PP321 (Karate, 1 lb/gal EC) was sprayed at 1.0 lb ai/A onto field plots located in Goldsboro, NC (application date 5/27/83); Vicksburg, MS (6/14/83); Champaign, IL (5/15/83); and Visalia, CA (5/03/83) (Table 1). Forty soil samples (1 inch diameter; 0- to 6- and 6- to 12-inch depths) were collected at each site at intervals up to 188 days posttreatment (Table 2). Samples were kept frozen until analysis.

The soil samples were analyzed for PP321 and its opposite enantiomer pair formed by epimerization, R157836, using ICI Analytical Method No. 70. The soils were extracted by ultrasonification with 50% acetone:hexane. The organic and aqueous phases were allowed to separate and the organic phase was decanted. The soil and aqueous phase were reextracted with 80% acetone:hexane. The organic extracts were combined, washed with 10% sodium chloride, and filtered through an activated Florisil column. The column eluate was analyzed using GLC with electron-capture detection. The detection limit for both PP321 and R157836 was 0.01 ppm. Recovery from forty-seven fortified (~0.006-7.2 ppm) soil samples averaged 97.5 ± 16.2% for PP321 and 98.3 ± 15.7% for R157836.

REPORTED RESULTS:

PP321 dissipated with a half-life of 14-28 days in soil located in North Carolina and California, and 28-60 days in Mississippi and Illinois (Table 2). Soil type rather than rainfall or soil temperature appeared to have the dominant influence on dissipation; both North Carolina and California sites had sandy loam soil, while Mississippi and Illinois had "heavier" soils (silt loam and silty clay loam, respectively). PP321 was not detected (<0.01 ppm) in the 6- to 12-inch soil depth at the North Carolina, Mississippi, and Illinois sites, and was <0.01 ppm in the soil at the California site.

R157836 was not detected in the 0- to 6-inch soil depth at the North Carolina site, and was <0.02 ppm at Mississippi, <0.02 ppm at Illinois, and <0.03 ppm at California. R157836 was not detected in the 6- to 12-inch depth at any site.

DISCUSSION:

1. From the data provided, it appeared (but was not stated) that the soils were not cropped. This would explain why the California field data was not accompanied with irrigation information.

2. No analyses were made for degradation products.

3. The application rate was about three times the maximum recommended per season.

Table 1. Soil and site characteristics.

Soil type	Location	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)	Slope (%)	Water table (feet)	Plot size (feet)
		%								
Sandy loam	Goldshoro, NC	67	29	4	2.0	6.0	2.4	<1	5	40 x 50
Silt loam	Vicksburg, MS	14	72	14	1.2	7.0	7.4	<1	9	25 x 50
Silty clay loam	Champaign, IL	17	51	32	3.9	7.9	39.6	<1	5	40 x 50
Sandy loam	Visalia, CA	51	38	11	0.8	7.6	8.0	<1	30	35 x 50

Table 2. PP321 (ppm) in soil at four locations in the U.S. treated with PP321 (1 lb/gal EC) at 1.0 lb ai/A in May/June, 1983.

Sampling interval (days)	Sampling depth (inches) 0-6	6-12	Cumulative rainfall (inches)	Soil temperature at 2 inch depth (°F)
		Goldsboro, NC		
0	0.31	ND[a]	--	--
7	0.41	ND	0.29	64-83
14	0.13	ND	2.98	68-83
21	0.19	ND	2.98	67-91
28	0.15	ND	5.55	70-90
63	0.09	ND	10.05	72-97
90	0.04	ND	10.32	75-99
126	0.02	ND	13.69	58-97
173	0.02	ND	17.72	44-83
		Vicksburg, MS		
0	0.24	ND	--	--
9	0.18	ND	5.19	67-84
15	0.20	ND	7.30	70-85
22	0.21	ND	7.37	72-88
29	0.13	ND	7.56	69-88
59	0.04	ND	9.25	69-88
91	ND	ND	10.35	71-87
121	ND	ND	12.12	56-80
188	ND	ND	24.27	36-72
		Champaign, IL		
0	0.18	ND	--	--
11	0.29	ND	0.00	43-84
14	0.20	ND	0.90	52-76
20	0.20	ND	1.03	48-79
28	0.22	ND	1.18	52-94
60	0.09	ND	5.95	64-105
87	0.03	ND	7.21	67-107
122	0.02	ND	9.25	58-92
179	0.01	ND	16.31	--
		Visalia, CA		
0	0.27	0.01	--	--
7	0.17	0.01	0.00	56-89
14	0.18	ND	0.00	61-91
21	0.15	ND	0.00	64-109
28	0.11	ND	0.00	71-112
59	0.03	ND	0.00	67-112
90	0.01	ND	0.00	69-114
120	ND	ND	0.01	73-114
181	ND	ND	0.74	57-96

a Not detected; detection limit was 0.01 ppm.

CASE GS -- PP321 STUDY 14 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC)

FICHE/MASTER ID None CONTENT CAT 01
Rapley, J.H., D.J. Arnold, and J. Vincent. 1981. Cypermethrin: Degradation in river and pond water and sediments. RJ 0175B. ICI Americas Inc., Wilmington, DE. Reference 7J.

FICHE/MASTER ID None CONTENT CAT 01
Rapley, J.H., D.J. Arnold, J. Vincent, and D. Moore. 1980. Cypermethrin: Degradation in river water and sediments. RJ 0119B. ICI Americas Inc., Wilmington, DE. Reference 6J.

SUBST. CLASS = S.

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

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Reference 6J is an interim report and reference 7J is the final report on the same aquatic metabolism study. Therefore, the reports were combined for this review.

CONCLUSIONS:

Metabolism - Anaerobic Aquatic

This portion of the study is scientifically invalid because the methods were inadequate to accurately assess the decline of cypermethrin in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because degradates were not adequately characterized, and samples were incubated at 16°C (below the recommended range).

Metabolism - Aerobic Aquatic

This portion of the study is scientifically invalid because the methods were inadequate to accurately assess the decline of cypermethrin in soil.

In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because degradates were not adequately characterized.

MATERIALS AND METHODS:

Sediments (Table 1) from rivers and ponds in England were added to pyrex glass cylinders (5 cm diameter) to a depth of 5 cm and flooded with river water (~pH 8.1) for a total depth of 15 cm. Benzene ring-labeled [^{14}C]cypermethrin (98% pure, specific activity 52.8 mCi/mM, 55:45 cis:trans isomers) was applied at ~0.14 kg ai/ha to the water. The cylinders were sealed with two-hole rubber stoppers. In half the flasks, glass tubing was extended through the stopper to just above the sediment surface and the water was aerated with CO_2-free air at ~0.1 liter/minute (Figure 1). In the remaining flasks, the glass tubing ended above the water surface. Effluent air was passed through two tubes of ethanolamine to collect volatiles. The incubation cylinders were kept in the dark at 16 ± 1°C throughout the study. Entire sediment:water systems were sampled 0, 2, 5, 12, 26, and 63 weeks posttreatment. The trapping solutions were sampled weekly.

Aliquots of all samples were analyzed for total radioactivity using LSC. The sediment and water phases were separated by filtering. The sediment was extracted by refluxing for 18 hours in methanol:water (50:50). The extract was removed and the sediment further extracted by refluxing for 18 hours in hexane:acetone (60:40). Radioactivity in the extracts was quantified using LSC. Radioactivity in the extracted soil was quantified using LSC following combustion. The sediment extracts and the water were analyzed by TLC on silica gel plates developed in toluene:diethyl ether:acetic acid (75:25:1) and petroleum spirit (80-100°):acetone:acetic acid (70:30:1). The plates were autoradiographed and radioactive compounds were identified by comparison to standards; radioactive compounds were scraped from the plates and quantified using LSC. Identity of some degradates was confirmed using GC coupled with MS. Radioactivity in the trapping solutions was quantified using LSC.

REPORTED RESULTS:

Metabolism - Anaerobic Aquatic

Total radioactivity in the samples decreased from 100 to 70-86% of the applied during the 26-week study (Table 2). Up to 32% of the recovered [^{14}C]residues adhered to the incubation flask.

[^{14}C]Cypermethrin degraded with a half-life of <2 weeks under anaerobic aquatic conditions (Table 3). The major degradate was $^{14}CO_2$ (47-63% of recovered by week 26); 3-phenoxybenzaldehyde (III), 3-phenoxybenzoic acid (IV), and 4'-hydroxy-3-phenoxybenzoic acid (VI) were the nonvolatile degradates identified.

Metabolism - Aerobic Aquatic

Total radioactivity in the samples decreased from 100 to 80-87% of the applied during the 26-week study (Table 2). Up to 12.2% of the recovered [^{14}C]residues adhered to the incubation flask.

[^{14}C]Cypermethrin degraded with a half-life of <2 weeks under aerobic aquatic conditions (Table 4). The major degradate was $^{14}CO_2$ (46-74% of the recovered by week 26); 3-phenoxybenzaldehyde (III), 3-phenoxybenzoic acid (IV), and 4'-hydroxy-3-phenoxybenzoic acid (VI) were the nonvolatile degradates identified.

DISCUSSION:

General

1. Up to ~50% of the [^{14}C]residues on the TLC plates (soil plus water data) were not characterized. The location of these residues on the plates was not reported, so it was uncertain if these were unidentified compounds that migrated or compounds that remained at the origin.

2. Identification of [^{14}C]residues in the ethanolamine was indirect and unsatisfactory. Sodium hydroxide was used as the trapping solution for one soil for 6 weeks. Total radioactivity in this solution was compared to total radioactivity in an ethanolamine solution attached to a duplicate sample. Since total [^{14}C]residues were similar in the sodium hydroxide and the ethanolamine, and since all [^{14}C]residues in the sodium hydroxide proved to be $^{14}CO_2$, it was assumed that all [^{14}C]residues in all ethanolamine solutions were $^{14}CO_2$.

3. From the data, it appears that cypermethrin (up to 28.9% of recovered) adsorbed to the incubation flask wall and was "protected" from degradation.

4. Incubation temperatures were only 16°C.

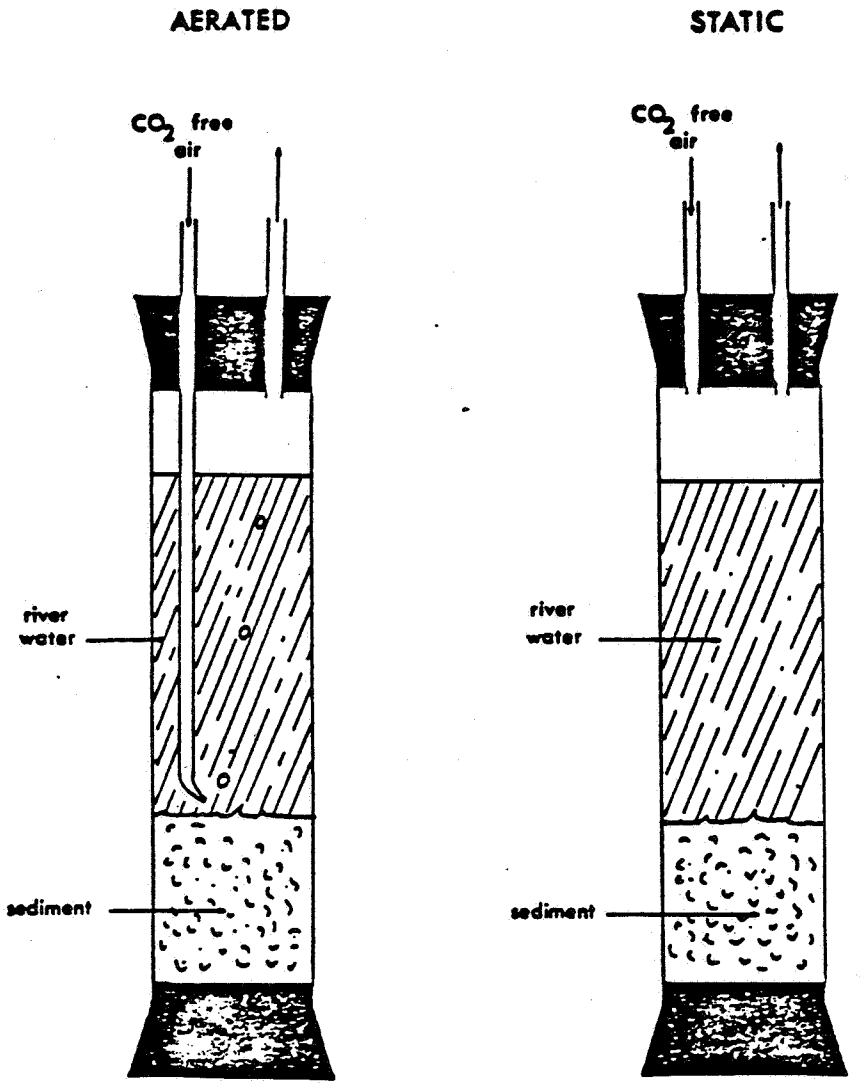


Figure 1. Incubation flasks used in the study.

Table 1. Soil characteristics.

Soil texture[a]	Coarse sand	Fine sand	Silt	Clay	Organic matter
			%		
Loamy coarse sand	53.6	33.7	7.6	5.1	3.0
Sandy loam	24.2	39.7	15.4	20.6	5.0
Coarse sand	78.1	14.4	5.0	2.5	1.2
Silty clay loam	6.6	22.1	26.7	44.6	21.6

[a] The soil was classified according to the New Jersey ADAS scale: coarse sand, 0.2-2 mm; 0.02-0.2 mm, fine sand; 0.002-0.02 mm, silt; <0.002 mm, clay.

Table 2. Total [^{14}C]residues (% of applied) in aerobic and anaerobic sediment:water systems treated with benzene ring-labeled [^{14}C]-cypermethrin at ~0.14 kg ai/ha.

		Sampling interval (weeks)					
		0	2	5	12	26	63
Aerobic	Loamy coarse sand	105.3	91.5	92.2	85.8	79.3	71.1
	Sandy loam	104.7	94.2	84.1	90.6	87.7	--
	Coarse sand	102.9	85.5	94.5	76.2	81.3	--
Anaerobic	Loamy coarse sand	100.0	88.5	87.7	71.5	70.6	--
	Sandy loam	104.1	95.0	81.7	87.4	86.2	--
	Silty clay loam	104.4	87.9	85.8	71.2	80.1	--

Table 3. [^{14}C]Cypermethrin and its degradates (% of recovered) in anaerobic sediment:water systems treated with benzene ring-labeled [^{14}C]-cypermethrin (98% pure) at ~0.14 kg ai/ha.

Sample fraction	[^{14}C]Compound	Sampling interval (weeks) 0	2	5	12	26
		Loamy coarse sand				
Sediment	Cypermethrin	--	4.6	2.5	6.8	0.7
	III	--	28.5	16.5	8.4	10.3
	IV	--	2.7	5.5	1.7	2.0
	VI	--	--	0.5	--	--
	Uncharacterized[a]	--	11.2	10.2	12.4	11.3
Water	Cypermethrin	69.6	3.9	1.4	--	--
	IV	--	11.9	11.3	--	--
	Uncharacterized[a]	6.4	8.3	16.9	8.3	3.1
Flask wall wash[b]	Cypermethrin	--	10.8	--	--	--
	Uncharacterized	2.4	1.0	4.0	1.1	0.3
$^{14}CO_2$		--	8.7	20.6	35.8	47.3
Unextractable		0.8	8.4	10.6	22.1	21.8
		Sandy loam				
Sediment	Cypermethrin	0.1	2.8	1.8	<0.1	0.4
	III	6.4	17.3	18.1	0.1	2.7
	IV	--	3.9	3.5	1.1	0.4
	VI	0.1	0.7	1.7	0.3	--
	Uncharacterized[a]	4.3	4.7	11.2	16.1	10.8
Water	Cypermethrin	74.1	3.8	0.5	--	--
	IV	--	20.8	5.6	--	--
	Uncharacterized[a]	9.1	23.5	30.1	14.4	9.9
Flask wall wash[b]	Cypermethrin	5.1	12.1	--	12.2	--
	Uncharacterized	0.4	1.1	3.7	0.8	0.5
$^{14}CO_2$		--	4.6	11.4	39.5	63.8
Unextractable		0.4	4.7	12.4	14.2	11.5
		Silty clay loam				
Sediment	Cypermethrin	0.1	5.4	2.4	2.1	0.4
	III	11.4	12.1	15.3	4.7	2.9
	IV	0.2	1.8	5.1	1.2	0.9
	VI	--	0.7	0.9	0.4	--
	Uncharacterized[a]	6.8	5.8	7.8	20.4	11.3
Water	Cypermethrin	66.8	7.0	7.8	--	--
	IV	--	8.4	18.8	--	--
	Uncharacterized[a]	8.9	21.0	11.1	7.7	9.4
Flask wall wash[b]	Cypermethrin	4.6	28.9	12.9	--	--
	Uncharacterized	0.3	3.2	4.3	7.9	1.5
$^{14}CO_2$		--	1.6	8.6	44.2	62.9
Unextractable		0.9	4.1	5.0	11.4	10.7

[a] Includes radioactivity in hexane:acetone extract, radioactivity on TLC plate, and radioactivity "lost" during analysis.

[b] [^{14}C]Residues that adhered to the incubation flask walls.

Table 4. [^{14}C]Cypermethrin and its degradates (% of recovered) in aerobic sediment:water systems treated with benzene ring-labeled [^{14}C]-cypermethrin (98% pure) at ~0.14 kg ai/ha.

Sample fraction	[^{14}C]Compound	Sampling interval (weeks) 0	2	5	12	26	63
		Loamy coarse sand					
Sediment	Cypermethrin	3.5	11.2	3.7	5.1	1.3	0.9
	III	5.3	6.0	17.9	12.7	13.5	4.1
	IV	<0.1	8.6	0.7	1.9	2.8	1.2
	VI	--	--	--	1.1	0.7	--
	Uncharacterized[a]	12.8	32.3	29.4	11.5	12.0	7.5
Water	Cypermethrin	57.2	2.3	0.8	--	--	--
	IV	--	4.2	0.2	--	--	--
	Uncharacterized[a]	17.3	10.7	7.4	1.6	0.5	1.4
Flask wall wash[b]	Cypermethrin	--	11.0	--	--	--	--
	Uncharacterized	3.3	1.2	0.5	0.7	0.5	0.3
$^{14}CO_2$		--	4.7	18.2	34.6	46.2	60.3
Unextractable		0.8	7.8	21.2	30.8	22.7	24.3
		Sandy loam					
Sediment	Cypermethrin	0.6	5.6	5.7	1.0	6.3	--
	III	1.1	6.6	16.8	17.4	10.1	--
	IV	0.8	7.1	0.4	0.8	0.7	--
	VI	0.3	0.7	0.1	0.9	0.3	--
	Uncharacterized[a]	8.2	40.4	19.6	14.6	5.6	--
Water	Cypermethrin	66.9	3.9	--	--	--	--
	IV	--	6.9	--	--	--	--
	Uncharacterized[a]	19.5	14.1	16.6	11.5	3.5	--
Flask wall wash[b]		2.4	3.0	2.2	0.4	0.3	--
$^{14}CO_2$		--	4.2	15.9	40.3	56.6	--
Unextractable		0.2	7.5	22.7	13.1	16.6	--
		Coarse sand					
Sediment	Cypermethrin	3.3	4.7	5.2	0.3	--	--
	III	1.4	13.6	24.9	9.3	--	--
	IV	5.8	9.5	0.9	0.9	--	--
	VI	--	1.7	<0.1	1.2	--	--
	Uncharacterized[a]	6.8	23.9	23.5	13.5	8.4	--
Water	Cypermethrin	56.9	1.1	<0.1	--	--	--
	IV	--	21.1	10.6	--	--	--
	Uncharacterized[a]	21.0	12.1	7.7	8.3	4.4	--
Flask wall wash[b]		5.0	1.0	<0.3	<0.3	1.0	--
$^{14}CO_2$		--	2.4	9.5	55.5	73.7	--
Unextractable		0.3	8.9	17.7	11.0	8.1	--

[a] Includes radioactivity in hexane:acetone extract, radioactivity on TLC plate, and radioactivity "lost" during analysis.

[b] [^{14}C]Residues that adhered to the incubation flask walls.

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).

PP321 (1 lb/gal EC) dissipated with a half-life of 14-28 days in sandy loam soils in North Carolina and California and 28-60 days in silt loam soil in Mississippi and silty clay loam soil in Illinois (Ussary, 1985). PP321 was <0.01 ppm in the 6- to 12-inch soil depth at all sites at all sampling intervals. R157836, the opposite enantiomer pair formed by epimerization, was <0.03 ppm in the 0- to 6-inch soil depth and was not detected (<0.01 ppm) in the 6- to 12-inch depth at all sites.

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 relevant to full registration requirements (Subdivision N) is summarized below.

Hydrolysis studies: One study (Collis and Leahey, 1984) was reviewed and is scientifically invalid because the test material was used at a rate exceeding its water solubility. In addition, this study would not fulfill data requirements because no information was provided on the alcohol moiety. All data (both cyclopropane and alcohol moieties) are required.

Photodegradation studies in water: One study (Curl et al., 1984a) was reviewed and is scientifically invalid because the test material was used at a rate exceeding its water solubility. In addition, this study would not fulfill data requirements because the solutions may not have been sterile throughout the study, no material balance was provided for the dark control, and a photolysis half-life could not be estimated. All data are required.

Photodegradation studies on soil: One study (Curl et al., 1984b) was reviewed and is scientifically invalid because the sampling protocol was inadequate (artificial light- and sunlight-irradiated soil), the material balance was inadequate (artificial light- and sunlight-irradiated soil), and the data were too variable (artificial light-irradiated soil) to accurately assess the decline of PP321 in soil. In addition, this study would not fulfill data requirements because the temperature was outside the range of normal conditions (artificial light-irradiated soil) and no precautions were taken to minimize loss of the test substance by volatilization. A photolysis half-life could not be estimated. Differences in photolysis rates between artificial and sunlight irradiated samples were not adequately explained. All data are required.

Photodegradation studies in air: No data were submitted, but no data are required because of the low vapor pressure of PP321.

Aerobic soil metabolism studies: One study (Bharti et al., 1985) was reviewed and is scientifically valid. This study partially fulfills data requirements by providing information on the metabolism of the acid moiety of PP321 in a sandy loam soil. A valid study (Harvey et al., 1981) using benzene ring-labeled [^{14}C]cypermethrin provides information on the aerobic metabolism of the alcohol moiety of cypermethrin (which is identical to the alcohol moiety of PP321) in soil. Considered together, these two studies fulfill data requirements for aerobic soil metabolism.

Anaerobic soil metabolism studies: No data were submitted, but all data are required.

Anaerobic aquatic metabolism studies: No PP321 data were submitted. A benzene ring-labeled [^{14}C]cypermethrin study (Rapley et al., 1980, 1981) that was provided was invalid and would not fulfill data requirements. No data are required because PP321 has no aquatic, forestry, or aquatic impact use.

Aerobic aquatic metabolism studies: No PP321 data were submitted. A benzene ring-labeled [^{14}C]cypermethrin study (Rapley et al., 1980, 1981) that was provided was invalid and would not fulfill data requirements. No data are required because PP321 has no aquatic or aquatic impact use.

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.

Laboratory volatility studies: No data were submitted, but no data are required because of the low vapor pressure of PP321.

Field volatility studies: No data were submitted, but no data are required because of the low vapor pressure of PP321.

Terrestrial field dissipation studies: One study (Ussary, 1985) was reviewed that does not fulfill data requirements because no analyses were made for degradation products. All data are required.

Aquatic field dissipation studies: No data were submitted; however, no data are required because PP321 has no registered aquatic food crop, aquatic noncrop, or aquatic impact use.

Forestry dissipation studies: No data were submitted; however, no data are required because PP321 has no forestry use.

Dissipation studies for combination products and tank mix uses: No data were submitted; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were submitted; however, no data are required because more than 50% of the PP321 dissipated prior to the recommended subsequent application of PP321.

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 [^{14}C]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.

Field accumulation studies on rotational crops: No data were submitted; however, the data requirement is deferred pending the receipt of acceptable confined rotational crop accumulation data.

Accumulation studies on irrigated crops: No data were submitted; however, no data are required because PP321 has no aquatic food crop or aquatic noncrop use.

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.

Field accumulation studies on aquatic nontarget organisms: No data were submitted; however, no data are required because PP321 has no forestry, aquatic noncrop, or aquatic impact use.

Reentry studies: No data were submitted, but data are required.

Spray Drift Data Requirements: The Agency is requiring Droplet Spectrum and Spray Drift Field Evaluation tests due to the toxicity of the chemical, its methods of application, and the likely exposure of off-site people and wildlife to the pesticide. The droplet spectrum study is to be performed to reflect the nozzle and other equipment types to be used in the application of PP321 to cotton. The spray drift field evaluation is to be performed to reflect the application equipment, use pattern, and typical locations of use, which includes different weather factors, in the application of PP321 to this crop. The spray drift droplet spectrum and field evaluation may be done together in order to evaluate the droplet spectrums that are associated with actual field use patterns.

The following label statements are required for Karate:

REENTRY

A 24-hour interim reentry restriction is imposed pending the submission and evaluation of adequate data for use on cotton.

ROTATIONAL CROP RESTRICTIONS

Do not rotate any crop except cotton into areas previously treated with Karate.

RESTRICTED USE PESTICIDE

"For retail sale and use by certified applicators or persons under their direct supervision and only for those uses covered by the certified applicator's certification. Applicators must ensure that all persons handling this pesticide under direct supervision are informed of the precautionary statements."

WORK SAFETY RULES

May be fatal if swallowed or inhaled. Do not breathe spray mist. If handled indoors provide mechanical exhaust ventilation.

Keep all unprotected persons, children, livestock, and pets away from treated area or where there is a danger of drift.

Do not rub eyes or mouth with hands. If you feel sick in any way, STOP work and get help right away. See State of Practical Treatment.

HANDLE THE CONCENTRATE ONLY WHEN WEARING THE FOLLOWING PROTECTIVE CLOTHING AND EQUIPMENT.

Wear a protective suit of one or two pieces that covers all parts of the body except the head, hands, and feet. Wear chemical resistant gloves, chemical resistant apron, and chemical resistant shoes, shoe coverings, or boots. Wear goggles or a face shield. Wear a pesticide respirator approved by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part II.

If handling the concentrate with a closed system, long sleeve shirt and long legged pants may be substituted for the protective suit.

WEAR THE FOLLOWING PROTECTIVE CLOTHING AND EQUIPMENT DURING APPLICATION, EQUIPMENT REPAIR, EQUIPMENT CLEANING, DISPOSAL OF THE SPRAY SOLUTION, AND DURING EARLY REENTRY TO TREATED AREAS.

Wear a protective suit of one or two pieces that covers all parts of the body except the head, hands, and feet. Wear chemical resistant gloves and chemical resistant boots, shoes, or shoe coverings. Wear goggles or a faceshield. A helmet with visor is acceptable during application from nonenclosed cockpits. Wear a pesticide respirator approved by the National Institute for Occupational Safety and Health under the provisions of 30 CFR II.

During application only from a tractor with a completely enclosed cab or aerially with an enclosed cockpit, long sleeve shirt and long legged pants may be worn in place of the above protective equipment. Chemical resistant gloves must be available in the cab or cockpit and must be worn while exiting. This clothing is inadequate to protect you during equipment repairs, equipment cleaning, spray solution disposal, or early reentry.

IMPORTANT! Before removing gloves, wash them with soap and water. Always wash hands, face, and arms with soap and water before smoking, eating, drinking, or toileting.

AFTER WORK. Take off all clothes and shoes. Shower using soap and water. Wear only clean clothes. Do not use contaminated clothing or equipment. Wash protective clothing and equipment with soap and water after each use. Respirators must be cleaned and filters replaced according to instructions included with the respirators. Personal clothing worn during use must be laundered separately from household articles. Clothing and protective equipment heavily contaminated or drenched with Karate 1E must be destroyed according to state and local regulations. HEAVILY CONTAMINATED OR DRENCHED CLOTHING CANNOT BE ADEQUATELY DECONTAMINATED.

HUMAN FLAGGERS ARE PROHIBITED UNLESS IN TOTALLY ENCLOSED VEHICLE.

Studies in which cyhalothrin rather than PP321 was the active ingredient were submitted to satisfy several data requirements for the PP321 registration 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 registration must be done with PP321 rather than cyhalothrin. A one-time exception has been made in the case of mobility studies submitted for registration because all radio-labeled 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.

REFERENCES

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.

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.

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.

Curl, E.A., J.P. Leahey, and S.J. Lloyd. 1984a. PP321: Aqueous photolysis at pH 5. RJ 0362B. ICI Americas Inc., Wilmington, DE. Reference 2J.

Curl, E.A., J.P. Leahey, and S. Lloyd. 1984b. PP321: Photodegradation on a soil surface. RJ 0358B. ICI Americas Inc., Wilmington, DE. Reference 3J.

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. Reference 18J.

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.

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 12J.

Rapley, J.H., D.J. Arnold, J. Vincent, and D. Moore. 1980. Cypermethrin: Degradation in river water and sediments. RJ 0119B. ICI Americas Inc., Wilmington, DE. Reference 6J.

Rapley, J.H., D.J. Arnold, and J. Vincent. 1981. Cypermethrin: Degradation in river and pond water and sediments. RJ 0175B. ICI Americas Inc., Wilmington, DE. Reference 7J.

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.

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.

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.

• Ussary, J.P. 1985. PP321 Dissipation in U.S. soils-1983. TMU 1809. ICI Americas Inc., Wilmington, DE. Reference 11J.

• Woods, T.M., D.W. Rewick, and J.P. Leahey. 1980. Cypermethrin: Rotational crop study. RJ 0161B. ICI Americas Inc., Wilmington, DE. Reference 13J.

The following study was not reviewed because the data are not necessary to fulfill mobility data requirements:

Weissler, M. and S.R. Hill. 1980. Cypermethrin: Leaching of formulated cypermethrin in soil columns. ICI Americas Inc., Wilmington, DE. RJ0137B. Acc. No. 073990. Reference 17J.

The following studies were not reviewed because they are literature reviews only:

Ellgehausen, H., J.A. Guth, and H.O. Esser. 1980. Factors determining the bioaccumulation potential of pesticides in the individual compartments of aquatic food chains. Ecotoxicol. Environ. Safety 4:134-157. ICI Americas Inc., Wilmington, DE. Acc. No. 073990. Reference 20J.

Macek, K., S. Petrocelli, and B.H. Sleight III. 1979. Considerations in assessing the potential for, and significance of, biomagnification of chemical residues in aquatic food chains. In Aquatic Toxicology, ASTM STP 667, L.L. Marking and R.A. Kimerle, eds. American Society for Testing and Materials, pp. 251-268. ICI Americas Inc., Wilmington, DE. Acc. No. 073990. Reference 19J.

The following study was not reviewed because it is not pertinent to environmental fate data requirements:

Hall J.S. and J.P. Leahey. 1983. Cyhalothrin: Fate in River Water. ICI Americas Inc., Wilmington, DE. RJ 0320B. Acc. No. 073990. Reference 10J.

The following studies were not reviewed because bioaccumulation studies done using cyhalothrin as the test substance cannot be used to register PP321:

Hammer, M.J. and I.R. Hill. 1985. Cyhalothrin: The accumulation of cyhalothrin and its degradation products by channel catfish and Daphnia magna in a soil/water system. ICI Americas Inc., Wilmington, DE. RJ 0427B. Acc. No. 073990. Reference 16J.

Leahey, J.P. and S. Parker. 1985. Cyhalothrin: Characterization of residues accumulated by carp continuously exposed to ^{14}C-cyhalothrin. ICI Americas Inc., Wilmingon, DE. RJ 0407B. Acc. No. 073990. Reference 15J.

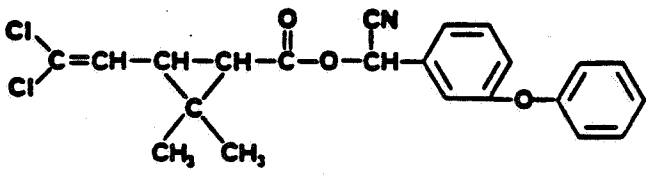
Shigeoka, T. 1984. PP-321 (Cyhalothrin): Accumulation in fish (carp) in a flow-through water system. ICI Americas Inc., Wilmington, DE. Mites Report No. 58-367. Acc. No. 073990. Reference 14J.

The following studies were not reviewed because they contain data on pesticide accumulation in birds only:

Curl, E.A. and S.D. Milner. 1980. Cypermethrin: Accumulation and depletion of radioactive residues in the tissues of mallard duck and bobwhite quail following daily dosing. ICI Americas Inc., Wilmington, DE. RJ 0147B. Acc. No. 073990. Reference 24J.

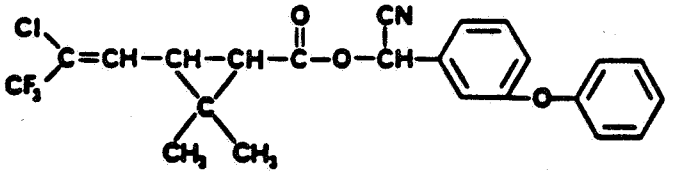
Knight, S.W. and J.P. Leahey. 1984. PP321: Evaluation of the potential for accumulation by quail and mallard. ICI Americas Inc., Wilmington, DE. RJ 0384B. Acc. No. 073990. Reference 23J.

APPENDIX



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

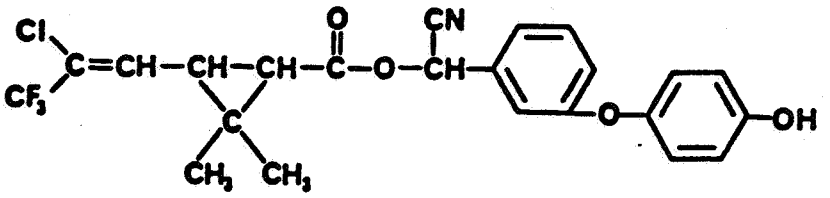
(Cypermethrin)



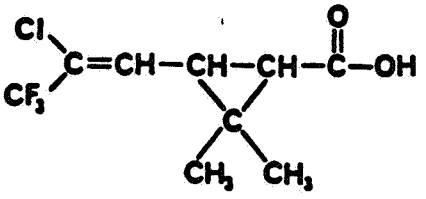
A 1:1 mixture of the enantiomers (S)-α-Cyano-3-phenoxy-benzyl (1R)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate and (R)-α-cyano-3-phenoxy-benzyl (1S)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate

(Karate, PP321)

Figure 1. Cypermethrin and PP321 (Karate).



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

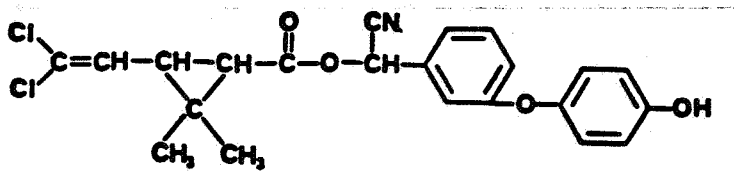


(1RS)-*cis*-3-(Z-2-Chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid

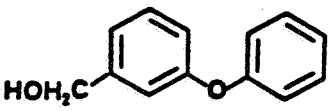
and

(1RS)-*trans*-3-(Z-2-Chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid

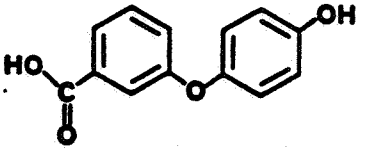
Figure 2. Degradates of PP321.



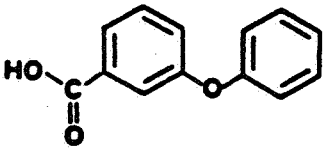
(RS)-a-Cyano-4'-hydroxy-3-phenoxybenzyl,*cis*, *trans*-3-(2, 2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate



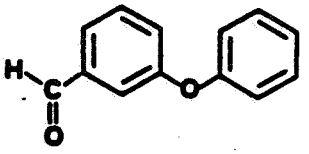
3-Phenoxybenzyl alcohol



4'-Hydroxy-3-phenoxybenzoic acid



3-Phenoxybenzoic acid



3-Phenoxybenzaldehyde

Figure 3. Degradates of cypermethrin.