

US EPA ARCHIVE DOCUMENT

EEB

Shaughnessy No.: 128897

MAR 24 1988

Date Out of EAB:

To: George LaRocca  
Product Manager #15  
Registration Division (TS-767)

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

Thru: Paul F. Shuda, Chief  
Exposure Assessment Branch/HED (TS-769C)

Attached, please find the EAB review of...

Reg./File#: 10182-OA

Chemical Name: PP321

Type Product: Insecticide

Product Name: KARATE

Company Name: ICI Americas Inc.

Purpose: Review of data and supplementary information presented  
by registrant at meeting held on October 15, 1987 to support the  
use of PP321 on cotton. Review of anaerobic soil metabolism study.

Action Code(s): 106

EAB #(s) : 80108

Date Received: 11/17/87

Total Reviewing Time: 9.2 days

Date Completed:

Deferrals to:  Ecological Effects Branch  
 Residue Chemistry Branch  
 Toxicology Branch

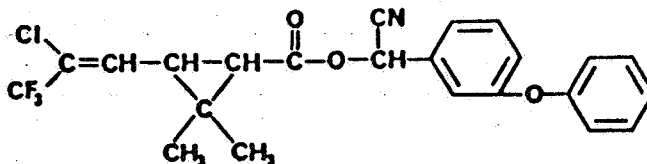
1. CHEMICAL: Common name: None

Chemical name: (+)-alpha-cyano-(3-phenoxyphenyl)methyl(+)-  
cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-  
dimethylcyclopropanecarboxylate.

Trade name(s): Karate, (PP321 is the active ingredient)

Formulations: 1 lb/gal EC

STRUCTURE



2. TEST MATERIAL: <sup>14</sup>C-Cyclopropane labeled PP321.

3. STUDY/ACTION TYPE: Review of supplementary data and information presented by the registrant at a meeting held on October 15, 1987 in support of the registration of PP321 for use on cotton, and review of anaerobic soil metabolism data.

4. STUDY IDENTIFICATION: Registrant's letter and supplementary information dated October 30, 1987. 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

5. REVIEWED BY:

Arthur Schlosser  
Chemist  
EAB/HED/OPP

Signature: Arthur O. Schlosser

Date: March 10, 1988

6. APPROVED BY:

Emil Regelman  
Supervisory Chemist  
Review Section #3, EAB/HED/OPP

Signature: [Signature]

Date: MAR 24 1988

7. CONCLUSIONS: The registrant's response to EAB comments on rotational crop data is acceptable. The requirement for confined rotational crop data is satisfied for currently registered application rates. Studies submitted indicate that significant residues will not be present in

crops rotated 30 days after application of PP321.

The study on fish accumulation is not acceptable because a preferred species of fish was not used. In addition, an explanation is needed for the apparent differences in BCF data reported for PP321 (5000, 4800 and 4600). A final summary table of relevant accumulation data along with calculations would be helpful.

The registrant's responses to EAB comments on leaching and adsorption/desorption are acceptable. This data requirement is considered to be satisfied.

Anaerobic soil metabolism: See attached review. This study was found to be unacceptable as presented because it appears that anaerobic conditions may not have been achieved during the study as required. Also, data on the "alcohol" portion of the test molecule were not submitted or referenced. See attached data review.

Reentry- See memo from Dr. James D. Adams to Ms. Christine Dively of February 25, 1988 (copy attached)

8. RECOMMENDATIONS: The data submitted on confined rotational crops are acceptable. No additional rotational crop data are needed to support current registered application rates. For the development of any future confined rotational crop data at higher rates it is recommended that control plants not be exposed to  $^{14}\text{CO}_2$ , plant residues be chemically identified if feasible and total and net plant residues be tabulated to facilitate review.

The fish accumulation data submitted are not acceptable to EAB because carp was used as the test species instead of bluegill sunfish or channel catfish which are preferred. The registrant should have submitted a protocol for EAB approval before starting the study or requested a waiver for the test species used. However, EAB will defer to EEB and will accept the study if they find that the species used is a satisfactory indicator of bioaccumulation. The registrant should also provide clarification of the apparent inconsistencies in the BCF values reported along with calculations.

The requirement for leaching and adsorption/desorption data is satisfied.

The data submitted for anaerobic soil metabolism are not acceptable as presented. It appears that anaerobic conditions may not have been achieved during the study as required. In addition, data on the "alcohol" portion of the test molecule have not been submitted or specifically referenced. This study may be accepted for the acid moiety if the registrant can demonstrate that anaerobic conditions were present as required or otherwise explain the apparent incon-

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sistency in carbon dioxide evolution observed between this and other studies submitted.

Reentry: See memo from Dr. James D. Adams to Ms. Christine Dively of February 25, 1988 (copy attached).

The following data are still required to support the registration of PP321 on cotton: (1) anaerobic soil metabolism (161-2) or explanation of apparent lack of anaerobic conditions in the study submitted, (2) fish residue accumulation (165-4) conducted according to guidelines and using a preferred fish test species if EEB does not find the present study acceptable.

9. BACKGROUND: A meeting was held on October 15, 1987 between ICI Americas and OPP personnel to discuss comments made in EAB review No. 70233 dated October 17, 1987. At this meeting the registrant addressed EAB's comments, provided explanations of their studies and presented supplementary data to support their position. No decisions as to the acceptability of data under discussion were made at this meeting. The current action is a review of written summaries, comments and supplementary data submitted formally as a follow-up to the meeting.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Rotational Crops Confined

EAB Comment: Additional data are needed on the uptake of the alcohol moiety into rotated crops using benzene ring-radiolabeled PP321 in a confined study.

ICI Response: (See attachment pp 4-6). The registrant states that the alcohol moiety of PP321 is identical to that of cypermethrin and that confined rotational crop data on the alcohol moiety of cypermethrin have been previously accepted by the Agency. In addition, EAB had agreed at a meeting in May 1983 that it was reasonable to reference data on the common moiety in support of PP321.

The cypermethrin study was carried out at an application rate five times that proposed for PP321 on cotton and resulted in maximum residues of 0.02 ppm at a 30 day planting interval.

EAB Response: The confined rotational crop studies are acceptable to support the proposed use on cotton and indicate that significant residues are not taken up at a 30 day planting interval. It is recommended, however, that for any future confined rotational crop studies, control samples should not be exposed to  $^{14}\text{CO}_2$  and plant residues should be chemically identified.

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Laboratory studies of pesticide accumulation in fish

(1) EAB Comment: Use of the term "cyhalothrin" is inconsistent.

ICI Response: (See attachment pp 8-9). The registrant acknowledged inconsistent use of the term "cyhalothrin" in the study and clarified the issue by pointing out that "cyhalothrin" should only have been used to describe the actual test material employed in the study ie. the Z-cis enantiomeric pairs (four isomers; pair A and pair B). See structures on page two of attached study.

EAB Response: The registrant's explanation is satisfactory.

(2) EAB Comment: Cyhalothrin was used in the study not PP321.

ICI Response: (See attachment page 10). The registrant states that at a meeting with EAB staff in May 1983 it was agreed that cyhalothrin data could be referenced in support of PP321. Cyhalothrin and PP321 metabolize similarly in soil. TOX has accepted the sub-chronic and chronic toxicological data on cyhalothrin to evaluate PP321 and a single ADI has been set for cyhalothrin and PP321.

EAB Response: The registrant's explanation is satisfactory.

(3) EAB Comment: Data were difficult to interpret and there were no tabulated data for residues.

ICI Response: ICI acknowledges these criticisms and explains that the studies were reported in Japanese and translated into English. The numerical data do exist and two tables of data are provided.

EAB Response: The registrant's response is satisfactory.

(4) EAB Comment: An inappropriate fish species was used.

ICI Response: Data on a large number of pyrethroids show that various species of fish exhibit very similar acute toxicity and bioaccumulation values. There is very little difference in this respect in a wide range of fish species (see Figures 7 and 8). This has also been shown for three species of fish with cyhalothrin and PP321 (bluegill sunfish, rainbow trout and carp)(see Figure 9). The study was carried out in Japan to satisfy the Japanese regulatory authorities as well as the USA/EPA. In the past ICI has submitted fish accumulation data using rainbow trout for the registration of cypermethrin and this species has been acceptable to the Agency. ICI therefore felt that since the carp was also an American species the fish species used in the cyhalothrin /PP321 study (Cyprinus carpio) would be acceptable to the Agency. The guidelines state that the "bluegill sunfish and the channel catfish are the preferred species, although other species may be appropriate".

EAB Response: Data in Figure 8 indicate a general similarity in accumulation for bluegill sunfish, carp and rainbow trout for several pyrethroid chemicals. However, no data are given for accumulation of PP321. The data given on fish toxicity are not directly relevant to accumulation. Approval for the use of a non-preferred test species should have been obtained before the study was conducted either by waiver or by submitting a protocol.

(5) EAB Comment: Test substance specifications were inconsistent.

ICI Response: (i) Technical cyhalothrin was supplied by ICI to the contractors (MITES) in Japan.

(ii) ICI Report No RJ0407B gives the radiochemical purity of cyhalothrin as 95.5% and its isomers as 4.43% ie. total of 99.9%. This refers to 95.5% of isomers (A', B', C, C', D and D'), and is the specification of the technical cyhalothrin supplied to MITES by ICI.

(iii) The MITES report No 58-367 gives the radiochemical purity of technical cyhalothrin as 80.5% and its isomers as 15% ie. total 95.5%. This is from analysis of the material supplied by ICI. The higher percentage of isomers refers to isomers A' and B' and is a result of the difficult (and in this case incomplete) separation of the isomers A from A' and B from B'. The amounts of isomers C, C', D and D' remained extremely small.

(iv) The ratio of the two enantiomeric pairs (isomers A and B) in the cyhalothrin supplied by ICI, in the test water and in the fish, was similar (see Figure 10a); and in each case the trans isomer content was less than 5%.

(v) However, the most important technical specification is the concentration of cyhalothrin and PP321 in the test water, and this is described and discussed under 7 below.

EAB Response: The registrant's explanation is acceptable.

(6) EAB Comment: Nominal test substance concentration was too low.

ICI Response: The guidelines stipulate that the concentration of the test substance must not exceed 1/10 of the 96-hour LC<sub>50</sub> of the test species. Figure 11 gives the 96-hour LC<sub>50</sub> values of cyhalothrin in three fish species. When allowance is made for the fact that the carp value is derived from a static test, the value for carp in a flow-through system would be expected to be similar or less than 0.4-0.5 ppb. As the 1/10 of this approximate 96-hour LC<sub>50</sub> value may be too close to its acute toxicity value for an exposure period of 28 days, ICI prefer to use the 1/20 of this value to avoid any toxicity effects in fish.

Available data on analogous pyrethroids: permethrin, fenvalerate and flucythrinate (see Figure 12) show that the concentration of the test substance does not influence the Biological Concentration factor (BCF), over a concentration range of up to fourteen-fold. ICI therefore believe that the concentration of the test substance used would not make any difference in the fish accumulation study.

EAB Response: The registrant's explanation is acceptable.

(7) EAB Comment: Data for characterization in water were poor.

ICI Response: Data in the study report were presented graphically and not tabulated, and results were not given separately for the enantiomeric pairs A and B. Information from the study reports is therefore summarized in Figures 13 and 14. Values for each enantiomeric pair (isomers A and B) and their ratios were not displayed in the reports. The ratio of isomer A: isomer B did not change during the course of the study. Although 40-50% of the total applied radioactivity was recovered in water, the important values are the actual concentration of the radioactivity of cyhalothrin and isomer B (PP321) measured in water and in fish. Low recovery from loss of the test material in the water would tend to give worse results for the accumulation in fish.

Ester hydrolysis products are several orders of magnitude less toxic to fish, considerably more polar and with much lower potential for accumulation in fish compared to the parent ester. Hence the important criterion in this study is to monitor the parent ester, analysis of which shows that the ratio of isomer A: isomer B remains constant throughout the course of the study.

EAB Response: The registrant's explanation is acceptable.

(8) EAB Comment: Measured concentrations of cyhalothrin in water were variable.

ICI Response: Pyrethroids are difficult compounds to maintain at constant concentrations in water because they readily adsorb to vessel surfaces and to debris (eg. excreta from fish) and are continuously removed from water in a flow-through system.

Examination of the available data on analogous pyrethroids shows that the variability observed with cyhalothrin is within the range of variability found with all these other pyrethroid compounds (see Figure 15).

The variability in the case of cypermethrin, data which was accepted by the Agency, is higher than for cyhalothrin (Figure 15). The crucial information needed in the study to calculate BCF is the concentration of the test substance in water and in fish. .... The pattern of accumulation and elimination of cyhalothrin and PP 321 are closely comparable to the spectrum of data for a wide range of pyrethroid insecticides. Comparisons are given in Figures 20 and 21.

EAB Response: The registrant's response is acceptable.

(9) EAB Comment: Data for trans isomers in fish tissue were not reported.

ICI Response: Data on the levels of the trans isomers of cyhalothrin were not reported because they were negligibly small (less than 3% of the total pyrethroid isomers and less than 0.002 mg/kg in any fish tissue: see Figure 17)

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EAB Response: The registrant's response is acceptable.

(10) EAB Comment: TLC plate type was not reported and LODs were not reported for LSC, TLC and HPLC.

ICI Response: TLC types are given on Page 3 of the Appendix of the MITES Report No 58-367. The LODs were not reported because the values were sufficiently above these limits for accurate determinations.

EAB Response: The registrant's response is acceptable.

General comment on the additional data presented.

The registrant has reported what appear to be three different values for the bioaccumulation factor of PP321 in carp: figure 18 indicates a 28 day BCF of 4800, figure 21 indicates a BCF of 5000 and a BCF of 4600 for the total fish is reported in the registrant's letter of October 26, 1987. An explanation of these reported values is needed along with the calculations on which they are based. A summary table of all relevant bioaccumulation data (total  $^{14}\text{C}$ , cyhalothrin and PP321) would be helpful.

Leaching and Adsorption/Desorption

EAB Comment: This adsorption/desorption study is not acceptable because concentrations of PP321 in the test solutions exceeded its solubility in water.

ICI Response: In order to derive  $K_d$  values, it is necessary to quantify the concentration of the test compound in both the aqueous and solid phases of a soil slurry, at equilibrium. For this study it was intended to use  $^{14}\text{C}$ -PP321 with the highest possible specific radioactivity (2.39 GBq per mmole). Despite this, with the expected very high soil  $K_d$  values (approximately 2000) the concentration of radio-carbon in the aqueous phases of the slurries at equilibrium would have been too low to allow accurate quantification. It was therefore decided to apply the  $^{14}\text{C}$ -PP321 to the test systems over the initial concentration range of 0.02-0.20ppm. It was recognized, however, that it was vital that the concentration of  $^{14}\text{C}$ -PP321 in the aqueous phases, at equilibrium, would not be constrained by the solubility of the compound. The actual concentrations of  $^{14}\text{C}$ -PP321 determined in the aqueous phase are presented on Figure 22. It is clear that for the vast majority of the test variants, the solution concentrations are below 0.004 ppm. Although a few solution concentrations above 0.004 ppm were detected, it is almost certain that this material was in solution during this test, as the solubility of the test material was enhanced by the presence of both the co-solvent (the  $^{14}\text{C}$ -PP321 was added in a volume of acetonitrile equivalent to 1% of the final volume) and dissolved soil organic matter. Both of these factors would be expected to increase, considerably, the solubility of PP321 compared to that in pure or buffer solutions.

The EAB review also criticized the somewhat variable Kd values obtained from the replicates of the soil slurries. ICI concurs that there was some variability of the data. However, this level of variability is inevitable in studies of this type and was probably due to the presence of minute amounts of particulate soil or soil organic matter in the equilibrium solutions even after vigorous centrifugation. Since the soil particles had an associated large radioactive residue, this would have had a profound effect on the measured solution concentrations and therefore on the derived Kd values.

In conclusion, ICI believes that this study is valid since the concentration of the test compound in the aqueous phases at equilibrium was not constrained by its water solubility. Further, very high Kd values were determined (1200-3200 for various test variants), thus indicating that PP321 has an extremely low leaching potential.

EAB Response: The registrant's explanation is acceptable. The data requirement for leaching and adsorption/desorption is considered to be fulfilled.

Anaerobic Soil Metabolism: See attached review.

Reentry: See memo from Dr. James D. Adams to Ms. Christine Dively of February 25, 1988.

11. COMPLETION OF ONE-LINER: Not applicable to this action.
12. CBI APPENDIX: Data submitted appear to be CBI and should be treated as such.

CASE GS -- PP321 STUDY 1 PM --  
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 CHEM -- PP321  
 BRANCH EAB DISC --

## FORMULATION 00 - ACTIVE INGREDIENT

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 FICHE/MASTER ID No MRID CONTENT CAT 01  
 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.  
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SUBST. CLASS = S.

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 DIRECT RVW TIME = 14 (MH) START-DATE END DATE  
 -----

REVIEWED BY: A. Schlosser  
 TITLE: Chemist  
 ORG: EAB/HED/OPP  
 TEL: 557-5736  
 -----

APPROVED BY: A. Schlosser  
 TITLE: Chemist  
 ORG: EAB/HED/OPP  
 TEL: 557-5736  
 -----

SIGNATURE: *Arthur C. Schlosser*DATE: *March 8, 1988*CONCLUSIONS:

Metabolism - Anaerobic Aquatic  
Metabolism - Anaerobic Soil

This report is unacceptable for fulfilling guideline requirements for anaerobic aquatic metabolism data because the soil was not flooded for 30 days before the addition of test material.

The report is unacceptable for fulfilling guideline requirements for anaerobic soil metabolism because it appears that anaerobic conditions may not have been achieved after the 30 day period of aerobic incubation. Evidence of this is suggested by the continued evolution of carbon dioxide in the anaerobic soil metabolism study under flooded conditions while little carbon dioxide was evolved when treated soils were flooded immediately without an aerobic incubation period. This study may be accepted if the registrant can show that anaerobic conditions were present under flooded conditions or can otherwise explain the continued evolution of carbon dioxide. A estimate of half-life under anaerobic conditions should also be provided.

No data were provided on the "alcohol" portion of the test substance. These data must be either submitted or specifically referenced.

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## MATERIALS AND METHODS:

Cyclopropane-labeled [ $^{14}\text{C}$ ]PP563 (containing "A" and "B" isomers) was applied at 100 or 500 g ai/ha to "pots" (25-g soil; 3.8-cm diameter x 3-cm depth) of sandy loam or loamy sand soil (Tables 1 and 2). Also, the "A" and "B" (PP321) isomers were applied separately at 100 g ai/ha to sandy loam soil. The soils were moistened to 40% of their water-holding capacity at zero suction, except for one set of samples that was flooded immediately after treatment. A second set of samples was flooded after 30 days of aerobic incubation. The treated pots of soil were placed in sealed-glass columns through which moistened carbon dioxide-free air was drawn (Figure 1). Air passing over the treated soil was drawn through one tube of 2-methoxyethanol and two tubes of ethanolamine. The soils were incubated at 10 or 20°C for the duration of the study. Soil, water, and trapping solutions were sampled at various intervals up to 181 days posttreatment.

The soils were extracted sequentially with acetonitrile on a wrist action shaker for 30 minutes at room temperature and acetonitrile:water (70:30) by refluxing for 3 hours. Aliquots of the extracts were analyzed for total radioactivity by LSC, and for specific compounds by 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 soil extracts were also analyzed for degradates and specific isomers using GC, HPLC, and MS. The extracted soil was analyzed by LSC following combustion. The water samples were concentrated and analyzed by LSC, TLC, and HPLC. Aliquots of the trapping solution were analyzed for total radioactivity by LSC.

## REPORTED RESULTS:

[ $^{14}\text{C}$ ]PP563 (a 60:40 mixture of isomers "A" and "B"), PP321 (isomer "B"), and isomer "A" degraded with an initial half-life between 14 and 30 days posttreatment in aerobic sandy loam soil (Table 3). A second half-life occurred between 30 and 60 days posttreatment for the mixture (PP563) and isomer "A"; isomer "B" did not reach a second half-life until approximately 90 days posttreatment. When the behavior of isomers "A" and "B" in the mixture were examined, both "A" and "B" degraded faster in combination than separately (Table 4). In the mixture, 91.8% of isomer "A" and 85.8% of isomer "B" degraded by 90 days posttreatment, while separately 90.1% of "A" and 78.4% of "B" degraded by 92 days posttreatment (too few samples were obtained to permit these data to be analyzed statistically with any degree of confidence). The "A": "B" mixture also degraded more completely than "A" or "B" alone; by day 90, 58.9% of the applied radioactivity in the mixture had been evolved as  $^{14}\text{CO}_2$ , but only 47.1% of the applied radioactivity was evolved as  $^{14}\text{CO}_2$  from the soil treated with the "A" isomer alone and only 35.6% was evolved from soil treated with the "B" isomer alone (Table 4). (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (up to 7.6% of the applied) and (RS)- $\alpha$ -cyano-3-(4-hydroxy-

phenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (up to 12.5% of the applied) were the major nonvolatile degradates in soil treated with PP563, "A" alone, and "B" alone (Table 3).

The "A":"B" mixture (PP563) degraded more slowly under anaerobic (flooded) conditions than under aerobic conditions (Tables 5 and 6). The difference between the "A" and "B" isomer degradation rate was less pronounced under anaerobic conditions; by 131 days posttreatment, 59% of the "A" isomer and 55% of the "B" isomer in the mixture had degraded. PP563 degraded more slowly when applied at 500 g ai/ha compared to 100 g ai/ha, degraded more slowly at 10°C than at 20°C, and degraded more slowly in loamy sand than sandy loam soil (Table 7).

No isomerization of the parent compounds and observed under any conditions during the studies.

#### DISCUSSION:

1. It appears the anaerobic conditions may not have been achieved under flooded conditions in the anaerobic soil metabolism study. It is noted that very little carbon dioxide was evolved in a study where treated soils were flooded immediately.
2. Studies in which cyclopropane-labeled [<sup>14</sup>C]PP321 was used provide no information on the fate of the alcohol half of the PP321 molecule in soil. Data on the "alcohol" portion of the molecule should be submitted or specifically referenced.
4. The soil that was used was collected in Berkshire, England and was classified by a method other than the USDA Soil Textural Classification System. The soil was not reclassified.
5. Recovery from fortified samples and detection limits were not reported.

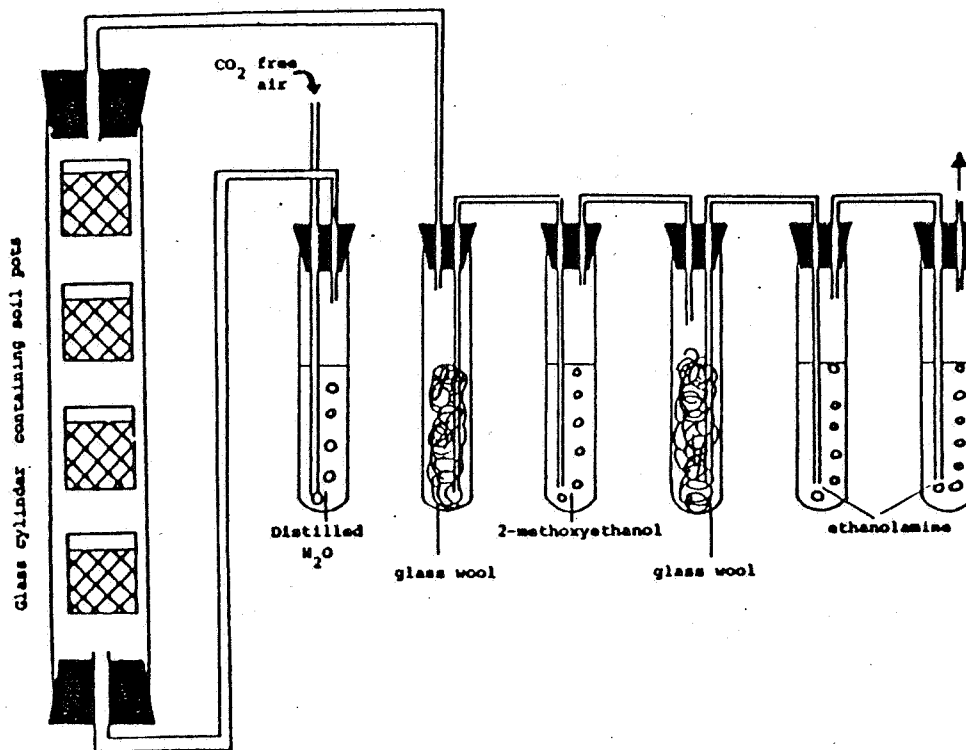


Figure 1. Continuous air-flow incubation apparatus.

Table 1. Test data.

| Study | Test substance <sup>a</sup> | Soil type <sup>b</sup> | Incubation conditions | Temperature | Application rate (g ai/ha) | Sampling intervals (days) |    |    |    |    |    |     |     |
|-------|-----------------------------|------------------------|-----------------------|-------------|----------------------------|---------------------------|----|----|----|----|----|-----|-----|
| A     | PP563                       | Sandy loam             | Aerobic               | 20°C        | 100                        | 0                         | 7  | 14 | 30 | 59 | 90 | --  | 180 |
| B     | PP563                       | Sandy loam             | Flooded after 30 days | 20°C        | 100                        | --                        | -- | -- | -- | 60 | 90 | --  | --  |
| C     | PP563                       | Sandy loam             | Aerobic               | 20°C        | 500                        | 0                         | 7  | -- | 30 | -- | 90 | --  | --  |
| D     | PP563                       | Sandy loam             | Aerobic               | 10°C        | 100                        | --                        | 7  | -- | 30 | -- | 90 | --  | --  |
| E     | PP563                       | Sandy loam             | Anaerobic (flooded)   | 20°C        | 100                        | 0                         | 7  | -- | 30 | 59 | -- | 131 | --  |
| F     | PP321 ("B" isomers)         | Sandy loam             | Aerobic               | 20°C        | 100                        | 0                         | -- | -- | 30 | 63 | 92 | --  | --  |
| G     | "A" isomers                 | Sandy loam             | Aerobic               | 20°C        | 100                        | 0                         | -- | -- | 30 | 63 | 92 | --  | --  |
| H     | PP563                       | Loamy sand             | Aerobic               | 20°C        | 100                        | 0                         | 7  | -- | 30 | -- | 90 | --  | 181 |

<sup>a</sup> All compounds were cyclopropane-labeled [<sup>14</sup>C] material. Refer to Table 2 of this report for isomer ratios.

<sup>b</sup> 18 Acres sandy loam: 28% coarse sand, 33% fine sand, 17% silt, 22% clay, 4.0-4.6% organic matter, pH 6.7, CEC 16.7-19.8 meq/100 g.

Frensham loamy sand: 38% coarse sand, 40% fine sand, 12% silt, 10% clay, 2% organic matter, pH 5.3, CEC 7.2 meq/100 g.

Table 2. Characteristics of the test substance.

| Test substance             | Total pyrethroid purity (%) <sup>a</sup> | Isomeric composition (%) <sup>b</sup> |      |     |      | Trans-isomers <sup>c</sup> |
|----------------------------|--|---------------------------------------|------|-----|------|----------------------------|
|                            |  | Cis-isomers                           |      |     |      |                            |
|                            |  | A'                                    | A    | B'  | B    |                            |
| PP563                      | 98.0                                     | 3.4                                   | 57.7 | 1.8 | 36.2 | 0.9                        |
| PP321<br>(isomer pair "B") | 98.7                                     | 0.1                                   | 0.7  | 2.6 | 95.1 | 1.5                        |
| Isomer pair "A"            | 100                                      | 1.1                                   | 96.5 | 0.6 | 1.1  | 0.7                        |

<sup>a</sup> Determined by TLC; all isomers are included.

<sup>b</sup> These isomers have a cis configuration about the 1,3 bond of the cyclopropane ring:

A' -  $\underline{E}(1R, 3R, \alpha R)$  and  $\underline{E}(1S, 3S, \alpha S)$  enantiomer pair

A -  $\underline{Z}(1R, 3R, \alpha R)$  and  $\underline{Z}(1S, 3S, \alpha S)$  enantiomer pair

B' -  $\underline{E}(1R, 3R, \alpha S)$  and  $\underline{E}(1S, 3S, \alpha R)$  enantiomer pair

B -  $\underline{Z}(1R, 3R, \alpha S)$  and  $\underline{Z}(1S, 3S, \alpha R)$  enantiomer pair

<sup>c</sup> These isomers have a trans configuration about the 1,3 bond of the cyclopropane ring:

C -  $\underline{Z}(1R, 3S, \alpha R)$  and  $\underline{Z}(1S, 3R, \alpha S)$  enantiomer pair

C' -  $\underline{E}(1R, 3S, \alpha R)$  and  $\underline{E}(1S, 3R, \alpha S)$  enantiomer pair

D -  $\underline{Z}(1R, 3S, \alpha S)$  and  $\underline{Z}(1S, 3R, \alpha R)$  enantiomer pair

D' -  $\underline{E}(1R, 3S, \alpha S)$  and  $\underline{E}(1S, 3R, \alpha R)$  enantiomer pair



| Sampling interval (days) | Parent <sup>b</sup> | Degradate         |                | Origin | Other | <sup>14</sup> C <sub>2</sub> | Unextractable |
|--------------------------|---------------------|-------------------|----------------|--------|-------|------------------------------|---------------|
|                          |                     | A <sup>c</sup>    | B <sup>d</sup> |        |       |                              |               |
| <u>PP563</u>             |                     |                   |                |        |       |                              |               |
| 0                        | 95.2                | <0.5 <sup>e</sup> | <0.5           | <0.5   | 0.9   | --                           | 0.1           |
| 7                        | 76.3                | 3.5               | 3.5            | 0.9    | 3.5   | 3.0                          | 2.3           |
| 14                       | 61.7                | 7.6               | 7.6            | 4.4    | 1.6   | 8.6                          | 5.7           |
| 30                       | 35.2                | 5.8               | 11.1           | 2.8    | 1.0   | 24.0                         | 12.0          |
| 59                       | 17.9                | 3.6               | 7.0            | 4.0    | 1.2   | 46.6                         | 17.6          |
| 90                       | 10.1                | 1.8               | 3.1            | 1.3    | <0.5  | 58.9 ✓                       | 18.9          |
| 180                      | 5.7                 | 5.7               | 2.0            | <0.5   | 0.9   | 70.4                         | 18.7          |
| <u>PP321 (B isomers)</u> |                     |                   |                |        |       |                              |               |
| 0                        | 98.9                | <0.5              | <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          |
| <u>A Isomers</u>         |                     |                   |                |        |       |                              |               |
| 0                        | 97.8                | <0.5              | <0.5           | <0.5   | 1.4   | --                           | <0.1          |
| 30                       | 39.1                | 5.6               | 7.5            | 6.4    | 0.6   | 21.9                         | 8.9           |
| 63                       | 18.1                | 3.7               | 9.1            | 3.0    | <0.5  | 40.0                         | 15.2          |
| 92                       | 10.8                | 1.2               | 5.4            | 0.6    | <0.5  | 47.1 ✓                       | 18.3          |

<sup>a</sup> CO<sub>2</sub> and unextractable data are from Table 7 in the original document. Characterization of extractables is from Table 8 in the original document.

<sup>b</sup> Distribution of specific isomers is presented in Table 4.

<sup>c</sup> (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

<sup>d</sup> (RS)- $\alpha$ -Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

<sup>e</sup> The detection limit was not specified.

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Table 5. Effect of flooding on the distribution of radioactivity (% of the applied) in sandy loam soil treated with cyclopropane-labeled [<sup>14</sup>C]PP563 at 100 g ai/ha and incubated at 20°C.<sup>a</sup>

| Sampling interval (days)                             | Parent <sup>b</sup> | Degradate         |                |        |       | <sup>14</sup> CO <sub>2</sub> | Unextractable |
|--|---------------------|-------------------|----------------|--------|-------|-------------------------------|---------------|
|  |                     | A <sup>c</sup>    | B <sup>d</sup> | Origin | Other |                               |               |
| <u>Aerobic (40% of WHC)</u>                          |                     |                   |                |        |       |                               |               |
| 0  | 95.2                | <0.5 <sup>e</sup> | <0.5           | <0.5   | 0.9   | --                            | 0.1           |
| 7  | 76.3                | 3.5               | 3.5            | 0.9    | 3.5   | 3.0                           | 2.3           |
| 14   | 61.7                | 7.6               | 7.6            | 4.4    | 1.6   | 8.6                           | 5.7           |
| 30   | 35.2                | 5.8               | 11.1           | 2.8    | 1.0   | 24.0                          | 12.0          |
| 59   | 17.9                | 3.6               | 7.0            | 4.0    | 1.2   | 46.6                          | 17.6          |
| 90   | 10.1                | 1.8               | 3.1            | 1.3    | <0.5  | 58.9                          | 18.9          |
| 180  | 5.7                 | 5.7               | 2.0            | <0.5   | 0.9   | 70.4                          | 18.7          |
| <u>Aerobic for 30 days, then flooded<sup>f</sup></u> |                     |                   |                |        |       |                               |               |
| 30 + 0   | 35.2                | 5.8               | 11.1           | 2.8    | 1.0   | 24.0                          | 12.0          |
| 30 + 30  | 17.7                | 10.8              | 6.3            | 3.2    | <0.5  | 37.3                          | 16.1          |
| 30 + 60  | 13.1                | 5.3               | 4.5            | 1.7    | <0.5  | 45.1                          | 19.7          |
| <u>Anaerobic (flooded)<sup>f</sup></u>               |                     |                   |                |        |       |                               |               |
| 0  | 93.2                | <0.5              | <0.5           | <0.5   | 2.0   | --                            | 0.1           |
| 7  | 84.7                | 1.8               | 0.9            | <0.5   | 1.8   | 0.2                           | 0.6           |
| 30   | 75.3                | 10.0              | 0.8            | 0.8    | 0.8   | 0.3                           | 1.5           |
| 59   | 60.5                | 22.4              | 1.4            | 2.8    | 0.7   | 0.4                           | 1.1           |
| 131  | 41.1                | 34.8              | 0.6            | 2.3    | 2.5   | 0.5                           | 2.8           |

<sup>a</sup> CO<sub>2</sub> and unextractable data are from Table 7 in the original document. Characterization of extractables is from Table 8 in the original document.

<sup>b</sup> Distribution of specific isomers is presented in Table 6.

<sup>c</sup> (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

<sup>d</sup> (RS)-α -Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

<sup>e</sup> The detection limit was not specified.

<sup>f</sup> Data include radioactivity in the flood water.

Table 6. Effect of flooding on the distribution of isomers (% of the applied radioactivity) in sandy loam soil treated with cyclopropane-labeled [ $^{14}\text{C}$ ]PP563 at 100 g ai/ha and incubated at 20°C.<sup>a</sup>

| Sampling interval (days)                             | Parent | Cis-isomers       |      |      |      | Trans-isomers |
|--|--------|-------------------|------|------|------|---------------|
|  |        | A'                | A    | B'   | B    |               |
| <u>Aerobic (40% of WHC)</u>                          |        |                   |      |      |      |               |
| 0  | 95.2   | 3.2               | 54.9 | 1.7  | 34.5 | 0.9           |
| 7  | 76.3   | 2.6               | 40.9 | 2.0  | 29.7 | 1.1           |
| 14   | 61.7   | 1.9               | 31.0 | 1.6  | 24.0 | 1.2           |
| 30   | 35.2   | 1.0               | 16.0 | 1.1  | 15.1 | 0.5           |
| 59   | 17.9   | <0.5 <sup>b</sup> | 7.5  | 0.6  | 8.0  | <0.5          |
| 90   | 10.1   | <0.5              | 4.5  | <0.5 | 4.9  | <0.5          |
| 180  | 5.7    | <0.5              | 2.4  | <0.5 | 2.8  | <0.5          |
| <u>Aerobic for 30 days, then flooded<sup>c</sup></u> |        |                   |      |      |      |               |
| 30 + 0   | 35.2   | 1.0               | 16.0 | 1.1  | 15.1 | 0.5           |
| 30 + 30  | 17.7   | 0.5               | 7.5  | 0.5  | 7.7  | 0.6           |
| 30 + 60  | 13.1   | 0.6               | 4.7  | <0.5 | 5.7  | 0.7           |
| <u>Anaerobic (flooded)<sup>c</sup></u>               |        |                   |      |      |      |               |
| 0  | 93.2   | 2.8               | 53.0 | 1.8  | 34.7 | 0.9           |
| 7  | 84.7   | 3.2               | 47.1 | 1.3  | 31.8 | 1.3           |
| 30   | 75.3   | 2.3               | 43.0 | 1.3  | 27.6 | 1.1           |
| 59   | 60.5   | 1.6               | 30.4 | 1.4  | 20.6 | 1.1           |
| 131  | 41.1   | 0.7               | 21.7 | 0.8  | 15.5 | 0.4           |

<sup>a</sup> Distribution of isomers is from Table 8 in the original document.

<sup>b</sup> The detection limit was not specified.

<sup>c</sup> Data include radioactivity in the flood water.

Table 7. Effect of temperature, application rate, and soil type on the distribution of radioactivity (% of the applied) in sandy loam or loamy sand soil treated with cyclopropane-labeled [<sup>14</sup>C]PP563 at 100 or 500 g ai/ha and incubated at 40% of moisture holding capacity.

| Sampling interval (days)                  | Parent | Degradate         |                |        |       | <sup>14</sup> CO <sub>2</sub> | Unextractable |
|---|--------|-------------------|----------------|--------|-------|-------------------------------|---------------|
|   |        | A <sup>b</sup>    | B <sup>c</sup> | Origin | Other |                               |               |
| <u>Sandy loam soil, 100 g ai/ha, 20°C</u> |        |                   |                |        |       |                               |               |
| 0   | 95.2   | <0.5 <sup>d</sup> | <0.5           | <0.5   | 0.9   | --                            | 0.1           |
| 7   | 76.3   | 3.5               | 3.5            | 0.9    | 3.5   | 3.0                           | 2.3           |
| 14  | 61.7   | 7.6               | 7.6            | 4.4    | 1.6   | 8.6                           | 5.7           |
| 30  | 35.2   | 5.8               | 11.1           | 2.8    | 1.0   | 24.0                          | 12.0          |
| 59  | 17.9   | 3.6               | 7.0            | 4.0    | 1.2   | 46.6                          | 17.6          |
| 90  | 10.1   | 1.8               | 3.1            | 1.3    | <0.5  | 58.9                          | 18.9          |
| 180                                       | 5.7    | 5.7               | 2.0            | <0.5   | 0.9   | 70.4                          | 18.7          |
| <u>Sandy loam soil, 100 g ai/ha, 10°C</u> |        |                   |                |        |       |                               |               |
| 0   | 95.2   | <0.5              | <0.5           | <0.5   | 0.9   | --                            | 0.1           |
| 7   | 96.5   | 1.0               | 1.0            | <0.5   | 2.0   | 0.2                           | 0.7           |
| 30  | 74.9   | 5.2               | 5.2            | 4.3    | <0.5  | 2.7                           | 4.0           |
| 90  | 28.8   | 5.5               | 6.9            | 3.7    | 0.9   | 21.2                          | 14.2          |
| <u>Sandy loam soil, 500 g ai/ha, 20°C</u> |        |                   |                |        |       |                               |               |
| 0   | 97.0   | <0.5              | <0.5           | <0.5   | 2.0   | --                            | 0.0           |
| 7   | 87.2   | 2.8               | 2.8            | <0.5   | 0.9   | 1.4                           | 1.2           |
| 30  | 60.5   | 6.7               | 4.3            | 6.7    | 0.8   | 11.0                          | 6.8           |
| 90  | 26.4   | 7.3               | 4.5            | 2.0    | <0.5  | 37.0                          | 14.3          |
| <u>Loamy sand soil, 100 g ai/ha, 20°C</u> |        |                   |                |        |       |                               |               |
| 0   | 97.5   | <0.5              | <0.5           | <0.5   | 2.0   | --                            | <0.1          |
| 7   | 94.1   | 1.9               | <0.5           | <0.5   | <0.5  | 0.8                           | 0.8           |
| 30  | 72.6   | 4.0               | 0.8            | 0.8    | 0.8   | 7.2                           | 6.1           |
| 90  | 46.6   | 2.7               | 3.2            | 4.2    | 4.2   | 25.4                          | 12.0          |
| 181                                       | 21.4   | 2.2               | 4.1            | 8.2    | 2.5   | 37.6                          | 14.7          |

<sup>a</sup> CO<sub>2</sub> and unextractable data are from Table 7 in the original document. Characterization of extractables is from Table 8 in the original document.

<sup>b</sup> (1RS)-Cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

<sup>c</sup> (RS)-α -Cyano-3-(4-hydroxyphenoxy)benzyl-(1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

<sup>d</sup> The detection limit was not specified.