Chemical Code: **109702**

Date Out: _____

ENVIRONMENTAL FATE AND GROUND WATER BRANCH
Review Action

To: George LaRocca, PM #13
Registration Division (7505C)

From: Akiva Abramovitch, Section Chief
Chemical Review Section #3
Environmental Fate & Ground Water Branch/EFED (7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (7507C) Henry Jacoby 3/4/96

Attached, please find the EFGWB review of...

DP Barcode:	D197021, D197873, D197879		
Chemical Name:	Cypermethrin	**Trade name:**	Ammo, Cymbush
Company Name:	FMC, Inc.		
ID #:	279-3084, 279-3027		
Purpose:	Review of 165-4 study for registration, status of data requirements, and New Use Registration requests for tomatoes and Brassica crops.		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
Insecticide	330, 606		3.0 days

STATUS OF STUDIES IN THIS PACKAGE:

Guideline #	MRID	Status[1]
165-4	42868201	A

STATUS OF DATA REQUIREMENTS:

	Status[2]
165-4	S

[1]Study Status Codes: A=Acceptable U=Upgradeable C=Ancillary I=Invalid.
[2]Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved.

1. CHEMICAL: Common name:

Cypermethrin.

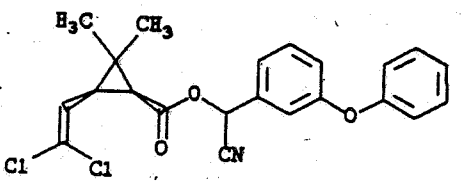
Chemical name (C.A.):

(RS)-Cyano(3-phenoxyphenyl)-methyl(1RS)-3-(2,2-dichloro-ethenyl)-2,2-dimethylcyclopropanecarboxylate.

Trade name(s):

Fligene CI, Siperin, Polytrin, Ammo, Arrivo, Basathrin, Amcocyper, Cypermar, Cyperkill, Cynoff, Cyperguard, Kafil Super, Demon, Cyperator, Ralothrin, Barricade, Flectron, Folcord, Ripcord, Ustaad, and Cyrux.

Structure:



Formulations:

Emulsifiable concentrate, ULV concentrate, and wettable powder.

Physical/Chemical properties:

Molecular formula: $C_{22}H_{19}Cl_2NO_3$.
Molecular weight: 416.3.
Physical state (mixed isomers): Viscous yellowish-brown semi-solid.
Melting point: 60-80 °C.
Solubility (20 °C): 0.01-0.2 mg/L water; >450 g/L acetone, chloroform, cyclohexanone, xylene; 337 /L ethanol; 103 g/L hexane.

2. TEST MATERIAL:

Study 1: Active ingredient.

2

3. STUDY/ACTION TYPE:

Review of bioaccumulation in fish study, status of data requirements, and New Use Registration Request for tomatoes and Brassica crops.

4. STUDY IDENTIFICATION:

Giroir, L.E., and L. Stuerman. 1993. [^{14}C]Cypermethrin bioconcentration by bluegill sunfish (Lepomis macrochirus). FMC Study No. 191E5491E1; ABC Laboratories Final Report No. 40018. Unpublished study performed by ABC Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ. (42868203)

5. REVIEWED BY:

James Breithaupt, Agronomist
Review Section 3
EFGWB/EFED/OPP

Signature: James Breithaupt
Date: 2/4/96

6. APPROVED BY:

Akiva Abramovitch, Chief
Review Section 3
EFGWB/EFED/OPP

Signature: Akiva Abramovitch
Date: MAR 4 1996

7. CONCLUSION:

New Use Registration on Tomatoes and Brassica Crops

Extremely high soil binding of parent cypermethrin, based on Kads values, will keep cypermethrin in the top soil and prevent movement to ground water. Only the degradate dichlorovinyl acid (DCVA) is mobile and may leach into ground water. Cypermethrin was moderately persistent in the laboratory aerobic and anaerobic soil metabolism studies, but dissipated rapidly in the field. Biodegradation was the only apparent means of dissipation in the laboratory studies, and it appears that another dissipation route is important in the field. The registrant has not reconciled the difference in persistence in the laboratory and field studies. Therefore, the submitted fate information does not present a consistent picture of cypermethrin dissipation in the environment to support the new uses on tomatoes and Brassica crops.

Submitted Studies in this Review

Bioaccumulation in Fish, DER 1, 165-4, MRID 42868203, Acceptable

Cypermethrin residues accumulated moderately in bluegill sunfish continuously exposed to benzyl or cyclopropyl ring-labeled cypermethrin at 0.20 ppb for 28 days. Maximum bioconcentration factors for the benzyl and cyclopropyl ring-labeled treatments were 111 and 161x for the edible (body, muscle, skin, and skeleton) tissues, 579 and 833x for the nonedible (fins, head, and internal organs) tissues, and 468 and 444x for whole fish. Maximum mean concentrations of total [^{14}C]residues were 21-29 ppb for edible tissues, 110-150 ppb for nonedible tissues, and 80-89 ppb for whole fish. Metabolites identified in the fish tissues were cyperamide (cyano-hydrated cypermethrin), m-phenoxybenzyl alcohol, m-phenoxybenzoic acid, m-phenoxybenzylaldehyde, cis-dichlorovinyl acid (DCVA), trans-DCVA, and a mixture of DCVA methyl ester isomers. Cyperamide, mPB aldehyde, mPB acid, and cis- and trans-DCVA were identified in the aquarium water. After 14 days of depuration, ≥81% of the accumulated [^{14}C]residues were eliminated from the fish tissues.

ENVIRONMENTAL FATE ASSESSMENT

Cypermethrin was moderately persistent in the laboratory aerobic and anaerobic soil metabolism studies, but dissipated rapidly in the field. Biodegradation was the only apparent means of dissipation in the laboratory, and it appears that another dissipation route is important in the field. The registrant has not reconciled the difference in persistence in the laboratory and field studies. Even though parent cypermethrin is moderately persistent and the degradate DCVA is mobile in soil, EFGWB is not aware of any detections of parent cypermethrin or DCVA in ground water.

Based on available information, cypermethrin is stable to hydrolysis at pH values of 5 and 7, but degrades rapidly in pH 9 aqueous buffer solutions (1 % acetonitrile cosolvent) with calculated half-lives of 1.8 and 2.5 days in acid (cyclopropyl) and alcohol (benzyl) labels, respectively. Cypermethrin is moderately stable in soil, degrading in aerobic and anaerobic soil with half-lives of 53-63 days for both the acid and alcohol labels. Photodegradation does not contribute significantly to degradation on soil. The primary degradates are cis/trans DCVA, mPBAcid, cyperamide and mPBAldehyde. Parent cypermethrin is not mobile in soil, having Freundlich K_{ads} values of 657, 1163, 1897, 416 and K_{des} values of 1263, 192, 602, and 262 on sand (0.23 % OC), sandy loam (1.05 % OC), silt loam (2.5 % OC), and clay loam (2.3 % OC) soils, respectively. K_{oc} values of 259,000, 111,000, 72,000, and 18,000 for adsorption and 549,000, 18,000, 23,000, and 12,000 for desorption, respectively. However, 13.2 % of the applied radioactivity was found

4

in the leachate as the degradate DCVA in an aged soil column leaching study. No other degradate appears to be mobile in soil.

Cypermethrin apparently dissipated with calculated half-lives of 3 days in California and Louisiana (upgradeable data). The degradates mPBAcid and trans-DCVA were found in inverse proportions in the field compared to the aerobic soil metabolism study. However, the DCVA degradate may have leached in the field as it formed.

Cypermethrin residues accumulated in bluegill sunfish with accumulation factors of 111 and 161x for the edible tissues, 579 and 833x for the nonedible tissues, and 468 and 444x for whole fish for the benzyl and cyclopropyl labels. Metabolites identified in the fish tissues were cyperamide (cyano-hydrated cypermethrin), m-phenoxybenzyl alcohol, m-phenoxybenzoic acid, m-phenoxybenzylaldehyde, cis-dichlorovinyl acid (DCVA), trans-DCVA, and a mixture of DCVA methyl ester isomers. Cyperamide, mPB aldehyde, mPB acid, and cis- and trans-DCVA were identified in the aquarium water. After 14 days of depuration, $\geq$81% of the accumulated [^{14}C]residues were eliminated from the fish tissues.

8. RECOMMENDATIONS: Inform the Registrant that:

(1) The submitted fate information does not present a consistent picture of cypermethrin dissipation in the environment. Therefore, EFGWB cannot determine how cypermethrin will dissipate when used for any New Use Registration at this time. The registrant should see the STATUS of DATA REQUIREMENTS section below for upgrading the 161-1, 161-3, 163-1, and 164-1 data requirements and for explaining the discrepancies in the data.

(2) The bioaccumulation in fish data requirement (165-4) is satisfied with the submitted study, MRID 42868203.

(3) The aged soil leaching-adsorption-desorption (163-1) data requirement may be satisfied with batch equilibrium data on the degradate DCVA.

Status of Data Requirements and Summary of Environmental Fate Data

Satisfied:

Aerobic Soil Metabolism (162-1); MRID 42156601, EFGWB 93-0048, 11/10/93. Cypermethrin degraded with a half-life of 60 days in sandy loam soil. The identified degradates were cis/trans DCVA and MPBAcid, bound residues, and CO_2.

5

Anaerobic Soil Metabolism (162-2); MRID 42156602, EFGWB 93-0048, 11/10/93. Half-life of 53-63 days for acid and alcohol labeled cypermethrin. The identified degradates were cis/trans DCVA and MPBAcid, bound residues, and CO_2.

Bioaccumulation in Fish (165-4); MRID 42868203, this review. Cypermethrin residues accumulated in bluegill sunfish with accumulation factors of 111 and 161x for the edible tissues, 579 and 833x for the nonedible tissues, and 468 and 444x for whole fish for the benzyl and cyclopropyl labels. Metabolites identified in the fish tissues were cyperamide (cyano-hydrated cypermethrin), m-phenoxybenzyl alcohol, m-phenoxybenzoic acid, m-phenoxybenzylaldehyde, cis-dichlorovinyl acid (DCVA), trans-DCVA, and a mixture of DCVA methyl ester isomers. Cyperamide, mPB aldehyde, mPB acid, and cis- and trans-DCVA were identified in the aquarium water. After 14 days of depuration, ≥81% of the accumulated [^{14}C]residues were eliminated from the fish tissues.

Upgradeable: (from 11/10/93 review)

Upgrading Instructions:

Hydrolysis (161-1). The registrant should explain the differences in persistence within the pH 5 buffer solutions between the two studies with differentially-labeled cypermethrin.

Soil Photolysis (161-3). The registrant should determine what competing processes are producing the degradate cyperamide (cyano-hydrated cypermethrin) in the dark controls since cyperamide was not found in the aerobic soil metabolism study reviewed on 11/10/93 (MRID 42156601).

Unaged and Aged Leaching-Adsorption-Desorption (163-1). The registrant should explain why the Freundlich K-values increased in sandy loam soil from adsorption to desorption and why the Freundlich K-values decreased from adsorption to desorption in the sandy loam, silt loam, and clay loam soils.

Terrestrial Field Dissipation. The registrant should identify the route(s) of dissipation in the field and the relative lack of formation of degradates in both studies combined with the rapid degradation. The dissipation rate in the field was faster than the aerobic soil metabolism rate, but the concentrations of degradates detected were far less than in the aerobic soil metabolism study.

Results from Upgradeable Studies:

Hydrolysis (161-1); MRID 42620501, EFGWB 93-0405. Cypermethrin was stable in pH 5 and 7 aqueous buffer solutions (1 % acetonitrile cosolvent) that were incubated at 25 °C in darkness for 30 days, but degraded rapidly in pH 9 solutions

6

that were incubated for 5 days. The calculated half-lives were 769 and 508 days for the pH 5, 188 and 635 days for the pH 7, and 1.8 and 2.5 days for the pH 9 acid (cyclopropyl) and alcohol (phenyl-ring) labels, respectively. The degradates were cis/trans DCVA, MPBAldehyde, and hydrocyanic acid.

Soil Photolysis (161-3); MRID 42129001, EFGWB 92-0396, 11/10/93. Half-life of 55 days on sandy loam soil. Cyperamide was the only significant degradate.

Unaged and Aged Leaching-Adsorption-Desorption (163-1); MRID's 42129002, 42129003, EFGWB 92-0626, 11/10/93. Parent cypermethrin does not appear to be mobile in soil with Freundlich K_{ads} values of 657, 1163, 1897, 416 and K_{des} values of 1263, 192, 602, and 262 on sand (0.23 % OC), sandy loam (1.05 % OC), silt loam (2.5 % OC), and clay loam (2.3 % OC) soils, respectively. K_{oc} values of 259,000, 111,000, 72,000, and 18,000 for adsorption and 549,000, 18,000, 23,000, and 12,000 for desorption, respectively. **Aged residues** of parent cypermethrin and the degradates MPB acid/MPB alcohol were relatively immobile in sandy loam soil columns that were aged for 30 days and leached with 20 inches of 0.01 N $CaCl_2$. Most of the applied radioactivity remained in the treated layer and upper 6 cm of the soil columns. The degradate cis/trans-DCVA was mobile in the soil columns and reached up to 13.2 % of the applied dose in the leachate.

Terrestrial Field Dissipation (California Study, 164-1); MRID 42459601, EFGWB 92-1194, 11/10/93.The half-lives were 3 days (0-7 day sampling intervals) and 51 days for the 7-150 day sampling intervals in a silt loam soil (0.1 % OC) in California treated with 0.6 lbs ai/A. Parent cypermethrin and degradates were not detected below 12 inches of depth.

Terrestrial Field Dissipation (Louisiana Study, 164-1); MRID 42459601, EFGWB 92-1194, 11/10/93. The first half-lives were 3 days (0-14 day sampling intervals) and 254 days for the 14-150 day sampling intervals in a loamy sand soil (0.4 % OC) in Louisiana treated with 0.6 lbs ai/A. Parent cypermethrin and its degradates DCVA and MPBAcid were not detected below 3 inches of depth in Louisiana.

Unsatisfied: (from 11/10/93 review)

Aqueous Photolysis (161-2); MRID 42395701, EFGWB 92-0626, 11/10/93. Study was unacceptable because the microbial contamination of solutions may have confounded the results.

Aged Leaching-Adsorption-Desorption (163-1) for the degradate DCVA, this review.

Spray Drift (201-1 and 202-1)

The registrant may propose to satisfy these data requirements through the Spray Drift Task Force, since they are a member.

Waived:

Photolysis in Air (161-4); Waived on 3/7/91.

Laboratory Volatility (163-2); Waived on 3/7/91.

Field Volatility (163-3); Waived on 3/7/91.

9. BACKGROUND:

A. Introduction

B. Directions for Use

Cypermethrin is a stomach and contact insecticide registered for use to control a wide range of pests, particularly lepidoptera, in cotton, fruit, and vegetables. Cypermethrin is a member of the pyretheroid family of chemicals. Single active ingredient formulations include emulsifiable concentrate, ULV concentrate (in vegetable oil carrier for cotton), and wettable powder. For cotton application, cypermethrin can be tank mixed with other cotton-registered products. Some or all applications of cypermethrin may be classified as RUP.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Refer to attached reviews.

11. COMPLETION OF ONE-LINER: One-liner was updated.

12. CBI APPENDIX: Not applicable.

8

DATA EVALUATION RECORD 1

CHEM 109702 Cypermethrin §165-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42868203

Giroir, L.E., and L. Stuerman. 1993. [^{14}C]Cypermethrin bioconcentration by bluegill sunfish (Lepomis macrochirus). FMC Study No. 191E5491E1; ABC Laboratories Final Report No. 40018. Unpublished study performed by ABC Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 35

REVIEWED BY: J. Harlin
TITLE: Staff Scientist
ORG: Dynamac Corporation
TEL: 301-417-9800

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: EFGWB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt

SIGNATURE:

CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study is acceptable and satisfies the 165-4 data requirement for cypermethrin.

2. Cypermethrin residues accumulated moderately in bluegill sunfish continuously exposed to benzyl or cyclopropyl ring-labeled cypermethrin at 0.20 ppb for 28 days. Maximum bioconcentration factors for the benzyl and cyclopropyl ring-labeled treatments were 111 and 161x for the edible (body, muscle, skin, and skeleton) tissues, 579 and 833x for the nonedible (fins, head, and internal organs) tissues, and 468 and 444x for whole fish. Maximum mean concentrations of total [^{14}C]residues were 21-29 ppb for edible tissues, 110-150 ppb for nonedible tissues, and 80-89 ppb for whole fish. Metabolites identified in the fish tissues were cyperamide (cyano-hydrated cypermethrin), m-phenoxybenzyl alcohol, m-phenoxybenzoic acid, m-phenoxybenzylaldehyde, cis-dichlorovinyl acid (DCVA), trans-DCVA, and a mixture of DCVA methyl ester isomers. Cyperamide, mPB aldehyde, mPB acid, and cis- and trans-DCVA were identified in the aquarium water. After 14 days of depuration, ≥81%

of the accumulated [^{14}C]residues were eliminated from the fish tissues.

METHODOLOGY:

Bluegill sunfish (Lepomis macrochirus; mean weight and length, 5.14 g and 55 mm, respectively) were held in culture tanks containing aerated well water at 22 ± 2 °C and irradiated for 16 hours/day for ≥14 days prior to the initiation of the study. Flow-through aquatic exposure systems were prepared using five 100-L aquaria, which were supplied with aerated well water (pH 7.8-8.2, total hardness 266-296 mg/L as $CaCO_2$, alkalinity 298-320 mg/L as $CaCO_2$; Table I) at a rate of 7.5-7.6 turnovers per day. The water supplied to two of the aquaria (one "radioanalysis" and one "metabolism" aquarium) was continuously treated at 0.20 ppb with benzyl ring-labeled [U-^{14}C]cypermethrin [(RS)-α-cyano-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate; radiochemical purity 98.6%, specific activity 35.4 mCi/mMol, FMC Corporation] dissolved in acetone. Two additional aquaria were treated at 0.20 ppb with cyclopropyl ring-labeled [^{14}C]cypermethrin (radiochemical purity 99.3%, specific activity 56.0 mCi/mMol, FMC Corporation) dissolved in acetone. To serve as the control, the water supplied to the fifth aquarium was treated with an equivalent amount of pesticide-free acetone. The aquaria were covered with glass throughout the experiment to minimize volatilization and evaporation. The flow-through systems were equilibrated for 1 week prior to the introduction of the fish.

Bluegill sunfish (120) were transferred into each aquarium. During the exposure period, water samples (1000 mL) were collected from all aquaria at 0, 1, 3, 7, 10, 14, 21, and 28 days; additional water samples (1500 or 2000 mL) were collected from the "metabolism" aquaria at 1, 7, 21, and 28 days. Six fish were collected from the "radioanalysis" and control aquaria at 0, 1, 3, 7, 10, and 14 days; 20 fish were collected at 21 and 28 days. Sixty fish were collected from the "metabolism" aquaria at 21 and 28 days. Following the 28-day exposure period, the water in the "radioanalysis" and control aquaria was siphoned off to a depth of approximately 8 cm, then the aquaria were filled with approximately 70 L of pesticide-free well water; the water was removed and the aquaria were refilled one additional time. During depuration, water samples (500 mL) and fish (6) were collected from the treated and control aquaria at 1, 3, 7, 10, 14, and 21 days. All water samples were stored frozen at -20 °C prior to analysis; the water samples from the "metabolism" aquaria were mixed with hexane (9:1, v:v) prior to storage. Three fish from each sampling interval were dissected into edible (body, muscle, skin, skeleton) and nonedible (fins, head, internal organs) tissues; the remaining three fish from each sampling interval were used for whole fish analysis. All fish samples were stored at -20 °C prior to analysis.

The water samples were thawed and analyzed for total radioactivity using LSC; subsamples of the edible, nonedible, and whole fish tissues were analyzed for total radioactivity using LSC following combustion.

The water samples were analyzed for specific [^{14}C]compounds using the scheme presented in Figures 2 and 3. The additional water samples (1, 7, 21, and 28 days) that had been collected from the "metabolism" aquaria and stored with hexane were thawed; the water and hexane fractions were separated, and aliquots of both fractions were analyzed for total [^{14}C]residues using LSC. The water fractions were extracted 4-5 times with water-saturated ethyl acetate (extraction procedure not further described), and the ethyl acetate extracts were combined with the corresponding hexane solution. The ethyl acetate-extracted water was acidified (pH 1) and again extracted 4-5 times with ethyl acetate; these extracts were added to the previous ethyl acetate:hexane extract solution. The ethyl acetate:hexane solution was dried with sodium sulfate and transferred to acetonitrile. The acetonitrile solution was concentrated under a nitrogen stream, then brought to volume (1 mL) with acetonitrile. Aliquots of the concentrated acetonitrile solutions were analyzed for total radioactivity using LSC. Additional aliquots were analyzed by HPLC using a Waters Nova-Pak C-18 radial compression column eluted with acetonitrile:water (80:20, v:v); the column was equipped with UV (224 nm) and radioactive flow monitoring. The samples were cochromatographed with unlabeled reference standards of cyperamide, m-phenoxybenzoic acid (mPB acid), m-phenoxybenzylaldehyde (mPB aldehyde), m-phenoxybenzyl alcohol (mPB alcohol), 3-(2'-hydroxyphenoxy)benzoic acid (2'-OH-MPB acid), 3-(4'-hydroxyphenoxy)benzoic acid (4'-OH-MPB acid), 2-hydroxy-3-phenoxybenzoic acid (2-OH-MPB acid), cis-dichlorovinyl acid (cis-DCVA), trans-dichlorovinyl acid (trans-DCVA), and DCVA methyl ester isomers. The acidified ethyl acetate-extracted water samples were analyzed for unextracted [^{14}C]residues using LSC. Extracted water samples that still contained >10% of the applied radioactivity were diluted with water and neutralized (pH 7); aliquots were analyzed using LSC. The diluted sample was placed on an Empore °C-18 disk, then drawn through the disc with a low vacuum. The disc was dried for approximately 10 minutes, then sequentially rinsed with methanol:ethyl acetate (1:1, v:v) and methanol. The rinses were combined, and the organic and aqueous fractions were separated. The aqueous fraction was applied to the Empore extraction disk, which was rinsed as previously described. The organic and aqueous fractions of the rinse were separated, and the organic fraction was added to the initial organic rinse fraction. Duplicate aliquots of the aqueous-soluble fraction were analyzed using LSC. The combined organic fractions were concentrated under a nitrogen stream, diluted with acetonitrile, and again concentrated. Aliquots of the organic concentrate were analyzed using LSC and HPLC as previously described.

//

The edible and nonedible tissue from the fish that had been collected from the "metabolism" aquarium (21 and 28 days) were analyzed for specific [^{14}C]compounds using the scheme presented in Figure 4. The fish tissues were extracted a minimum of four times by homogenization with acetone:iso-octane (1:1, v:v); after each extraction, the samples were centrifuged, then vacuum-filtered. The extracted tissues were analyzed for total radioactivity using LSC following combustion. The fish extracts were concentrated under a nitrogen stream, diluted with iso-octane, and partitioned a minimum of four times with iso-octane-saturated acetonitrile; like fractions were combined and concentrated under a nitrogen stream. Aliquots of the acetonitrile, iso-octane, and aqueous extract fractions were analyzed by LSC. The aqueous-soluble extracts from the nonedible tissues were lyophilized, then analyzed using LSC and HPLC as previously described.

To minimize the interference by tissue components, the concentrated acetonitrile extracts from the nonedible tissue were concentrated, diluted with cyclohexane:methylene chloride (85:15, v:v), and filtered through a Bio-rad Biobeads SX-3 column. [^{14}C]Residues (fractions GPC-1 and GPC-2) were eluted from the columns with cyclohexane:methylene chloride (85:15, v:v), concentrated under a nitrogen stream, and diluted with acetonitrile. Aliquots of both fractions were analyzed for total radioactivity using LSC. Aliquots of the GPC-2 fraction were methylated with diazomethane by frequent shaking for 30 minutes. The reaction mixture was reduced to dryness to remove the diazomethane, then reconstituted in acetonitrile. Aliquots of the original and methylated GPC-2 fractions were analyzed by one-dimensional TLC on normal-phase silica gel plates developed in hexane:ethyl acetate:acetic acid (60:40:1 or 75:25:1), and on reverse-phase plates developed in acetonitrile:water (80:20, v:v). [^{14}C]Residues on the plates were located and quantified using a radioanalytic imaging system, and were identified by comparison to unlabeled reference standards that had been cochromatographed with the samples and visualized under UV light.

DATA SUMMARY:

[^{14}C]Cypermethrin residues accumulated in bluegill sunfish that were continuously exposed to benzyl or cyclopropyl ring-labeled [^{14}C]cypermethrin [(RS)-α-cyano-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate; radiochemical purities ≥98.6%], at 0.20 ug/L, for 28 days under flow-through aquarium conditions. Maximum bioconcentration factors for the benzyl and cyclopropyl ring-labeled treatments were, respectively, 111 and 161x for the edible (body, muscle, skin, and skeleton) tissues, 579 and 833x for the nonedible (fins, head, and internal organs) tissues, and 468 and 444x for whole fish. Maximum mean concentrations of total [^{14}C]residues were 21-29 ppb for edible tissues, 110-150 ppb for nonedible tissues, and 80-89 ppb for whole fish. Metabolites identified in the fish tissues were:

cyperamide (Metabolite A),

m-phenoxybenzyl alcohol (mPB alcohol; Metabolite G),

m-phenoxybenzoic acid (mPB acid; Metabolite B),

m-phenoxybenzylaldehyde (mPB aldehyde; Metabolite C),

cis-dichlorovinyl acid (cis-DCVA; Metabolite D),

trans-dichlorovinyl acid (trans-DCVA; Metabolite E), and

a mixture of DCVA methyl ester isomers (Metabolite F).

After 14 days of depuration, ≥81% of the accumulated [^{14}C]residues were eliminated from the fish tissues.

In fish exposed to benzyl ring-labeled [U-^{14}C]cypermethrin, maximum bioconcentration factors were 111x for the edible tissue, 579x for the nonedible tissue, and 468x for the whole fish (Table III). Maximum mean concentrations of total [^{14}C]residues were 21 ppb for edible tissues (day 28), 110 ppb for nonedible tissues (day 21), and 89 ppb for whole fish (day 21). In the edible fish tissues at 21 and 28 days, cypermethrin was 77.8-82.5% of the recovered (13.20-14.79 ppb), cyperamide was 0.7-4.4% (0.14-0.70 ppb), mPB alcohol was 8.7% (1.40 ppb), and mPB acid was 6.8% (1.30 ppb; Table XXII). In the nonedible tissues at 21 and 28 days, cypermethrin was 48.0-68.1% of the recovered (55.66-85.24 ppb), cyperamide was 0.7-1.2% (0.82-1.40 ppb), mPB aldehyde was 1.7-2.0% (1.98-2.46 ppb), trans-cypermethrin was 0.2% (0.27 ppb); and mPB alcohol was 10.3% (11.93 ppb; Table XXIV). Unidentified extractable [^{14}C]residues totaled ≤1% of the recovered in the edible plus nonedible tissues; unextracted [^{14}C]residues comprised 4.3-4.4% and 9.5-11.7% in the edible and nonedible tissues, respectively (Tables XXII and XXIV). By day 14 of the 21-day depuration period, 77-82% of the accumulated [^{14}C]residues were eliminated from the edible, nonedible, and whole fish samples (Table XIV).

Benzyl ring-labeled [^{14}C]residues in the water of the radioanalysis and metabolite aquaria were 0.14-0.24 and 0.13-0.27 ug/L, respectively (Table III). Cypermethrin was 0.083 ppb after 1 day of exposure, and 0.051-0.070 ppb at later intervals; mPB aldehyde was a maximum of 0.050 ppb, mPB acid was a maximum of 0.064 ppb, and cyperamide was a maximum of 0.010 ppb (Tables XVIII and XIX). During the study, the temperature of the treated water was 21-22 °C, the pH ranged from 7.6 to 8.4, and the dissolved oxygen content ranged from 6.5 to 8.5 mg/L (Table X).

In fish exposed to cyclopropyl ring-labeled [^{14}C]cypermethrin, maximum bioconcentration factors were 161x for the edible (body, muscle, skin, and skeleton) tissue, 833x for the nonedible (fins, head, and internal organs) tissue, and 444x for the whole fish (Table

IV). Maximum mean concentrations of total [^{14}C]residues were 29 ppb for edible tissues, 150 ppb for nonedible tissues, and 80 ppb for whole fish, all at day 28 of the exposure period. In the edible tissues, cypermethrin was 50.1-65.2% of the recovered (13.04-13.68 ppb), cis-DCVA was 21.9-24.9% (4.60-6.47 ppb), trans-DCVA was 3.3-4.4% (0.69-1.14 ppb), and DCVA methyl ester isomers (Metabolite F) totaled 1.7-2.0% (0.41-0.44 ppb; Table XXIII). In the nonedible tissues, cypermethrin was 30.0-45.6% (36.07-59.30 ppb), cis-DCVA was 20.6-21.4% (25.77-26.78 ppb), trans-DCVA was 6.3-9.8% (8.24-11.78 ppb), and DCVA methyl ester isomers totaled 1.7-2.6% (2.27-3.15 ppb; Table XXV). Unidentified extractable [^{14}C]residues totaled ≤1% of the recovered in the edible plus nonedible tissues; unextracted [^{14}C]residues comprised 4.9-6.9% and 7.4-8.3% in the edible and nonedible tissues, respectively (Tables XXIII and XXV). By day 14 of the 21-day depuration period, 83-95% of the accumulated [^{14}C]residues were eliminated from the edible, nonedible, and whole fish samples (Table XV).

Attached, [illegible] EHGWB review of.

Cyclopropyl-labeled [^{14}C]residues in the water of the radioanalysis and metabolite aquaria were 0.13-0.25 and 0.11-0.23 ug/L, respectively (Table IV). Cypermethrin was 0.07 ppb after 1 day of exposure, 0.009 ppb after 7 days, and 0.06-0.07 ppb after 21 and 28 days; cis-DCVA was 0.039-0.05 ppb and trans-DCVA was 0.003-0.01 ppb (Tables XX and XXI). During the study, the temperature of the treated water was 21-22 °C, the pH ranged from 7.6 to 8.3, and the dissolved oxygen content ranged from 6.7 to 8.5 mg/L; values were comparable for the control water (Table XI).

COMMENTS:

1. Based on the reanalysis of water and fish samples stored at -20 °C, the study authors concluded that cypermethrin and its metabolites were stable during storage. "Odd-shaped" peaks observed in the water radiohistograms were attributed to peak splitting that resulted from the co-injection with ethyl acetate.

2. "Unaccounted for" radioactivity, the difference between total [^{14}C]residues measured by LSC of unextracted tissue and total [^{14}C]residues measured by summing the various extracts and extracted tissues, ranged up to 20.4% of the recovered (acetonitrile partition of the day-21 non-edible tissue for the cyclopropyl label). The study authors attributed the "unaccounted for" radioactivity to losses during the various analytical procedures.

3. During the 49-day study, one fish from the benzyl label treatment and seven control fish died. The study authors attributed these mortalities to stress during transfer at study initiation, since they occurred in the early part of the study.

4. Radioactive residues were shown to bind to the glass walls of the storage containers.

5. The study authors calculated half-lives for depuration of benzyl and cyclopropyl ring-labeled [^{14}C]cypermethrin to be 1.2 days. This is consistent with the hydrolysis study that showed rapid degradation in pH 9 water.

Cypermethrin Review

Page _____ is not included in this copy.

Pages 16 through 55 are not included in this copy.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

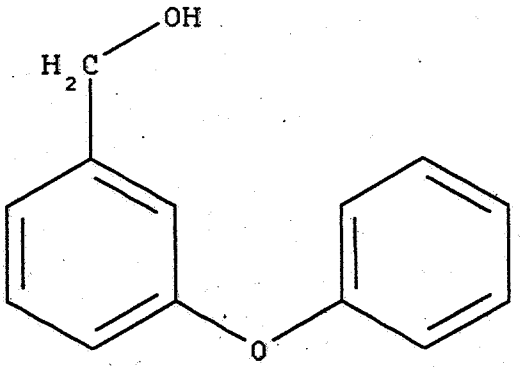
_____ Information about a pending registration action.

X FIFRA registration data.

_____ The document is a duplicate of page(s) _____.

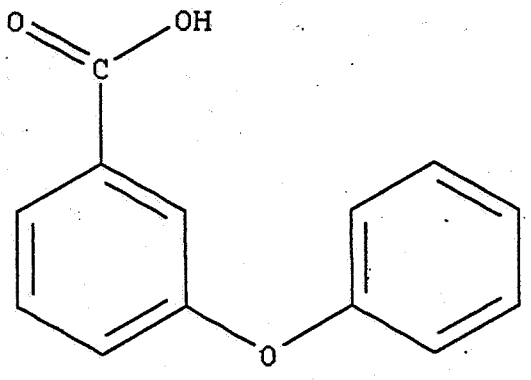
_____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.



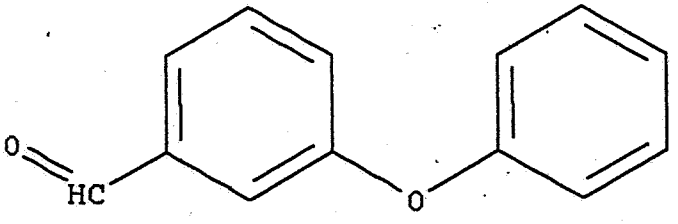
m-Phenoxybenzyl alcohol

(mPB Alcohol)



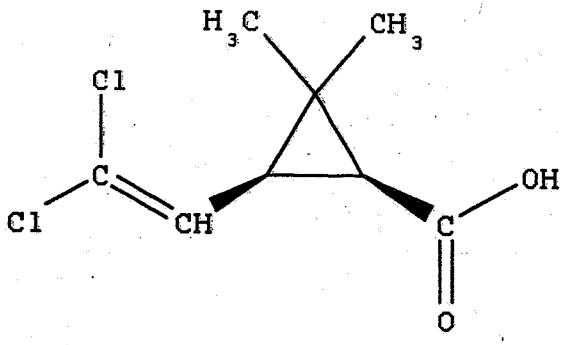
m-Phenoxybenzoic acid

(mPB Acid)



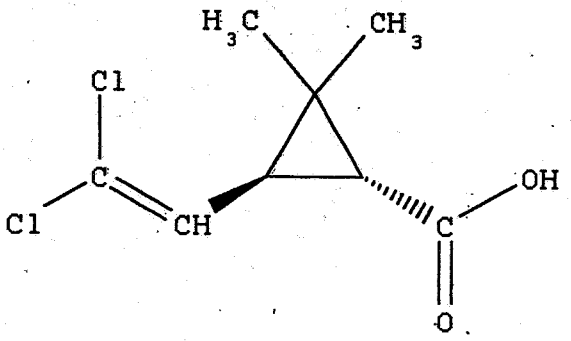
m-Phenoxybenzylaldehyde

(mPB Aldehyde)



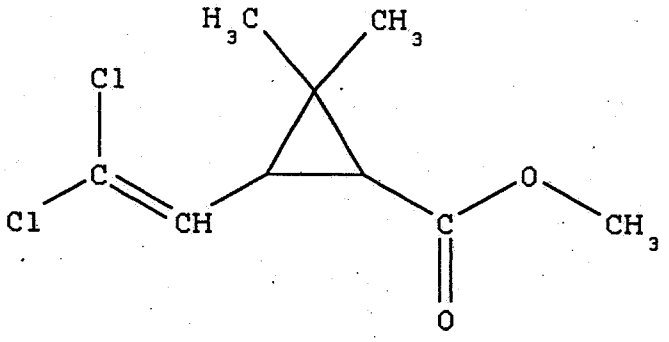
cis-Dichlorovinyl acid

(cis-DCVA)



trans-Dichlorovinyl acid

(trans-DCVA)



DCVA Methyl ester

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on February 23, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer: JAB	Section Head:	Date: MAR 8 1996

Common Name: CYPERMETHRIN
Smiles Code:
PC Code # :109702 CAS #:66841-24-5 Caswell #:

Chem. Name :α-CYANO-3-PHENOXYBENZYL-(+/-)cis,trans-3-(2,2-DICHLORO-VINYL)-2,2-DIMETHYL CYCLOPROPANE CARBOXYLATE
Action Type: Insecticide

Trade Names: AMO; BARRICADE; CYMBUSH
(Formul'tn): VARIOUS EC AND ULV FORMULATIONS
Physical State:

Use :COTTON/PECANS
Patterns :
(% Usage) :
:

Empirical Form: $C_{22}H_{19}NCl_2O_3$
Molecular Wgt.: 416.28 Vapor Pressure: 6.70E -9 Torr
Melting Point : °C Boiling Point: °C
Log Kow : pKa: @ °C
Henry's : E Atm. M3/Mol (Measured) 1.83E -8 (calc'd)

Solubility in ...					Comments
Water	0.20E	ppm	@20.0	°C	
Acetone	E	ppm	@	°C	
Acetonitrile	E	ppm	@	°C	
Benzene	E	ppm	@	°C	
Chloroform	E	ppm	@	°C	
Ethanol	E	ppm	@	°C	?
Methanol	E	ppm	@	°C	
Toluene	E	ppm	@	°C	
Xylene	E	ppm	@	°C	
	E	ppm	@	°C	
	E	ppm	@	°C	

Hydrolysis (161-1)
[S] pH 5.0:769 AND 508 DAYS FOR ACID AND ALCOHOL LABELS
[ ] pH 7.0:188 AND 635 DAYS FOR ACID AND ALCOHOL LABELS
[ ] pH 9.0:1.8 AND 2.5 DAYS FOR ACID AND ALCOHOL LABELS
[ ] pH :DEG WERE DCVA, MPBALDEHYDE, AND HYDROCYANIC ACID
[ ] pH :DCVA AND MPBAldehyde increased to 79 and 65 % of
[ ] pH :applied by 5 dys, respectively, at pH 9.

58
59

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on February 23, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Photolysis (161-2, -3, -4)
[S] Water:100-120 DAYS, pH 5.3, 26C
[ ] :
[ ] :
[ ] :

[S] Soil :8-16 DAYS IN SdLm pH 7.25
[S] Air :SOIL HALF-LIFE OF 55 DAYS ON SD LM. CYPERAMIDE MAIN DEG.

Aerobic Soil Metabolism (162-1)

	SOIL	pH	%OM	T1/2
[S]	ClLm	7.5	12.2	1-3 WKS
[S]	LmSd	6.1	1.8	2 "
[S]	PEAT	9.4	72.0	3 "

[V] 60 DAYS IN SD LM SOIL. DEGRADATES WERE cis- AND trans-DCVA AT
[ ] 24.2 % BY 62 DAYS AND 3-PHENOXY BENZOIC ACID (MPB-ACID) AT 8.4 %.
[ ] CO2 WAS 36-46 % AND BOUND RESIDUES WERE 28-31 % BY 150 DAYS.

Anaerobic Soil Metabolism (162-2)
[V] CYCLOPROPYL LABEL--53 DAYS, PHENYL-LABEL--63 DAYS. DEGRADATES
[ ] WERE CIS AND TRANS DCVA, MPBAcid, AND CO2. DCVA AND MPBAcid WERE
[ ] MAXIMUM OF 13 AND 20 % & 14.3 AND 13.6 % OF APPLIED ON SOIL AND
[ ] IN WATER, RESPECTIVELY. CO2 INCREASED TO 10.9-11.3% BY 60 DAYS
[ ] OF ANAEROBIC CONDITIONS. SOIL-BOUND INCREASED TO 13.2 AND 21%
[ ] BY 60 ANAEROBIC DAYS FOR ACID AND ALCOHOL LABELS, RESPECTIVELY.
[ ]

Anaerobic Aquatic Metabolism (162-3)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Aerobic Aquatic Metabolism (162-4)
[V] <2 WEEKS
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

60

59

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on February 23, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Soil Partition Coefficient (Kd) (163-1)

[S] 1911 IN LmSd, pH 5.4, 2.1%OM

	TEXTURE	OC	pH	CEC	KADS	KOC	KDES	KOC
[ ]	SD	.23	6.0	0.6	657	258652	1263	549130
[ ]	SD LM	1.05	6.9	5.2	1163	110762	191	18190
[ ]	SI LM	2.6	7.4	13.2	1897	72405	602	22977
[ ]	CL LM	2.3	7.0	14.1	416	18326	262	11542

Soil Rf Factors (163-1)

[S] 0.08 SILTY CLAY
[S] 0.13 SILTY CL LM
[S] 0.12-0.16 LOAMY SAND
[S] AGED MOBILITY-73-93% OF RADIOACTIVITY REMAINED IN TOP 6 CM OF
[ ] SOIL COLUMN. 13% OF RADIOACTIVITY WAS FOUND IN LEACHATE AS
[ ] THE DEGRADATE DCVA.

Laboratory Volatility (163-2)

[ ]
[ ]

Field Volatility (163-3)

[ ]
[ ]

Terrestrial Field Dissipation (164-1)

[S] 7-30 DAYS IN UPPER 6" LOAM IN CA AND ARK; CYPERMETHRIN WAS
[ ] <0.15 PPM IN THE 6-12" DEPTH AND DID NOT APPEAR TO LEACH .
[S] 3 DAYS FOR 1st HALF-LIFE AND 50-250 DAYS FOR 2ND HALF-LIFE.
[ ] MPBACID AND DCVA WERE ONLY DEGRADATES DETECTED. NO PARENT
[ ] OR DEGRADATES WERE DETECTED BELOW 6-12 INCHES OF DEPTH.
[ ]
[ ]
[ ]
[ ]
[ ]

Aquatic Dissipation (164-2)

[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Forestry Dissipation (164-3)

[ ]
[ ]

60

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on February 23, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[ ]
[ ]

Accumulation in Rotational Crops, Field (165-2)
[ ]
[ ]

Accumulation in Irrigated Crops (165-3)
[ ]
[ ]

Bioaccumulation in Fish (165-4)
[S] TROUT 1200X WHOLE; DEPURATION T1/2 = 8 DAYS
[S] CATFISH 9X EDIBLE, 14X WHOLE; DEPURATION 70-80% IN 14 DAYS

Bioaccumulation in Non-Target Organisms (165-5)
[V] 165-4 111x, 579x, and 468x for edible, non-edible, and whole
[ ] fish, respectively for benzyl labeled. 161, 833, and 444x

Ground Water Monitoring, Prospective (166-1)
[ ] for cyclopropyl labels.
[ ]
[ ]
[ ]

Ground Water Monitoring, Small Scale Retrospective (166-2)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Large Scale Retrospective (166-3)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Miscellaneous Data (158.75)
[ ]
[ ]
[ ]

~~62~~
61

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on February 23, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Field Runoff (167-1)
[ ]
[ ]
[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Droplet Spectrum (201-1)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

3-phenozybenzoic acid (primary degradate; has long half-life in sediments, as do the other degradates)
Dichlorovinyl acids (CIS AND TRANS DCVA)
3-phenoxybenzaldehyde
Kd for 3-phenoxybenzoic acid = 10.
3-phenoxybenzylmethyl alcohol

62

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on February 23, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Comments

Degradation is faster in soils with low cation exchange capacity and organic matter.
Field monitoring study showed that cypermethrin will be transported via runoff of sediments to adjacent aquatic sites. Leaching potential of cypermethrin is low but may be higher for the degradates.

Cypermethrin, at 500 gm AI/HA, did not affect release of CO2 from soils.

References: EAB FILES
Writer : RWH PJH, JAB

64
63