Date Out: 11/10/93

109702

Chemical Code:

DP Barcode:D173229, D175226, D175741, D180874, D183311, D187908

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To: Linda Deluise, PM 52
Special Review and Reregistration Division (H7508W)

George Larocca, PM 13
Registration Division (H7505C)

From: Akiva Abramovitch, Section Head
Chemistry Review Section 3
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Henry Jacoby 11/10/93

Attached, please find the EFGWB review of...

Common Name:	Cypermethrin	Trade name:	Ammo, Cymbush
Company Name:	FMC		
ID #:	279-3084		
Purpose:	Review of 161-1,2,3, 161-1,2, 163-1, and 164-1 studies for reregistration. Also, proposed new use on tomatoes.		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
Insecticide	330, 604, 620, 606	92-0626, -0396, -1194, 93-0048, -0405, -0986	9 days

STATUS OF STUDIES IN THIS PACKAGE:

Guideline #	MRID	Status[1]
161-1	42620501 42665961	U
161-2	42129003 42395701	I
161-3	42129001	U
162-1	42156601	A
162-2	42156602	A
163-1	42129002 42129003	U
164-1	42549601	U

STATUS OF DATA REQUIREMENTS ADDRESSED IN THIS PACKAGE:

Guideline #	Status[2]
161-1	P
161-2	N
161-3	P
162-1	S
162-2	S
163-1	P
164-1	P

[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 W=Waived.

1. CHEMICAL: Common name:

Cypermethrin.

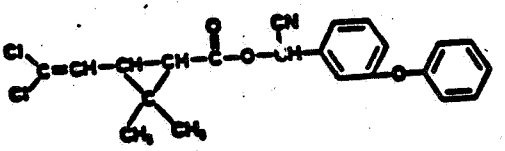
Chemical name (C.A.):

(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, unmerin, 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:

Studies 1-7: Active ingredient.
Study 8: 2.5 EC.

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3. STUDY/ACTION TYPE:

Review of hydrolysis, photodegradation in water and on soil, aerobic and anaerobic soil metabolism, mobility (batch equilibrium and aged column leaching), and terrestrial field dissipation studies. Also, proposed new use on tomatoes.

4. STUDY IDENTIFICATION:

Clifton, J.L. 1992. Environmental fate studies: Hydrolysis studies of cypermethrin in aqueous buffered solutions. Project ID: 191E1192E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (42620501)

Curry, S.J. 1991. Leaching of ^{14}C-cypermethrin in soil following aerobic aging. Laboratory Project ID: 191E3190E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (42129002)

Estigoy, L., L.O. Ruzo, and K. Shepler. 1991a. Photodegradation of ^{14}C-acid and ^{14}C-alcohol cypermethrin in buffered aqueous solution at pH 7 by natural sunlight. PTRL Project No. 247/248W. PTRL Report No. 247/248W-1. FMC Study No. 191E1290E1. FMC Report No. PC-0163. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Richmond, CA, and submitted by FMC Corporation, Princeton, NJ. (42141501)

Estigoy, L., L.O. Ruzo, and K. Shepler. 1991b. Photodegradation of ^{14}C-acid] and ^{14}C-alcohol]cypermethrin in/on soil by natural sunlight. PTRL Project No. 249/250W. FMC Study No. 191E1390E1. FMC Report No. PC-0159. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Richmond, CA and submitted by FMC Corporation, Princeton, NJ. (42129001)

Estigoy, L., L.O. Ruzo, and K. Shepler. 1992. Photodegradation of [^{14}C-acid] and [^{14}C-alcohol]cypermethrin in buffered aqueous solution at pH 7 by natural sunlight. PTRL Project No. 247/248W. PTRL Report No. 247/248W-1. FMC Study No. 191E1290E1. FMC Report No. PC-0163. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Richmond, CA, and submitted by FMC Corporation, Princeton, NJ. (42395701).

Froelich, L.W. 1991. Soil mobility studies: Adsorption/desorption studies of cypermethrin. Laboratory Project ID: 191E3290E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (42129003)

Leppert, B.C. 1992. Ammo 2.5 EC insecticide - terrestrial field dissipation. Study No. 191E4191E1. Unpublished study performed by FMC Corporation, Richmond CA, Pan-Agricultural Laboratories, Inc., Madera, CA, and Pest Management Enterprises, Inc., Cheneyville, LA; and submitted by FMC Corporation, Richmond, CA. (42459601)

Ramsey, A.A. 1990. Environmental fate studies: Aerobic soil metabolism of cypermethrin in a sandy loam soil. FMC Study No. 191E2190E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (42156601).

Ramsey, A.A. 1991. Environmental fate studies: Anaerobic soil metabolism of cypermethrin in a sandy loam soil. FMC Study No. 191E2590E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (42156602).

5. REVIEWED BY:

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

Signature: James Breithaupt
Date: 11/8/93

6. APPROVED BY:

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

Signature: E.B. Conrad-Perkins for ADA
Date: 11/8/93

7. CONCLUSION:

New Use Registration on Tomatoes

The data requirements are not completely satisfied for a New Use Registration on tomatoes. EFGWB is particularly concerned about the mobility of the degradate DCVA and the persistence of cypermethrin in acid and neutral water and under some soil conditions. Also, the field dissipation of cypermethrin has not been fully explained. 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.

Submitted Studies

Hydrolysis (MRID 42620501, DER 1, 161-1, Upgradeable)

The hydrolysis study may be upgraded if the registrant can explain the difference in persistence of acid labeled (188 days) and alcohol labeled (635 days) cypermethrin in sterile, aqueous pH 7 buffered solutions.

Cypermethrin was stable in buffered aqueous (1 % acetonitrile) solutions at pH 5 and 7 that were incubated at 25 °C in darkness for 30 days, but degraded rapidly at pH 9. The calculated half-lives were 769 and 508 days at pH 5, 188 and 635 days at pH 7, and 1.8 and 2.5 days at pH 9 for the acid and alcohol labels, respectively. The parent compound hydrolyzed at the carboxyl-carbon to form cis/trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA), 3-phenoxybenzaldehyde (MPBAldehyde), and hydrocyanic acid. At pH 9, DCVA and MPBAldehyde increased to 78.7 and 64.9 % of the applied radioactivity by 5 days, respectively.

Aqueous photolysis (MRID 42395701, DER 2, 161-2, Unacceptable)

The aqueous photolysis study is unacceptable and does not satisfy the 161-2 data requirement since the photodegradation of cypermethrin and its degradates may have been confounded with microbial degradation. The dark pH 7 buffer solutions for acid- and alcohol-labeled cypermethrin and the irradiated alcohol-labeled solutions showed growth of gram negative bacteria at the end of the study. There was minimal degradation of cypermethrin even in the contaminated dark controls, which is consistent with the above hydrolysis study. The half-life of alcohol-labeled cypermethrin was 20 days in the irradiated, contaminated buffer solution versus the 36 day half-life for acid-labeled cypermethrin in the irradiated, non-contaminated buffer solution. In contrast, the half-life for alcohol-labeled cypermethrin was 3X that for acid-labeled cypermethrin in the hydrolysis study. Therefore, the rate of degradation of cypermethrin due to aqueous photolysis is uncertain.

The degradates identified in the aqueous photolysis study were the aerobic soil metabolism degradates MPBAcid (3-phenoxybenzoic acid) and DCVA, which suggests that some light-catalyzed hydrolysis or biodegradation may be occurring.

Soil photolysis (MRID 42129001, DER 3, 161-3, Upgradeable)

The photodegradation on soil study is upgradeable but does not satisfy the 161-3 data requirement for acid- and alcohol-labeled cypermethrin at this time. 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 in this review.

Cypermethrin degraded with a registrant-calculated half-life of approximately 55 days on a Thurston fine sandy loam soil (pH 6.9) that was irradiated with natural sunlight in California. In the corresponding dark controls, the half-lives for acid and alcohol labeled cypermethrin were 100 and 75 days, respectively. In both the irradiated and dark control soils, cyperamide was the only significant degradate. Cyperamide concentrations in both dark control and irradiated soils were similar throughout the study and increased from 1.7-3.4 % of the applied dose at day 7 to 9.2-13.3 % at 35 days. Even though there was more parent compound present in the dark control samples at 35 days, the cyperamide concentrations exceeded those of the irradiated samples. Therefore, it is apparent that photolysis is not the primary means of degrading cypermethrin to cyperamide. During the 35-day experiments, the cumulative light energy was 243-251 W-minute/cm^2, and soil surface temperatures ranged from 11.5 to 34.6 °C in both the dark and irradiated samples.

Aerobic soil metabolism (MRID 42156601, DER 4, 162-1, Acceptable)

Cypermethrin (both labels) degraded with a half-life of 60 days in sandy loam soil (pH 7) that was incubated in darkness at 25 °C and 75% of field moisture capacity. The identified nonvolatile degradates were cis/trans DCVA, which reached a maximum of 24.2 % of the applied dose by 62 days, and MPBAcid, which reached a maximum of 8.4 % at day 30. CO_2 increased to 35.8-46.1 % of the applied dose by the end of the study (150 days). Soil-bound residues reached 28-32 % by the end of the study.

Anaerobic soil metabolism (MRID 42156602, DER 5, 162-2, Acceptable)

Acid- and alcohol-labeled ^{14}C-cypermethrin degraded with half-lives of 53 and 63 days, respectively, in sandy loam soil (pH 7) that was incubated anaerobically (flooded) at 25 °C in darkness for 60 days at 75% of field capacity, following 32 days of aerobic incubation. The identified non-volatile degradates were DCVA at maximum concentrations of 13 and 20 % on soil and in water, respectively, and MPBAcid at a maximum of 14 % in both matrices. Soil-bound material increased to 13 and 21 % for the acid and alcohol labels, respectively. CO_2 increased to 11 % by 60 days of anaerobiosis.

Soil Mobility (163-1)

The 163-1 data requirement may be satisfied if the unaged batch equilibrium study (MRID 42129003) and aged soil column leaching study (MRID 42129002) are upgraded, and if the registrant provides adsorption-desorption data on the degradate cis/trans DCVA.

Unaged Batch Equilibrium (MRID 42129003, DER 6, 163-1, Upgradeable)

The registrant should explain the increasing Freundlich K-values in sandy soil from adsorption to desorption and the decreasing Freundlich K-values from adsorption to desorption in the sandy loam, silt loam, and clay loam soils. The registrant should also explain the tighter binding of cypermethrin on sandy, sandy loam, and silt loam soils than on a clay loam soil. The sandy and sandy loam soils that showed tighter binding of cypermethrin had significantly less surface area and organic carbon than the clay loam soil, making this result anomalous. If this unaged soil mobility study and the aged soil column leaching study in this review (MRID 42129002) are upgraded, the 163-1 data requirement may be satisfied.

Unaged cypermethrin was immobile in sand, sandy loam, silt loam, and clay loam soils (pH 6-7.4) with Freundlich K_{ads} values of 657 (0.4 % OC), 1163 (1.8 % OC), 1897 (4.5 % OC), and 416 (3.9 % OC), respectively. Freundlich K_{des} values were 1263, 191, 602, and 262, respectively. K_{oc} values ranged from 18,190 - 549,130 for adsorption and desorption.

Aged Soil Column Leaching (MRID 42129002, DER 7, 163-1, Upgradeable)

The soil column leaching study may be upgraded to acceptable if the batch equilibrium study is upgraded.

Residues of parent cypermethrin and the degradates MPB acid and 3-phenoxyphenylmethanol (MPB alcohol) were relatively immobile in sandy loam soil (pH 7, 1.05 % OC) columns that were aged for 30 days and leached with 20 inches of 0.01 N $CaCl_2$. About 73-93 % of the applied radioactivity remained in the treated layer and upper 6 cm of the soil columns. However, the degradate cis/trans-DCVA was mobile in the soil columns. Up to 13.2 % of the applied radioactivity was found in the leachate as cis/trans DCVA.

Terrestrial Field Dissipation (MRID 42459601, DER 8, 164-1, Upgradeable)

The 164-1 data requirement may be satisfied for the 2.5 EC, 2E, 3E, and 40 WP formulations of cypermethrin if the registrant can identify the route of dissipation of cypermethrin in the field. The registrant should also explain the relative lack of formation of degradates in both studies combined with the rapid dissipation. The first half-life in the 164-1 study for both locations was 3 days for the 0-7 day and 0-14 day sampling intervals in California and Louisiana, respectively, which is far less than the reported half-life in the aerobic soil metabolism study in this review (60 days). While the study shows dissipation, it does not explain the environmental fate of cypermethrin.

Cypermethrin (2.5 EC), at 0.6 lb ai/A, dissipated with reviewer-calculated first half-lives of 3 days in bareground plots of California silt loam (0-7 days) and Louisiana loamy sand soil (0-14 days), followed by half-lives of 51 and 254 days in California and Louisiana for the remaining sampling intervals, respectively. The identified cypermethrin degradates were MPBAcid (both sites) and trans-DCVA (Louisiana site only). Cypermethrin was detected only once (0.01 ppm) in the 6-12 inch soil depth at 2 days after treatment in California, and was not detected below 3-6 inches of depth in Louisiana. Also, no degradates were detected below 3 inches of depth. DCVA was not detected in the California field dissipation study while the MPBacid degradate was detected as late as 62 days after treatment. This is inconsistent with the aerobic soil metabolism study in this review (MRID 42156601) where the degradate DCVA was produced in greater quantity and was more persistent than the MPBacid degradate. However, DCVA may have formed and leached at levels lower than detection since it was found in the leachate at 13 % of the applied dose in an aged soil column leaching study (MRID 42129002).

The extraction methods used in this study were very harsh but may have been necessary due to the low application rate and high adsorption of cypermethrin.

ENVIRONMENTAL FATE ASSESSMENT

Based on available data, cypermethrin is a moderately persistent chemical that primarily degrades by biodegradation. Hydrolysis proceeds only at pH 9 and photodegradation does not appear to be important. The degradate DCVA appears to be mobile in soil, but cypermethrin and the other degradates did not demonstrate mobility. Cypermethrin is stable in water, not susceptible to photodegradation, and is moderately persistent to soil metabolism. However, the high Freundlich K_{ads} and K_{des} values indicate that parent compound is tightly bound to soil particles and is not likely to move to ground water. One degradate, DCVA, is mobile and could contaminate ground water if cypermethrin is used in highly vulnerable areas.

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. The reported half-lives in soil photolysis, aerobic soil metabolism, and anaerobic soil metabolism are 53-63 days for both the acid and alcohol labels. The primary degradates are cis/trans DCVA, MPBAcid, cyperamide and MPBAldehyde. Parent cypermethrin does not appear to be mobile in soil with Freundlich K_{ads} and K_{des} values of 191 - 1867 and K_{oc} values of 18,000 - 540,000 on sand, loamy sand, silt loam, and clay loam. However, 13.2 % of the applied radioactivity was found in the leachate as the degradate DCVA in an aged soil column leaching study. No other degradate appears to be mobile in soil.

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8. RECOMMENDATIONS: Inform the Registrant that:

(1) The data requirements are not completely satisfied for a New Use Registration on tomatoes. EFGWB is particularly concerned about the mobility of the degradate DCVA and the persistence of cypermethrin in acid and neutral water and under some soil conditions.

(2) The aerobic soil metabolism (MRID 42156601) and anaerobic soil metabolism (MRID 42156602) studies are acceptable and satisfy the 162-1, and 162-2 data requirements.

(3) The hydrolysis study (MRID 42620501) may be upgraded if the registrant can explain the difference in persistence of acid labeled (188 days) and alcohol labeled (635 days) cypermethrin in sterile, aqueous pH 7 buffered solutions.

(4) The soil photolysis (MRID 42129001, 161-3) study may be upgraded to acceptable if the registrant can determine what competing processes are producing the degradate cyperamide (cyano-hydrated cypermethrin) in both irradiated and dark control samples when cyperamide was not detected in the aerobic soil metabolism study.

(5) The leaching-adsorption-desorption data requirement may be satisfied if the registrant upgrades the soil mobility studies (MRID's 42129002 and 42129003) and provides batch equilibrium information on the degradate cis/trans DCVA. The registrant should explain the increasing Freundlich K-values in sandy soil from adsorption to desorption and the decreasing Freundlich K-values from adsorption to desorption in the sandy loam, silt loam, and clay loam soils. The registrant should also explain the tighter binding of cypermethrin on sandy, sandy loam, and silt loam soils than on a clay loam soil.

(6) The terrestrial field dissipation study (MRID 42549601, 164-1) may be upgraded to acceptable if the registrant can identify the route of dissipation in the field and explain the relative lack of formation of degradates in both studies combined with the rapid dissipation. If upgraded, the 164-1 data requirement may be satisfied for the 2.5 EC, 2E, 3E, and 40 WP formulations of cypermethrin.

(7) The aqueous photolysis study (MRID 42395701) is unacceptable and does not satisfy the 161-2 data requirement because microbial contamination of solutions appear to have confounded the results.

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Status of Data Requirements and Summary of Environmental Fate Data

Satisfied:

Aerobic Soil Metabolism (162-1); MRID 42156601, EFGWB 93-0048. 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.

Anaerobic Soil Metabolism (162-2); MRID 42156602, EFGWB 93-0048. 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.

Upgradeable:

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 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. Half-life of 55 days on sandy loam soil. Cyperamide was the only significant degradate.

Leaching-Adsorption-Desorption (163-1); MRID's 42129002, 42129003, EFGWB 92-0626. Unaged cypermethrin was immobile in sand, sandy loam, and silt loam soils, and clay loam soils with 0.2-2.6 % OC with Freundlich K_{ads} values of 416 - 1897. Freundlich K_{des} values were 191 - 1263 and K_{oc} values ranged from 18,190 - 549,130. 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. 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.

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Terrestrial Field Dissipation (Louisiana Study, 164-1); MRID 42459601, EFGWB 92-1194. 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:

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

Bioaccumulation in Fish (165-4). No data have been submitted.

Confined Crop Accumulation (165-1); The study should be submitted to the Health Effects Division.

Field Crop Accumulation (165-2); The study should be submitted to the Health Effects Division.

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.

Spray Drift (201-1 and 202-1)

Because the registrant is a member of the Spray Drift Task Force, EFGWB concurs with the request that the droplet size spectrum and field drift evaluation data submissions be delayed until the final report of the Task Force is to be submitted (December 1994). EFGWB agrees that these data requirements may be satisfied through the work of the Spray Drift Task Force, provided that HED or EEB have no need of these data in advance of the Task Force's final report to be submitted in December 1994. This recommendation is in accordance with PR Notice 90-3 (4/10/90), allowing registrants to fulfill the spray drift (201-1 and 202-1) data requirements through the Task Force. If the registrant elects to satisfy these data requirements through the Task Force, the procedures outlined in PR Notice 90-3 should be followed.

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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.

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DATA EVALUATION RECORD 1

CHEM 109702 Cypermethrin §161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42620501
Clifton, J.L. 1992. Environmental fate studies: Hydrolysis studies of cypermethrin in aqueous buffered solutions. Project ID: 191E1192E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 22

REVIEWED BY: R. Morris
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J. Breithaupt

SIGNATURE:

CONCLUSIONS:

Degradation - Hydrolysis

1. The hydrolysis study is upgradeable and does not satisfy the 161-1 data requirement at this time. The registrant should explain the difference in persistence of acid labeled (188 days) and alcohol labeled (635 days) cypermethrin in sterile aqueous pH 7 buffer solutions.

2. Cypermethrin was stable in buffered aqueous (1 % acetonitrile) pH 5 and 7 solutions that were incubated at 25 °C in darkness for 30 days, but degraded rapidly at pH 9. The calculated half-lives were 769 and 508 days at pH 5, 188 and 635 days at pH 7, and 1.8 and 2.5 days at pH 9 acid and alcohol labels, respectively. The parent compound hydrolyzed at the carboxyl-carbon to form cis/trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA), 3-phenoxybenzaldehyde (MPBAldehyde), and hydrocyanic acid. At pH 9, DCVA and MPBAldehyde increased to 78.7 and 64.9 % of the applied dose by 5 days, respectively.

METHODOLOGY:

Cyclopropyl ring-labeled [^{14}C]cypermethrin [(*RS*)-cyano(3-phenoxyphenyl)methyl (1*RS*)-*cis*,*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate; labeled at the 1-carbon position; radiochemical purity 99.4%, specific activity 49.7 mCi/mMol, Amersham] or phenyl ring-labeled [^{14}C]cypermethrin (uniformly labeled; radiochemical purity 98.3%, specific activity 29.1 mCi/mMol, Sigma), dissolved in filter-sterilized acetonitrile, were added at 11-12 ppb and 9-12 ppb, respectively, to sterile (autoclaved) amber glass vials containing filter-sterilized aqueous buffer solutions adjusted to pH 5 (0.01 M acetate), pH 7 (0.01 M Tris), or pH 9 (0.01 M borate). The cosolvent (acetonitrile) was 1% by volume. The vials were sealed with Teflon-lined caps, shaken vigorously, and incubated in darkness at 25 ± 1 °C. The pH 5 and 7 solutions were incubated for 30 days; the pH 9 solutions were incubated for 120 hours. Duplicate vials of the pH 5 and 7 solutions were removed immediately posttreatment and at 2, 4, 7, 14, 21, and 30 days posttreatment; duplicate vials of the pH 9 solution were removed immediately posttreatment and at 12, 24, 36, 48, 72, and 120 hours posttreatment.

The test solutions were acidified (pH 2) using 1 N HCl then transferred to C-18 Bond Elut cartridges. The amber glass vials were rinsed with acetonitrile, and aliquots of the rinsates were analyzed by LSC. The C-18 Bond-Elut cartridges were eluted with buffer and then centrifuged to remove all the eluate; aliquots of the eluate were analyzed by LSC. The cartridges were next extracted with methylene chloride, and aliquots of the methylene chloride extracts were analyzed by LSC. Additional aliquots of the methylene chloride extracts and the acetonitrile rinsates from the vials were analyzed by TLC on silica gel plates developed in toluene:ethyl acetate:glacial acetic acid (75:25:1, v:v:v). Radioactive areas were located by radioscanning; unlabeled reference standards were chromatographed and visualized under UV light to confirm R_f values. Radioactive areas were scraped from the plates and analyzed by LSC. To confirm identification of the degradates, additional aliquots of methylene chloride extracts and the acetonitrile rinsates were analyzed by HPLC on a C-18 column eluted with acetonitrile:0.01 M acetic acid (80:20, v:v) using UV (214 nm) detection; eluate fractions were collected and analyzed by LSC. The C-18 matrix from the Bond-Elut cartridges was analyzed by LSC following combustion.

In order to obtain degradates for additional analyses, 1 L of pH 9 buffer solution was treated with cyclopropyl or phenyl ring-labeled [^{14}C]cypermethrin at a nominal concentration of 10 ppb. The solution was incubated for 3 days and extracted with methylene chloride on a C-18 Bond Elut cartridge as described above. The methylene chloride extracts were analyzed by TLC as described above prior to concentration under a stream of nitrogen; the concentrates were analyzed by GC/MS.

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DATA SUMMARY:

Cyclopropyl ring-labeled [^{14}C]cypermethrin [(*RS*)-cyano(3-phenoxyphenyl)methyl (1*RS*)-*cis*,*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate; labeled at the 1-carbon position; radiochemical purity 99.4%] and phenyl ring-labeled [^{14}C]cypermethrin (uniformly labeled; radiochemical purity 98.3%), at 9-12 ppb, were relatively stable in pH 5 and 7 sterile aqueous buffer solutions incubated in darkness at 25 ± 1 °C for up to 30 days. In aqueous buffer solutions adjusted to pH 9, cyclopropyl and phenyl ring-labeled [^{14}C]cypermethrin, at 9-12 ppb, degraded with a registrant-calculated half-life of 1.8 and 2.5 days, respectively, when incubated in darkness at 25 ± 1 °C for up to 120 hours (Table XV). The degradate identified in the solutions treated with cyclopropyl ring-labeled [^{14}C]cypermethrin was

(1*RS*)-*cis*,*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA),

detected at pH 9 only. In the phenyl ring-labeled [^{14}C]cypermethrin solutions,

3-phenoxybenzaldehyde (MPBAldehyde),

was detected at all pH values.

In pH 5 buffered solutions treated with cyclopropyl ring-labeled [^{14}C]cypermethrin, cypermethrin was 98.1-98.6% of the applied radioactivity immediately posttreatment, 96.5-99.0% at 2-21 days posttreatment, and 95.1-95.4% at 30 days posttreatment (Table XIV). Material balances were 78.2-92.5% of the applied radioactivity with no discernible pattern (Table V).

In pH 5 buffered solutions treated with phenyl ring-labeled [^{14}C]cypermethrin, cypermethrin was 97.0-98.0% of the applied immediately posttreatment, 93.6-97.1% at 2-14 days posttreatment, and 92.1-94.4% at 21-30 days posttreatment (Table XIV). MPBAldehyde was ≤0.7% of the applied at all sampling intervals (Table XI). Material balances were 77.2-92.6% of the applied with no discernible pattern (Table V).

In pH 7 buffered solutions treated with cyclopropyl ring-labeled [^{14}C]cypermethrin, cypermethrin was 98.7-98.8% of the applied immediately posttreatment, 97.4-98.8% at 2-4 days posttreatment, 92.8-95.9% at 7-14 days, and 87.8-91.9% at 21-30 days posttreatment (Table XIII). Material balances were 74.9-96.7% of the applied with no discernible pattern (Table IV).

In pH 7 buffered solutions treated with phenyl ring-labeled [^{14}C]cypermethrin, cypermethrin was 96.6-96.8% of the applied immediately posttreatment, 95.5-98.2% at 2-14 days, and 92.5-93.9% at 21-30 days posttreatment (Table XIII). MPBAldehyde was ≤0.7% of the

applied immediately posttreatment, ≤1.4% at 2-4 days posttreatment, 1.9-3.0% at 7-14 days posttreatment, 5.8-6.2% at 21 days posttreatment, and not detected at 30 days posttreatment (Table IX). Material balances were 77.1-94.8% of the applied with no discernible pattern (Table IV).

In pH 9 buffered solutions treated with cyclopropyl ring-labeled [^{14}C]cypermethrin, cypermethrin was 96.2-97.0% of the applied immediately posttreatment, 72.3-73.2% at 12 hours, 58.6-59.1% at 24 hours, 43.6-46.0% at 36 hours, 34.6-34.8% at 48 hours, 23.4-23.9% at 72 hours, and 13.9-16.0% at 120 hours (Table XII). DCVA was not detected immediately posttreatment, was 22.5-24.0% at 12 hours, 35.2-35.3% at 24 hours, 49.6-49.7% at 36 hours, 53.0-58.0% at 48 hours, 68.3-70.9% at 72 hours, and 77.2-80.1% at 120 hours (Table VI). Material balances were 72.4-100.1% of the applied with no discernible pattern (Table III).

In pH 9 buffered solutions treated with phenyl ring-labeled [^{14}C]cypermethrin, cypermethrin was 90.1-90.8% of the applied immediately posttreatment, 71.8-74.0% at 12 hours, 64.4-71.3% at 24 hours, 57.1-58.7% at 36 hours, 50.5-50.8% at 48 hours, 33.7-39.1% at 72 hours, and 21.9-23.6% at 120 hours (Table XII). MPBAldehyde was not detected immediately posttreatment, was 13.5-14.1% at 12 hours, 20.5-24.1% at 24 hours, 29.6-32.3% at 36 hours, 38.9-39.6% at 48 hours, 53.7-55.4% at 72 hours, and 62.7-67.0% at 120 hours (Table VII). Material balances were 91.5-125.3% of the applied with no discernible pattern (Table III).

COMMENTS:

1. The reported solubility of cypermethrin in water with no cosolvent is 7.6 ppb. In this study, the concentration of cypermethrin in the aqueous solutions with 1 % acetonitrile was 9-12 ppb. Subdivision N guidelines state that the test substance must be in solution at all sampling intervals. Even though the solubility of cypermethrin in the aqueous co-solvent was not reported, it is very likely that the cosolvent was more than adequate to prevent supersaturation from the additional 1-4 ppb concentration.

2. All organic solvent extracts were stored in a freezer prior to analyses for an unspecified time period at -17 °C. Aqueous samples were stored in a refrigerator prior to analyses for an unspecified time period at 3 °C. The study author stated storage stability experiments demonstrated that unlabeled cypermethrin in acetonitrile was stable stored at -17 °C for up to 8 months.

3. The study author stated that the variability of the material balances was due to the binding of cypermethrin to glass. Cypermethrin recovered in the rinsates was 26.7-45.5% and 19.3-46.8% of the applied in the pH 5 cyclopropyl and phenyl ring-labeled solutions, respectively; 21.0-33.7% and 16.5-39.1% in the pH 7 cyclopropyl and phenyl ring-labeled solutions, respectively; and 1.9-15.4% and 11.3-

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39.1% in the pH 9 cyclopropyl and phenyl ring-labeled solutions, respectively.

Cypermethrin Review

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DATA EVALUATION RECORD 2

CHEM 109702 Cypermethrin §161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42395701
Estigoy, L., L.O. Ruzo, and K. Shepler. 1992. Photodegradation of [^{14}C-acid] and [^{14}C-alcohol]cypermethrin in buffered aqueous solution at pH 7 by natural sunlight. PTRL Project No. 247/248W. PTRL Report No. 247/248W-1. FMC Study No. 191E1290E1. FMC Report No. PC-0163. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Richmond, CA, and submitted by FMC Corporation, Princeton, NJ.

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. The aqueous photolysis study is unacceptable and does not satisfy the 161-2 data requirement since the photodegradation of cypermethrin and its degradates may have been confounded with microbial degradation. The dark buffer solutions for acid and alcohol labeled cypermethrin and the irradiated alcohol-labeled solutions showed growth of gram negative bacteria at the end of the study while incubated at an average temperature of 25.3 °C. The half-life of the alcohol-labeled cypermethrin in the contaminated buffer solution was 20 days, versus the 36-day half-life in the non-contaminated acid-labeled cypermethrin buffer solution. Therefore, it appears that the contamination may have led to an increased rate of degradation of cypermethrin.

2. This study contains additional information on degradates and supersedes MRID 42141501, another recently-submitted aqueous photolysis study.

METHODOLOGY:

Cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the 1-carbon position; radiochemical purity 95.4%, specific activity 300,200 dpm/ug, FMC Corporation) was dissolved in acetonitrile. Aliquots (2 mL) of the stock solution were mixed with filter-sterilized (0.22 um) 0.0048 M pH 7 phosphate buffer solution (8 mL) in quartz and foil-covered Pyrex tubes. The resulting solutions were vortexed; the final concentration of ^{14}C-cypermethrin and acetonitrile in the solutions was 0.1 ppm and 20% by volume, respectively. The tubes were placed at a 60° vertical angle in a circulating water bath located outdoors in Richmond, California (37.45°N, 122.26°W) between March and April, 1991; the samples were maintained at 22.6-28.8 °C (mean 25.1 ± 0.6 °C). The daily sunlight intensity ranged from 57 to 24592 uW/cm^2; the daily light energy ranged from 3.44 to 10.56 W-minute/cm^2; and the cumulative light energy for the 30-day period was 281.59 W-minute/cm^2 (Table VA). A thermocouple and a photodetector probe were located inside the water bath to monitor environmental conditions. Filter-sterilized air was continuously drawn through the sample tubes, then through ethylene glycol (one tube) and 10% NaOH (two tubes) trapping solutions (Figure 4). Tubes of untreated buffer solution were incubated with the samples to monitor for bacterial contamination at the start and completion of the experiment. Duplicate tubes of the irradiated and dark control solutions were collected for analysis at 0, 8, 14, 22, and 30 days posttreatment. The trapping solutions were collected for analysis at 14 and 30 days posttreatment.

Phenyl ring-labeled ^{14}C-cypermethrin (uniformly labeled; radiochemical purity 96.9%, specific activity 188,800 dpm/ug, FMC Corporation) was dissolved in acetonitrile and mixed with phosphate buffer solution as previously described. The samples were irradiated with sunlight in Richmond, California, between January and March 1991. During the experiment, the temperature of the solutions was maintained at 21.6-27.1 °C (mean 25.3 ± 0.5 °C). The daily sunlight intensity ranged from 59 to 86479 uW/cm^2; the daily light energy ranged from 1.14 to 9.81 W-minute/cm^2 and the cumulative light energy for the 35-day period was 250.84 W-minute/cm^2 (Table VB). Duplicate tubes of the irradiated and dark control solutions were collected for analysis at 0, 7, 14, 21, 28, and 35 days posttreatment. The trapping solutions were collected for analysis at 14 and 35 days posttreatment.

All samples were "generally" analyzed within 72 hours after collection, and were stored frozen (<0 °C) when not in use. The samples were combined with an acetonitrile rinse of their respective sample tubes, and aliquots of the combined solutions were analyzed for total radioactivity using LSC. Additional aliquots of the solutions were analyzed for cypermethrin and its degradates by HPLC using a Supelco C-18 column eluted with a water to acetonitrile linear gradient, and with radioactivity and UV (254 nm) detection. Column eluate fractions (0.5 mL) were collected and analyzed by LSC.

HPLC recovery efficiencies averaged 95.4 ± 6.3% for the cyclopropyl label and 97.5 ± 9.0% for the phenyl label; the quantification and detection limits were 50 and 10 dpm, respectively. Additional aliquots of the final samples (30 or 35 days) were analyzed by two-dimensional TLC on silica gel plates developed in cyclohexane (saturated with formic acid):ether (3:1, v:v) in the first direction and toluene (saturated with formic acid):ether (10:1, v:v) in the second direction. Samples were cochromatographed with reference standards of cypermethrin and the degradates (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DV acid); (RS)-carbamoyl(3-phenoxyphenyl)-methyl(1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (cyperamide); and 3-phenoxybenzoic acid (MPB acid). ^{14}C-Compounds were identified by comparison to the R_f values of the reference standards. Radioactive areas were located using a linear analyzer or autoradiography, and identified by comparison to the standards.

Aliquots of the trapping solutions were analyzed for total radioactivity using LSC. ^{14}C-Residues in the NaOH trapping solutions were confirmed to be CO_2 by barium chloride precipitation.

Aliquots of the untreated buffer solutions were analyzed using MacKonkey and blood plates; no additional microbial analytical methodology was provided.

In an attempt to generate additional degradate material for identification, an acetonitrile solution of cyclopropyl ring-labeled ^{14}C-cypermethrin was mixed with pH 7 buffer solution (0.4 and 1.6 L, respectively) and irradiated with sunlight for 30 days. There was a constant flow of air through the solution. At 30 days, an aliquot of the irradiated solution was analyzed using HPLC as described; the remaining solution was extracted with ethyl acetate. The aqueous layer which contained 22% of the applied radioactivity was lyophilized and the resulting residues were redissolved in water. Aliquots of the aqueous solution were analyzed by HPLC using a Dionex PCX-500 column eluted with an acidified water:acidified acetonitrile gradient, and with radioactivity and UV (254 nm) detection. Additional aliquots were analyzed by two-dimensional TLC as described.

The concentrated aqueous solution was further extracted and analyzed according to the flowchart presented in Figure 12. The solution was extracted twice with ethyl acetate (Fraction 1), acidified to pH 1, and again extracted with ethyl acetate (Fraction 2). The extracted acid solution was adjusted to pH 6 and evaporated under vacuum to near dryness. The "white salt" that formed upon drying was washed with acetonitrile followed by methanol; the wash solutions were combined (Fraction 3). The salt was then dissolved in water (Fraction 4) and concentrated under nitrogen. Precipitates that formed during the concentration procedure were separated from the "relatively salt-free" supernatant (Fraction 5); the precipitates were dissolved in water to produce a "salt-enriched" solution

(Fraction 6). Prior to analysis, Fractions 1 and 5 were concentrated under nitrogen, and any precipitates formed during concentration were removed by filtration and centrifugation. Individual fractions were analyzed by LSC and by HPLC using a Phenomenex Ultracarb (20) ODS column and a Brownlee RP-18 guard column eluted with linear gradient of water to acidified acetonitrile, and with radioactivity and UV (250 nm) detection. Column eluate fractions were collected and analyzed by LSC. Also, fractions that were found to contain more than one radioactive component were purified by TLC. Radioactive components in Fractions 1 and 2 were isolated by one-dimensional TLC on silica gel plates developed in ethyl acetate:toluene:acetic acid (80:15:5, v:v:v). Radioactive components in Fraction 3 were isolated by one-dimensional TLC on silica gel plates developed in methanol:water (9:1, v:v). ^{14}C-Compounds were scraped from the TLC plates, desorbed from the silica with ethyl acetate followed by methanol, concentrated under nitrogen, and analyzed using EI/CI MS.

DATA SUMMARY:

Cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin (radiochemical purities ≥95.4%), at 0.1 ppm, photodegraded with registrant-calculated half-lives of 36.1 and 20.2 days, respectively, in pH 7 aqueous buffered solutions that were irradiated with sunlight in California for 30 or 35 days. ^{14}C-Cypermethrin degraded slightly (<10% of the applied) in nonsterile dark control solutions during 30-35 days of incubation. The irradiated phenyl ring-labeled solution and both dark control solutions were not sterile during the experiment, and the cyclopropyl ring-labeled solution was described only as being free of gram negative bacilli. In the irradiated solutions, the major degradates identified were 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DV acid) and 3-phenoxybenzoic acid (MPB acid).

Cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the 1-carbon position; radiochemical purity 95.4%), at 0.1 ppm, photodegraded with a registrant-calculated half-life of 36.1 days in "gram negative bacilli"-free, pH 7 aqueous buffered solutions that were irradiated outdoors at 22.6-28.8 °C for 30 days in California. The cumulative sunlight energy for the 30-day period was 281.59 W-minute/cm^2. In duplicate irradiated samples at 30 days posttreatment, cypermethrin was 47.7 and 55.3% of the applied,

> 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DV acid)

was 3.8 and 10.1%, and Unknown A was 18.5 and 23.9% (Table VIA). Following extraction of the aqueous layer of the 30-day sample, 14.1% of the applied was in the ethyl acetate (acidic) fraction, 3.3% was in the aqueous fraction, 2.5% was in the ethyl acetate fraction, and 2.1% was in the acetonitrile:methanol fraction (Table VII). Based on TLC analysis of the aqueous layer, it was determined that Unknown A was comprised of at least eight components, each at 0.8-5.4% of the

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applied radioactivity (Table X). Also at 30 days, up to 24 unidentified minor ^{14}C-compounds, each present at ≤4% of the applied, totaled 18.4 and 27.6% of the applied, and $^{14}CO_2$ totaled 5.8%.

In the nonsterile dark control solutions at 30 days posttreatment, cypermethrin comprised 81.3-87.4% of the applied, Unknown A was 5.4-5.9%, unidentified ^{14}C-compounds totaled 10.3-13.9%, and $^{14}CO_2$ was 1.5%.

During the experiment, the material balance for the irradiated samples ranged from 96.2 to 111.5% of the applied, and for the dark controls ranged from 87.9 to 104.3% (Table IIA).

Phenyl ring-labeled ^{14}C-cypermethrin (uniformly labeled; radiochemical purity 96.9%), at 0.1 ppm, photodegraded with a registrant-calculated half-life of 20.2 days in nonsterile pH 7 aqueous buffered solutions that were irradiated outdoors at 21.6-27.1 °C for 35 days in California. The cumulative light energy for the 35-day period was 250.84 W-minute/cm^2. In duplicate irradiated samples, ^{14}C-cypermethrin was 86.9 and 91.3% of the applied immediately posttreatment, 57.9 and 69.9% at 14 days, 39.3 and 51.9% at 21 days, and 22.4 and 28.2% at 35 days (Table VIB). The major degradate,

3-phenoxybenzoic acid (MPB acid)

increased to a maximum of 33.3-35.9% of the applied at 35 days posttreatment; minor degradates included up to 29 unidentified ^{14}C-compounds, each at ≤8.9% and totaling up to 35.0% of the applied, and one unidentified ^{14}C-compound that was detected only once, at 11.2% in one of duplicate samples collected at 7 days. $^{14}CO_2$ totaled 1.4% of the applied during the 35-day experiment.

In the nonsterile dark control solutions at 35 days posttreatment, cypermethrin was 82% of the applied, MPB acid was 6.3%, 24 unidentified degradates totaled 11.7%, and $^{14}CO_2$ was ≤0.1%.

During the experiment, the material balance for the irradiated samples ranged from 83.6 to 114.5% of the applied, and for the dark controls ranged from 84.8 to 111.7% (Table IIB).

COMMENTS:

1. The photodegradation of cypermethrin and its degradates in the buffer solutions may have been confounded with microbial degradation. Untreated buffer solutions were incubated with the treated samples to serve as solution sterility checks; however, the value of the checks were limited because the solutions were tested only on MacKonkey and blood agars for gram negative enterics (sewage coliforms, streptococcus, staphylococcus, etc.). Also, the relationship between the sterility of the untreated buffers and the samples was tenuous.

Because of the pattern of contamination, it appeared that contamination may have occurred either during the transfer of the stock solution into the sample tubes or during incubation. This would suggest that individual tubes rather than an entire sample set were contaminated (in this case, it would have been more accurate to test the sterility of the samples themselves).

The untreated buffer stock solution tested immediately posttreatment did not contain gram negative bacilli. The untreated solutions incubated with the phenyl ring-labeled sample set and the untreated buffer solutions incubated with both dark controls contained gram negative bacilli at the termination of the experiments. The cyclopropyl ring-labeled sample set was reported to contain no gram negative bacilli. The study authors stated that "Since minimal degradation occurred in the dark controls and there was agreement between the light-exposed acid and alcohol labels, it is anticipated that no adverse impact on the study results occurred." While it is true that degradation in the dark controls was <10% of the applied (half-lives >300 days), the rate at which cypermethrin degraded in the contaminated phenyl ring-labeled solution (alcohol label) was approximately twice that of cypermethrin in the cyclopropyl ring-labeled solution (acid), 20 compared to 35 days, respectively.

2. The concentration of cosolvent (acetonitrile) used by the study authors was 20% by volume; Subdivision N guidelines require that the concentration of cosolvent not exceed 1% in volume. It was stated that the high concentration of acetonitrile was needed because of the low solubility of cypermethrin in water, which was reported to be 0.3 ppm at 25 °C; however, the concentration of cypermethrin used in this experiment was only 0.1 ppm. It is possible that the study authors failed to differentiate between the solubility of cypermethrin and its tendency to readily adsorb to glass.

3. In one of the two phenyl ring-labeled solutions sampled at 7 days posttreatment, one unidentified degradate was detected at 11.2% of the applied. The study authors considered this compound to be "transient", and apparently did not attempt to identify the compound further.

4. Because the concentration of cypermethrin in solution was variable (as a result of the tendency of cypermethrin to adsorb to the container), the study authors defined "% of the applied" as the percentage of the average concentration of ^{14}C-residues in solution at a given sampling interval, and adjusted the data accordingly. EPA was informed of this approach in advance, and did not object (Appendix A4, EPA return fax dated March 26, 1991). The actual concentration of ^{14}C-residues in solution was never determined, however, because an acetonitrile rinse of the sample tubes was added to the sample solutions prior to analysis.

5. To determine the photoreactivity of ^{14}C-cyclopropyl and ^{14}C-phenyl ring-labeled cypermethrin, irradiated and dark control samples were

irradiated without duplicates for up 5 days. Both labels showed minimal degradation (4-7%) after 5 days of exposure to January sunlight intensity.

6. The registrant-calculated half-life for the cyclopropyl ring-labeled dark control was 332.5 days. The authors stated that a half-life was not calculated for the phenyl ring-labeled dark control, since only three data points were obtained.

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DATA EVALUATION RECORD 3

CHEM 109702 Cypermethrin §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42129001

Estigoy, L., L.O. Ruzo, and K. Shepler. 1991b. Photodegradation of ^{14}C-acid and ^{14}C-alcohol cypermethrin in/on soil by natural sunlight. PTRL Project No. 249/250W. FMC Study No. 191E1390E1. FMC Report No. PC-0159. Unpublished study performed by Pharmacology and Toxicology Research Laboratory, Richmond, CA and submitted by FMC Corporation, Princeton, NJ.

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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. The photodegradation on soil study is upgradeable and does not satisfy the 161-3 data requirement for cyclopropyl (acid) and phenyl-ring (alcohol) labeled cypermethrin at this time. The registrant should determine what degradation/metabolism process(es) are producing the degradate cyperamide in the dark controls since cyperamide was not detected in the aerobic soil metabolism study.

2. Cypermethrin degraded with a registrant-calculated half-life of approximately 55 days on a Thurston fine sandy loam soil (pH 6.9) that was irradiated with natural sunlight in California. In the corresponding dark controls, the half-lives were 100 and 75 days for the acid and alcohol labels, respectively. In the irradiated and dark control soils, cyperamide was the only significant degradate. Cyperamide concentrations in both dark control and irradiated soils were similar throughout the study and increased from 1.7-3.4 % of the applied dose at day 7 to 9.2-13.3 % at 35 days. Even though there was more parent compound present in the dark control samples at 35

days, the cyperamide concentrations exceeded those of the irradiated samples. Therefore, it is apparent that a process other than photolysis is producing cyperamide at the later sampling intervals. During the 35-day experiments, the cumulative light energy was 243-251 W-minute/cm^2, and soil surface temperatures ranged from 11.5 to 34.6 ^oC.

METHODOLOGY:

Sieved (2 mm) sandy loam soil (76% sand, 13% silt, 11% clay, 1.8% organic matter content, pH 6.9, CEC 5.2 meq/100 g) was mixed with distilled water, and the resulting slurries were applied to Petri dishes, then air-dried. The soil was remoistened with deionized water to increase the soil moisture to 75% of field capacity.

Cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the 1-carbon position; radiochemical purity 95.4%, specific activity 97,500 dpm/ug, FMC Corporation), dissolved in acetonitrile, was evenly applied at 20 ppm to the soil surfaces. The samples were placed perpendicular to the sun's path within two water-jacketed stainless steel chambers located outdoors in Richmond, California (37.45°N, 122.26°W) between February and March, 1991 (Figure 4). One chamber was covered with a quartz plate, the second with a rubber-covered glass plate that excluded light. The daily sunlight intensity ranged from 56 to 86479 $\mu W/cm^2$; the daily light energy ranged from 1.74 to 10.03 W-minute/cm^2, and the cumulative light energy for the 35-day period was 242.74 W-minute/cm^2 (Table VA). Sunlight intensity and energy were measured with a photodetector probe oriented at a 30° angle with respect to the vertical, and located approximately 4 feet above and 6 feet behind the soil chambers. The soil samples were maintained at 11.5-34.6 °C (mean 23.7 $\pm$ 0.4) in the irradiated chamber and 12.0-32.3 °C (mean 23.8 $\pm$ 0.3) in the dark chamber using circulating coolant through the water jacket; the temperatures were monitored using thermocouples attached to the soil surface. Humidified air was continuously drawn through the sample tubes, then through ethylene glycol (one tube) and 10% NaOH (two tubes) trapping solutions (Figure 4). Duplicate dishes of irradiated and dark control soil were removed for analysis at 0, 7, 14, 21, 28, and 35 days posttreatment. The trapping solutions were sampled at 21 and 35 days posttreatment.

Phenyl ring-labeled ^{14}C-cypermethrin (uniformly labeled; radiochemical purity 96.9%, specific activity 188,800 dpm/ug, FMC Corporation) was dissolved in acetonitrile and applied to Petri dishes containing sandy loam soil as previously described. The samples were irradiated with sunlight in Richmond, California, between January and March, 1991. The daily sunlight intensity ranged from 59 to 86479 uW/cm^2; the daily light energy ranged from 1.14 to 9.07 W-minute/cm^2, and the cumulative light energy for the 35-day period was 250.84 W-minute/cm^2 (Table VB). During the experiment, the temperature of the irradiated soil was maintained at 19.8-34.6 ^oC (mean 24.6 $\pm$ 0.2), and of the dark control was maintained at 12.3-

29.3 °C (mean 24.5 ± 0.1). Duplicate dishes of irradiated and dark control soil were removed for analysis at 0, 7, 14, 21, 28, and 35 days posttreatment. The trapping solutions were sampled at 21 and 35 days posttreatment. All samples were stored frozen at <0 °C when not in use.

The soil was transferred into centrifuge tubes, then extracted with acetone by shaking on a wrist action shaker for 16 hours. The slurries were centrifuged and the supernatant removed, and the soil was then sequentially extracted once with acetone and once with acetone:water (90:10, v:v), each time by shaking for 1 hour. The acetone and acetone:water extracts were combined, and aliquots were analyzed for total radioactivity by LSC. Additional aliquots of the extracts were analyzed for cypermethrin and its degradates by HPLC using a Supelco C-18 column eluted with a water to acetonitrile linear gradient, and with radioactivity and UV (254 nm) detection. Column eluate fractions (0.5 mL) were collected and analyzed by LSC. HPLC recovery efficiencies averaged 99.2 ± 10.6% for the cyclopropyl label and 101.5 ± 5.0% for the phenyl label; the quantification and detection limits were 50 and 10 dpm, respectively. Additional aliquots of the final samples (30 or 35 days) were analyzed by two-dimensional TLC on silica gel plates developed in cyclohexane (saturated with formic acid):ether (3:1, v:v) in the first direction and toluene (saturated with formic acid):ether (10:1, v:v) in the second direction. Samples were cochromatographed with reference standards of cypermethrin and the degradates (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DV acid); (RS)-carbamoyl(3-phenoxyphenyl)-methyl(1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (cyperamide); 3-phenoxybenzoic acid (MPB acid); and 3-phenoxybenzaldehyde cyanohydrin (MPB Ald cyanohydrin). ^{14}C-Compounds were identified by comparison to the R_f values of the reference standards. Radioactive areas were located using a linear analyzer or autoradiography, and identified by comparison to the standards.

The extracted soil was air-dried and a subsample was analyzed by LSC following combustion. Soil samples retaining >10% of the applied radioactivity following extraction were refluxed with acetonitrile: water (70:30, v:v) for 1 hour, then filtered. The supernatant was analyzed using LSC and TLC as described, and the refluxed soil was analyzed using LSC following combustion.

Aliquots of the trapping solutions were analyzed for total radioactivity using LSC. ^{14}C-Residues in the NaOH trapping solutions were confirmed to be CO_2 by barium chloride precipitation.

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DATA SUMMARY:

Cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin (radiochemical purities ≥95.4%), at 20 ppm, degraded with a registrant-calculated half-life of approximately 55 days on sandy loam soil that was irradiated with natural sunlight in California for 35 days. In the corresponding dark controls, ^{14}C-cypermethrin decreased from 86.4-105.0% of the applied immediately posttreatment to 72.9-78.4% at 35 days (Tables VIA and VIB). During the 35-day experiments, the cumulative light energy was 243-251 W-minute/cm^2, and soil surface temperatures ranged from 11.5 to 34.6 °C in the irradiated chamber and 12.0 to 32.3 °C in the dark chamber. Material balances for the irradiated soil and the dark controls were 91.5-108.6% of the applied immediately posttreatment and 89.6-104.2% at 35 days (Tables IIA and IIB).

In the irradiated soil at 35 days posttreatment, cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin comprised 63.0-69.9% of the applied in the soil, the degradate

> (RS)-carbamoyl(3-phenoxyphenyl)-methyl(1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (cyperamide)

comprised 8.9-10.5%, and numerous unidentified ^{14}C-compounds, each ≤4.5%, totaled 1.5-5.3% (Tables VIA and VIB). During the experiments, unextracted ^{14}C-residues increased from 1.1-4.8% of the applied immediately posttreatment to 14.9-34.0% at 28 days, then decreased to 9.0-15.2% at 35 days; when 50-80% of the unextracted ^{14}C-residues were extracted by refluxing, the majority (quantitative data not provided) were identified as ^{14}C-cypermethrin (Tables VIA, VIB, VIIA, and VIIB). After 35 days, $^{14}CO_2$ totaled 4.0% of the applied from the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin and 0.5% from the soil treated with phenyl ring-labeled ^{14}C-cypermethrin; volatilized organic ^{14}C-residues totaled <0.1%.

In the dark control soil at 35 days posttreatment, ^{14}C-cypermethrin comprised 72.9-78.4% of the applied, cyperamide was 12.6-13.5%, unidentified acetone-extractable compounds totaled ≤2.2%, and unextracted ^{14}C-residues were 7.4-10.2% (Tables VIA and VIB). After 35 days, $^{14}CO_2$ totaled 1.3% of the applied from the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin and 0.6% from the soil treated with phenyl ring-labeled ^{14}C-cypermethrin; volatilized organic ^{14}C-residues totaled <0.1%.

COMMENTS:

1. It is apparent that a process other than photolysis is producing cyperamide, since both the irradiated and dark control samples contained similar amounts of cyperamide. However, no cyperamide was found in the aerobic soil metabolism study in this review.

2. The results of the TLC analyses of ^{14}C-residues extracted from the soil by refluxing were not presented as numerical values, but only as copies of the autoradiographs.

3. Half-lives were calculated by the study authors based on the concentration of cypermethrin in the acetone and acetone:water sample extracts (data presented in Tables VIA and VIB). Cypermethrin extracted from the soil by refluxing was not considered.

Cypermethrin Review

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Pages 69 through 89 are not included in this copy.

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DATA EVALUATION RECORD 4

CHEM 109702 Cypermethrin §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42156601
Ramsey, A.A. 1990. Environmental fate studies: Aerobic soil metabolism of cypermethrin in a sandy loam soil. FMC Study No. 191E2190E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. The aerobic soil metabolism study is acceptable and satisfies the 162-1 data requirement.

2. Cypermethrin degraded with a half-life of 60 days in sandy loam soil that was incubated in darkness at 25 °C and 75% of field moisture capacity. Three nonvolatile degradates were identified: cis-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis-DCVA), trans-DCVA, and 3-phenoxybenzoic acid (MPBAcid).

METHODOLOGY:

Sieved (2-mm) sandy loam soil (76% sand, 13% silt, 11% clay, 1.8% organic matter content, pH 6.9, CEC 5.2 meq/100 g), moistened to 75% of field capacity, was weighed (50 g dry weight equivalent) into 250-mL biometer flasks and treated at approximately 3.0 ppm with cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the C-1

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position; radiochemical purity 96.3%, specific activity 4.88 mCi/mMol, Amersham) plus unlabeled cypermethrin (purity 99.3%), dissolved in absolute ethanol. Additional soil subsamples were treated at 3.0 ppm with phenyl ring-labeled ^{14}C-cypermethrin (uniformly labeled; radiochemical purity 97.1%, specific activity 5.14 mCi/mMol, Sigma Chemical) plus unlabeled cypermethrin (purity 99.2%), dissolved in absolute ethanol. The soils were mixed, the sidearm of each sample flask was filled with a 0.2 N KOH solution, and the sample flasks were sealed with rubber stoppers. The soil samples were incubated in darkness at 25 ± 1 °C and kept moistened to 75% of field moisture capacity. "The pH of the potassium hydroxide trapping solutions was monitored at least weekly and was changed when the pH dropped below 11." At each potassium hydroxide change, CO_2-free air was drawn through selected sample flasks, then through 0.1 N hydrogen sulfate and ethylene glycol trapping solutions (Figure 2). Duplicate flasks of soil and the corresponding trapping solutions were sampled at 0, 1, 3, 7, 14, 30, 44, 62, 91, 122, and 150 days posttreatment.

The soil samples were extracted according to the scheme presented in Figure 1. Both the cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin-treated soil samples were extracted twice with acetonitrile:water (70:30, v:v) by blending for approximately 5 minutes and once with acetonitrile:water by refluxing for 1 hour. After each extraction, the samples were centrifuged and the supernatants decanted. Portions of the extracted soils were analyzed for unextracted radioactivity using LSC following combustion. The acetonitrile:water extracts were combined and partitioned three times with methylene chloride. The combined methylene chloride fractions were dried over anhydrous sodium sulfate and concentrated under vacuum. Aliquots of the aqueous and methylene chloride fractions were analyzed for total radioactivity using LSC. Because significant amounts of radioactivity were noted in the aqueous fraction of the cyclopropyl ring-labeled soil extracts, the aqueous fraction of these samples was further partitioned with ethyl acetate beginning with the 14-day posttreatment samples. The ethyl acetate-extracted aqueous solution was then acidified to pH 1 and partitioned two more times with ethyl acetate. The initial ethyl acetate extract and the combined acidified ethyl acetate extracts were concentrated prior to use. The organic and aqueous extracts and the extracted soil were stored at approximately 4 °C "for short periods" during analysis, and at approximately -17 °C for "longer term storage".

The methylene chloride (both labels), ethyl acetate, and acidified ethyl acetate solutions were analyzed using one-dimensional TLC on silica gel plates developed in toluene:ethyl acetate:glacial acetic acid (75:25:1, v:v:v) or toluene:ethyl acetate:methanol (75:25:1, v:v:v). Unlabeled reference standards (Table I) were cochromatographed with the extracts, then visualized under UV light. ^{14}C-Compounds on the plates were located using autoradiography, then scraped from the glass, eluted from the silica with methanol, and quantified by LSC. Recoveries from TLC analyses were reported to be

>95% for both labels. Also, selected cyclopropyl ring-labeled soil extracts were analyzed by HPLC with UV (214 nm) detection using a C-18 column eluted with acetonitrile:0.01 M acetic acid. Eluate fractions were collected and analyzed using LSC. ^{14}C-Compounds were identified by comparing their retention times to those of unlabeled reference standards, and by GC/MS or LC/MS.

In an attempt to characterize unextracted ^{14}C-residues in the soil, portions of one of the two extracted 150-day posttreatment soil samples were further analyzed according to the scheme presented in Figure 3. The samples were refluxed in 0.25 N hydrochloric acid for 1 hour; after cooling, the supernatant was removed and partitioned twice with ethyl acetate. Aliquots of the ethyl acetate and aqueous fractions were analyzed by LSC. ^{14}C-Residues remaining in the refluxed soil were differentiated into fulvic acid, humic acid, and humin fractions using standard NaOH extraction procedures.

Aliquots of the KOH trapping solutions were analyzed for total radioactivity using LSC. Additional aliquots were either acidified with 0.25 N hydrochloric acid saturated with dry ice chips to quantify acid volatiles or precipitated with barium chloride to quantify $^{14}CO_2$. Aliquots of the hydrogen sulfate and ethylene glycol trapping solutions were analyzed using LSC.

The rubber stoppers used to seal the flasks containing the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin were "extracted" with methylene chloride. The methylene chloride was evaporated in the cold, and the residue was dissolved in methanol and cochromatographed with DCVA methyl ester standard. The identity of the DCVA methyl ester standard was confirmed by GC/MS.

DATA SUMMARY:

Cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin (radiochemical purities 96.3 and 97.1%, respectively), at 3.0 ppm, degraded with a registrant-calculated half-life of 60 days in sandy loam soil that was incubated in darkness at 25 ± 1 °C and 75% of field moisture capacity for up to 150 days. ^{14}C-Cypermethrin decreased from 96.7-97.1% of the recovered immediately posttreatment to 46.1-51.5% at 44 days, 33.9-46.7% at 62 days, and 15.7-19.1% at 150 days (Tables IX and X). The major nonvolatile degradates were cis- and trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis- and trans-DCVA) in the cyclopropyl ring-label treatment and 3-phenoxybenzoic acid (MPBAcid) in the phenyl ring-label treatment. The only significant volatile degradate was $^{14}CO_2$.

In the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin,

cis-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid and

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trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid

(cis- and trans-DCVA) increased to a maximum average of 0.73 ppm (24.2% of the recovered) at 62 days, then decreased to 0.13 ppm (4.4%) at 150 days (Table IX). Two ^{14}C-compounds were isolated but not identified: "AC1" (R_f 0.12) was a maximum 0.03 ppm (1.0% of the recovered), and "AC2" (R_f 0.02) was a maximum 0.13 ppm (4.2%). Also, a "mixture" of unidentified compounds (R_f 0.10-0.34), comprised up to 0.19 ppm (6.3% of the recovered); the study author reported that "this fraction is likely composed of at least 5 components none of which occur in >3.3% of the applied ^{14}C." Also, "unassigned" radioactivity (unknown ^{14}C-compounds, none >1.33% of the applied, and background) totaled a maximum 6.0% of the recovered. By 150 days posttreatment, unextracted ^{14}C-residues and $^{14}CO_2$ had increased to 28.3 and 34.4% of the recovered, respectively. Analysis of the unextracted ^{14}C-residues in the 150-day soil samples determined that 11.5% of the applied radioactivity was associated with the humic acid fraction, 7.3% with the acid hydrolyzable fraction, 6.6% with the fulvic acid fraction, and 2.9% with the humin fraction. In duplicate samples, material balances were 89.0 and 91.4% of the applied immediately posttreatment, ranged from 87.1 to 104.2% at 1 through 62 days, and ranged from 76.3 to 86.8% at 91 through 150 days (Table II).

In the soil treated with <u>phenyl ring-labeled ^{14}C-cypermethrin</u>,

3-phenoxybenzoic acid (MPBAcid)

increased to a maximum average of 0.25 ppm (8.4% of the recovered) at 30 days, then decreased to 0.05 ppm (1.7%) at 150 days (Table X). One ^{14}C-compound was isolated but not identified; "AB1" (R_f 0.10) was a maximum 0.08 ppm (2.6% of the recovered). Also, "unassigned" ^{14}C-compounds, none >1.26% of the applied, plus background totaled a maximum 6.8% of the recovered. By 150 days posttreatment, unextracted ^{14}C-residues and $^{14}CO_2$ had increased to 31.8 and 46.1% of the recovered, respectively. Analysis of the unextracted ^{14}C-residues in the 150-day soil samples determined that 14.8% the applied radioactivity was associated with the humic acid fraction, 7.9% with the fulvic acid fraction, 4.8% with the humin fraction, and 3.7% with the acid hydrolyzable fraction. Material balances were 96.8 and 102.8% of the applied in duplicate samples immediately posttreatment, and ranged from 89.9 to 101.8% with no discernable pattern at 1 through 150 days (Table III).

<u>COMMENTS</u>:

1. Individual unidentified ^{14}C-compounds were a maximum average of 0.13 ppm (4.2% of the recovered) from the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin, and 0.08 ppm (2.6%) from the soil treated with phenyl ring-labeled ^{14}C-cypermethrin. The study author

stated that an "exaggerated application rate (10X) was selected to facilitate the analysis and identification of any residues occurring at 0.01 ppm under normal field application rates (0.1 ppm in this study)."

The study author suggested that "AC1", isolated at up to 0.13 ppm from the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin, was comprised of more than one component "due to its highly polar nature".

2. Volatile ^{14}C-residues trapped in the rubber stoppers from the flasks containing cyclopropyl ring-labeled ^{14}C-cypermethrin were identified as methyl ester that was hydrolyzed to the free acid DCVA when stirred at room temperature in base. The study author stated that the ester was an artifact that formed by esterification in the presence of methanol, and that the recovery values for this portion of the experiment did not include the estimated 10% DCVA trapped in the rubber stoppers.

3. Tables IX and X are incorrectly labeled as "% of applied ^{14}C". Footnotes to the Tables indicate that the data were normalized to 100%; the data, therefore, are presented in terms of "% of recovered".

4. The study author stated that storage stability experiments demonstrated that ^{14}C-cypermethrin was stable in soil stored at approximately -17 °C for approximately 10 weeks and in organic extracts stored at -17 °C for approximately 4 months. Supporting data were not provided.

5. The metabolic pathway proposed for cypermethrin in aerobic soil is presented in Figure 8. The study authors stated that MPBAacid presumably arises by oxidation of the corresponding aldehyde (MPBAaldehyde); MPBAaldehyde is formed following hydrolysis.

6. In sterilized sandy loam soil treated with either cyclopropyl or phenyl ring-labeled ^{14}C-cypermethrin and incubated aerobically as described for 60 days, ^{14}C-cypermethrin comprised 95.8-97.6% of the applied (Table XI).

Cypermethrin Review

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Pages 95 through 111 are not included in this copy.

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DATA EVALUATION RECORD 5

CHEM 109702 Cypermethrin §162-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42156602
Ramsey, A.A. 1991. Environmental fate studies: Anaerobic soil metabolism of cypermethrin in a sandy loam soil. FMC Study No. 191E2590E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Metabolism - Anaerobic Soil

1. The anaerobic soil metabolism study is acceptable and satisfies the 162-2 data requirement for cis- and trans- cypermethrin.

2. Cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin degraded with half-lives of 53.3 and 63 days, respectively, in soil that was incubated anaerobically (flooded) at 25 °C in darkness for 60 days at 75% of field capacity, following 32 days of aerobic incubation. Three nonvolatile degradates were identified: cis-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis-DCVA), trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (trans-DCVA), and 3-phenoxybenzoic acid (MPBAcid).

METHODOLOGY:

Sieved (2-mm) sandy loam soil (76% sand, 13% silt, 11% clay, 1.8% organic matter content, pH 6.9, CEC 5.2 meq/100 g), moistened to 75% of field capacity, was weighed (50 g dry weight equivalent) into 250-mL biometer flasks and treated at approximately 3.0 ppm with

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cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the C-1 position; radiochemical purity 97.6%, specific activity 4.88 mCi/mMol, Amersham) plus unlabeled cypermethrin (purity 99.3%), dissolved in absolute ethanol. Additional soil subsamples were treated at 3.0 ppm with phenyl ring-labeled ^{14}C-cypermethrin (uniformly labeled; radiochemical purity 97.1%, specific activity 5.14 mCi/mMol, Sigma Chemical) plus unlabeled cypermethrin (purity 99.2%), dissolved in absolute ethanol. The soils were mixed, the sidearm of each sample flask was filled with a 0.2 N KOH solution, and the sample flasks were sealed with rubber stoppers. The soil samples were incubated in darkness at 25 ± 1 °C and kept moistened to 75% of field moisture capacity for 32 days. Following the 32-day aerobic incubation, microcrystalline cellulose (0.5 g) was added to each sample and the treated soils were flooded with Super Q water. "The pH of the potassium hydroxide trapping solutions was monitored at least weekly and was changed when the pH dropped below 11." At each potassium hydroxide change, CO_2-free air was drawn through selected sample flasks, then through 0.1 N hydrogen sulfate and ethylene glycol trapping solutions (Figure 2). Duplicate flasks of soil and the corresponding trapping solutions were sampled following the application of ^{14}C-cypermethrin, immediately postflooding (32 days posttreatment), and at 14, 30, 45, and 60 days postflooding (46, 62, 77, and 92 days posttreatment).

The soils and floodwater were separated by decantation and extracted according to the scheme presented in Figure 1. The floodwater was acidified to pH 1, then extracted twice with either methylene chloride or ethyl acetate; aliquots of the organic and aqueous fractions were analyzed using LSC. Both the cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin-treated soil samples were extracted twice with acetonitrile:water (70:30, v:v) by blending for approximately 5 minutes and once with acetonitrile:water by refluxing for 1 hour. After each extraction, the samples were centrifuged and the supernatants decanted. Portions of the extracted soils were analyzed for unextracted radioactivity using LSC following combustion. The acetonitrile:water extracts were combined and partitioned three times with methylene chloride. The combined methylene chloride fractions were dried over anhydrous sodium sulfate and concentrated under vacuum. Aliquots of the aqueous and methylene chloride fractions were analyzed for total radioactivity using LSC. The organic and aqueous extracts and the extracted soil were stored at approximately 4 °C "for short periods" during analysis, and at approximately -17 °C for "longer term storage".

The organic extracts from the floodwater and the soil were analyzed using one-dimensional TLC on silica gel plates developed in toluene:ethyl acetate:glacial acetic acid (75:25:1, v:v:v) or toluene:ethyl acetate:methanol (75:25:1, v:v:v). Unlabeled reference standards (Table I) were cochromatographed with the extracts, then visualized under UV light. ^{14}C-Compounds on the plates were located using autoradiography, then scraped from the glass, eluted from the silica with methanol, and quantified by LSC. Recoveries from TLC

analyses were reported to be >95% for both labels. Also, selected cyclopropyl ring-labeled soil extracts were analyzed by HPLC with UV (214 nm) detection using a C-18 column eluted with acetonitrile:0.01 M acetic acid. Eluate fractions were collected and analyzed using LSC. ^{14}C-Compounds were identified by comparing their retention times to those of unlabeled reference standards, and by GC/MS or LC/MS.

In an attempt to characterize unextracted ^{14}C-residues in the soil, portions of one of the two extracted 60-day postflooding soil samples were further analyzed according to the scheme presented in Figure 3. The samples were refluxed in 0.25 N hydrochloric acid for 1 hour; after cooling, the supernatant was removed and partitioned twice with ethyl acetate. Aliquots of the ethyl acetate and aqueous fractions were analyzed by LSC. ^{14}C-Residues remaining in the refluxed soil were differentiated into fulvic acid, humic acid, and humin fractions using standard NaOH extraction procedures.

Aliquots of the KOH trapping solutions were analyzed for total radioactivity using LSC. Additional aliquots were either acidified with 0.25 N hydrochloric acid saturated with dry ice chips to quantify acid volatiles or precipitated with barium chloride to quantify $^{14}CO_2$. Aliquots of the hydrogen sulfate and ethylene glycol trapping solutions were analyzed using LSC.

The rubber stoppers used to seal the flasks containing the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin were "extracted" with methylene chloride. The methylene chloride was evaporated in the cold, and the residue was dissolved in methanol and cochromatographed with DCVA methyl ester standard. The identity of the DCVA methyl ester standard was confirmed by GC/MS.

DATA SUMMARY:

Cyclopropyl and phenyl ring-labeled ^{14}C-cypermethrin (radiochemical purities 97.6 and 97.1%, respectively), at 3.0 ppm, degraded with registrant-calculated half-lives of 53 and 63 days, respectively, in sandy loam soil that was incubated anaerobically (flooded) in darkness at 25 ± 1 °C for 60 days, following 32 days of aerobic incubation. ^{14}C-Cypermethrin decreased from 97.2-97.3% of the recovered in the soil plus floodwater immediately posttreatment to 65.9-67.2% at flooding (32 days posttreatment), 40.9-51.7% at 30 days postflooding (62 days posttreatment), 33.7-37.4% at 45 days (77 days posttreatment), and 29.2-33.9% at 60 days (92 days posttreatment; (Tables VII and VIII). The major nonvolatile degradates were cis- and trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis- and trans-DCVA) in the cyclopropyl ring-label treatment and 3-phenoxybenzoic acid (MPBAcid) in the phenyl ring-label treatment. The only significant volatile degradate was $^{14}CO_2$.

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In the soil:water system containing cyclopropyl ring-labeled ^{14}C-cypermethrin,

cis-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid and

trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid

(cis- and trans-DCVA) increased to a maximum average of 1.00 ppm (33.3% of the recovered) at 30 days postflooding, then decreased to 0.79 ppm (26.3%) at 60 days (Table VII). Three ^{14}C-compounds were isolated but not identified: "ANC1" (R_f 0.02) was a maximum 0.16 ppm (5.4% of the recovered), "ANC2" (R_f 0.09) was a maximum 0.13 ppm (4.3%), and "ANC3" (R_f 0.26-0.28) was a maximum 0.02 ppm (0.6%). Also, "unassigned" radioactivity (unknown ^{14}C-compounds, none >1.2% of the applied, and background) totaled a maximum 11.1% of the recovered. By 60 days posttreatment, unextracted ^{14}C-residues and $^{14}CO_2$ had increased to 13.2 and 10.9% of the recovered, respectively. Analysis of the unextracted ^{14}C-residues in the 60-day soil:water samples determined that 3.7% of the applied radioactivity was associated with the humic acid fraction, 4.2% with the acid hydrolyzable fraction, 3.5% with the fulvic acid fraction, and 1.4% with the humin fraction. In duplicate samples, material balances were 100.8 and 103.1% of the applied immediately posttreatment, ranged from 95.9 to 98.5% from immediately postflooding through 45 days, and were 85.1 and 88.1% at 60 days (Table II).

In the soil treated with phenyl ring-labeled ^{14}C-cypermethrin,

3-phenoxybenzoic acid (MPBAcid)

increased to a maximum average of 0.78 ppm (25.9% of the recovered) at 60 days postflooding (Table VIII). One ^{14}C-compound was isolated but not identified; "ANB1" (R_f 0.32) was a maximum 0.08 ppm (2.6% of the recovered). Also, "unassigned" radioactivity (unknown ^{14}C-compounds, none >1.3% of the applied, and background) totaled a maximum 6.3% of the recovered. By 60 days posttreatment, unextracted ^{14}C-residues and $^{14}CO_2$ had increased to 20.9 and 11.3% of the recovered, respectively. Analysis of the unextracted ^{14}C-residues in the 60-day soil:water samples determined that 10.9% of the applied radioactivity was associated with the humic acid fraction, 3.1% with the acid hydrolyzable fraction, 4.6% with the fulvic acid fraction, and 3.2% with the humin fraction. In duplicate samples, material balances were 102.0 and 107.4% of the applied immediately posttreatment, ranged from 97.0 to 100.7% from immediately postflooding through 45 days, and were 95.7 and 96.7% at 60 days (Table III).

COMMENTS:

1. Individual unidentified ^{14}C-compounds were a maximum average of 0.16 ppm (5.4% of the recovered) from the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin, and 0.08 ppm (2.6%) from the soil treated with phenyl ring-labeled ^{14}C-cypermethrin. The study author stated that an "exaggerated application rate (10X) was selected to facilitate the analysis and identification of any residues occurring at 0.01 ppm under normal field application rates (0.1 ppm in this study)."

   The study author suggested that "ANC1" and "ANC2", isolated at up to 0.16 and 0.13 ppm from the soil treated with cyclopropyl ring-labeled ^{14}C-cypermethrin, were acidic in nature and were probable breakdown products of cis- and trans-DCVA. Insufficient material was available to analyze "ANC1" and "ANC2" using MS.

2. Volatile ^{14}C-residues trapped in the rubber stoppers from the flasks containing cyclopropyl ring-labeled ^{14}C-cypermethrin were identified as methyl ester that was hydrolyzed to the free acid DCVA when stirred at room temperature in base. The study author stated that the ester was an artifact that formed by esterification in the presence of methanol, and that the recovery values for this portion of the experiment did not include the DCVA trapped in the rubber stoppers.

3. Tables VII and VIII are incorrectly labeled as "% of applied ^{14}C". Footnotes to the Tables indicate that the data were normalized to 100%; the data, therefore, are presented in terms of "% of recovered".

4. In the aerobic soil metabolism study (Study 2, MRID 42156601), the study author stated that storage stability experiments demonstrated that ^{14}C-cypermethrin was stable in soil stored at approximately -17 °C for approximately 10 weeks and in organic extracts stored at -17 °C for approximately 4 months. Supporting data were not provided.

5. Microcrystalline cellulose was added to the soil at the time of flooding "to provide additional substrate to assure that all residual oxygen was depleted rapidly and completely."

6. The study author stated that the redox potential (mV) of each soil:water system was measured at the time of analysis to assure that anaerobic conditions (-mV) were maintained during the study. The data were not provided.

7. The proposed metabolic pathway for cypermethrin in anaerobic soil is presented in Figure 6. The study author suggested that MPBAcid arises from MPBAldehyde, which forms during hydrolysis. The author also suggested that a disproportionation reaction such as a Cannizzaro-type reaction; a metal ion-mediated oxidation, such as Fehling's reaction; or a dehydrogenase reaction (whereby 3-

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phosphoglyceraldehyde is converted to 3-phosphoglyceric acid) occurred during the experiment.

Cypermethrin Review

Page _____ is not included in this copy.

Pages 118 through 135 are not included in this copy.

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_____ 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.

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DATA EVALUATION RECORD 6

CHEM 109702 Cypermethrin §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42129003
Froelich, L.W. 1991. Soil mobility studies: Adsorption/desorption studies of cypermethrin. Laboratory Project ID: 191E3290E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 4

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. The batch equilibrium study is upgradeable and does not satisfy the unaged portion of the 163-1 data requirement at this time. The registrant should reconcile the increasing Freundlich K-values in sandy soil from adsorption to desorption and the decreasing Freundlich K-values from adsorption to desorption in the sandy loam, silt loam, and clay loam soils. The registrant should also reconcile the tighter binding of cypermethrin on sandy, sandy loam, and silt loam soils than on a clay loam soil. The sandy and sandy loam soils that demonstrated tighter binding of cypermethrin had significantly less organic carbon than the clay loam soil.

2. Unaged cypermethrin was immobile in sand, sandy loam, silt loam, and clay loam soils (pH 6-7.4) with Freundlich K_{ads} values of 657 (0.4 % OC), 1163 (1.8 % OC), 1897 (4.5 % OC), and 416 (3.9 % OC), respectively. Freundlich K_{des} values were 1263, 191, 602, and 262, respectively. K_{oc} values ranged from 18,190 - 549,130 for adsorption and desorption.

METHODOLOGY:

Sand, sandy loam, silt loam, and clay loam soils (Table I) were air-dried and sieved (2 mm). Based on the results of preliminary experiments, a 1:20 soil:solution ratio and a 24-hour equilibration period were selected for the definitive study. In addition, Teflon tubes were selected for use in the definitive study because cypermethrin adsorbed to Teflon surfaces significantly less than to glass, polycarbonate, or polysulfone surfaces.

To determine adsorption, aliquots of a 0.01 N $CaCl_2$ solution were added to sterile Teflon tubes. Cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the 1-carbon position, radiochemical purity 98.1%, specific activity 56.3 mCi/mg, Amersham), dissolved at nominal concentrations of 0.005, 0.04, 0.1, 0.2, or 0.4 ug/mL in 0.01 M $CaCl_2$ solutions containing 2 % acetonitrile, was added to each tube. The solutions were allowed to equilibrate with the wall surfaces for 30 minutes, then aliquots of the solutions were analyzed by LSC. Soil (1 g) was added to each tube. The slurries were equilibrated for 24 hours at 25 $\pm$ 1 °C in a shaking water bath in the dark. Following equilibration, the slurries were centrifuged, and the supernatants were decanted and their volume recorded. Triplicate aliquots of the supernatants were analyzed for total radioactivity by LSC.

To determine desorption, the supernatants from the adsorption samples were replaced with pesticide-free 0.01 N $CaCl_2$ solution and the soil:solution slurries were shaken for 24 hours in the dark. After the desorption period, the slurries were centrifuged and the supernatants were decanted. Aliquots of the supernatants were analyzed by LSC. The soils were dried with a nitrogen stream, and triplicate subsamples were analyzed by LSC following combustion. The remaining dry soil was removed from the centrifuge tubes, which were then rinsed with acetonitrile, and duplicate aliquots of the acetonitrile rinses were analyzed by LSC.

DATA SUMMARY:

Based on batch equilibrium experiments, cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the 1-carbon position, radiochemical purity 98.1%), at nominal concentrations of 0.005, 0.04, 0.1, 0.2, and 0.4 ug/mL, was immobile in sand, sandy loam, and silt loam soils, and slightly mobile in clay loam soil:solution slurries (1:20) that were equilibrated for 24 hours at 25 $\pm$ 1 °C. Freundlich K_{ads} values were 657 for sand, 1163 for sandy loam, 1897 for the silt loam, and 416 for clay loam soils; respective K_{oc} values were 285652, 110762, 72405, and 18326 (Table XII).

Following desorption in pesticide-free $CaCl_2$ solution (1:20 soil:solution ratio) for 24 hours, 3.72-18.88% of the radioactivity that had been adsorbed to the soils was desorbed (Tables III-VI). Freundlich K_{des} values were 1263 for the sand soil, 191 for the sandy

loam soil, 602 for the silt loam soil, and 262 for the clay loam soil.

The material balances for the definitive study were 63.8-79.1% for the sand soil, 74.5-137.0% for the sandy loam soil, 82.6-114.5% for the silt loam soil, and 95.7-111.7% for the clay loam soil (Tables XIII-XVI).

COMMENTS:

1. The registrant did not reconcile the increasing Freundlich K-values in sandy soil from adsorption to desorption and the decreasing Freundlich K-values from adsorption to desorption in the sandy loam, silt loam, and clay loam soils. The registrant also did not reconcile the tighter binding of cypermethrin on sandy, sandy loam, and silt loam soils than on a clay loam soil. The sandy and sandy loam soils that demonstrated very tight binding of cypermethrin had significantly less organic carbon than the clay loam soil, respectively.

2. The author suggested that the low material balance obtained for the sandy soil may have been due to particulate matter (possibly organic matter) floating in the supernatant and decanted with the aqueous phase. The author stated that if these particles had adsorbed ^{14}C-cypermethrin, then the combustion analysis for the sand soil would yield lower amounts of radioactivity, thereby decreasing the recovery.

3. Recovery efficiencies and method detection limits were not reported.

4. The solubility of cypermethrin was reported to be 0.3 ppm at pH 7 and 25 °C.

Cypermethrin Review

Page _____ is not included in this copy.

Pages 139 through 155 are not included in this copy.

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DATA EVALUATION RECORD 7

CHEM 109702 Cypermethrin §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42129002
Curry, S.J. 1991. Leaching of ^{14}C-cypermethrin in soil following aerobic aging. Laboratory Project ID: 191E3190E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. The aged soil column leaching study may be upgraded to acceptable if the unaged batch equilibrium study (MRID 42129003) in this review is upgraded.

2. Residues of parent cypermethrin and the degradates 3-phenoxybenzoic acid (mPB acid)/3-phenoxyphenylmethanol (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 $CaCl_2$. About 73.2-92.8% of the applied radioactivity remained in the treated layer and upper 6 cm of the soil columns. However, the degradate (1RS)-cis,trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis/trans-DCVA) was mobile in the soil columns. Up to 13.2 % of the applied radioactivity was found in the leachate as cis/trans DCVA.

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METHODOLOGY:

Sieved (2-mm), air-dried sandy loam soil (76% sand, 13% silt, 11% clay, 1.8% organic matter content, pH 6.9, CEC 5.2 meq/100 g) was weighed (30 g) into biometer flasks and treated at 0.55 ppm with either cyclopropyl ring-labeled ^{14}C-cypermethrin (labeled at the 1-carbon position; radiochemical purity 98.2%, specific activity 56.3 mCi/mMol, Amersham) or phenyl ring-labeled ^{14}C-cypermethrin (uniformly labeled; radiochemical purity 96.9%, specific activity 35.4 mCi/mMol, Sigma Chemical), dissolved in ethanol. The ethanol was allowed to evaporate, and each sample was mixed using a spatula. The soil moisture was adjusted to 75% of field moisture capacity at 0.33 bar. The sidearm of each flask contained a 0.2 M KOH solution for trapping evolved $^{14}CO_2$. The flasks were sealed with rubber stoppers and the treated soil samples were incubated aerobically in darknessat approximately 25 °C. At weekly intervals, the flasks were removed and weighed, and the soil moisture was adjusted to maintain 70-80% of field capacity. At 30 days posttreatment, the flasks of soil were removed for analysis; trapping solutions were sampled and refreshed at various intervals during the incubation. Following the 30-day aging period, the soil was air-dried and ground. Subsamples were analyzed by LSC following combustion.

Duplicate 19.5-inch glass columns (25-mm id) were filled with sieved (2-mm) sandy loam soil (Figure 1). The soils were saturated with 0.01 N $CaCl_2$ by capillary action and allowed to drain to approximate soil moisture at field capacity conditions; the length of the soil columns after saturation was at least 30 cm. A 10-g (dry weight) subsample of the aged, treated soils was evenly distributed on top of each soil column, and the treated layer was covered with 10 g of untreated soil and filter paper. The columns were wrapped with aluminum foil and leached with the equivalent of 20 acre-inches of a 0.01 N $CaCl_2$ solution. Leaching was completed within 28-52 hours. The leachate was collected in 100-mL fractions, aliquots of which were analyzed using LSC. The remaining leachate was pooled prior to further analysis. Following leaching, the soil columns were frozen, then thawed for 10-30 minutes, and the partially frozen soil core was extruded from the column. The top layer containing the aged soil and 10 g of overlaid untreated soil were removed, and the remaining soil was divided into five 6-cm segments that were analyzed by LSC following combustion. Following removal of the soil, the glass columns were rinsed sequentially with 2% Isoclean and methanol; the rinse from each column was combined into a single sample and analyzed for total radioactivity by LSC.

Subsamples of the soil collected during the aerobic incubation period and from all soil segments that contained >0.01 ppm of ^{14}C-residues were extracted in a blender with acetonitrile:water (70:30, v:v) for 5 minutes (Figure 2). The slurries were centrifuged and the supernatant decanted; the extraction procedure was repeated two more times. The remaining soil was transferred to a round-bottom flask, refluxed for 30 minutes with acetonitrile:water (70:30, v:v), and

centrifuged as described. The supernatants from each extraction and the reflux were combined to form a single soil extract; the volume was measured and duplicate aliquots were analyzed using LSC. The soil extract was adjusted to pH 2 with concentrated HCl and the extract was immediately partitioned three times with equal volumes of methylene chloride. The organic and aqueous fractions were separated and analyzed by LSC. The methylene chloride fraction was dried over anhydrous sodium sulfate, partially concentrated by rotary evaporation, and then further concentrated under a nitrogen stream. The concentrated methylene chloride fraction was redissolved in "suitable solvents" and analyzed by one-dimensional TLC and reverse-phase HPLC.

For HPLC analyses, the extracts were analyzed on a Beckman Ultrasphere ODS column and eluted with a 20% 0.01 M acetic acid:80% acetonitrile isocratic gradient and with radioactive flow monitoring and UV (214 nm) detection. Column fractions were collected and analyzed by LSC. Radioactive peaks were compared to the retention times of unlabeled reference standards of unlabeled cis/trans cypermethrin, (1RS)-cis,trans-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis/trans-DCVA), 3-phenoxybenzoic acid (mPB acid), and 3-phenoxyphenylmethanol (mPB alcohol) that had been chromatographed in the same systems. The identities of cypermethrin and its degradates were confirmed using GC/MS. The quantitation limit for cypermethrin and its degradates was 0.001 ppm. HPLC column recoveries ranged from 68.8 to 107.5%.

For TLC analyses, the extracts were dissolved in methylene chloride (phenyl ring-labeled) or hexane:methyl t-butyl ether (50:50; cyclopropyl ring-labeled) and spotted on normal phase silica gel plates, which were then developed in toluene:ethyl acetate:acetic acid (75:25:1, v:v:v). ^{14}C-Compounds were located using autoradiography, quantified using a TLC linear analyzer, and identified by comparison to reference standards. Unlabeled reference standards, which were cochromatographed with the phenyl ring-labeled extracts but on separate TLC plates under similar conditions for the cyclopropyl ring-labeled samples, were located with short-wavelength UV light. The quantitation limit for cypermethrin and its degradates was 0.001 ppm.

The leachate fractions from each column were combined and analyzed by LSC. The combined leachate fractions were adjusted to pH 2 and partitioned with methylene chloride. The methylene chloride fractions were concentrated and analyzed as described for the soil methylene chloride fractions.

The KOH trapping solutions from the aerobic aging portion of the study were analyzed for $^{14}CO_2$ using two referenced methods (not provided for review). In one method, aliquots of the trapping solutions were acidified with 2 N HCl, then saturated with nonradioactive CO_2 (dry ice chips), and the remaining solution was

analyzed by LSC. In the second method, the identity of CO_2 was confirmed by barium carbonate precipitation.

DATA SUMMARY:

Based on column leaching studies, aged (30 days) ^{14}C-cypermethrin residues had low mobility in 30-cm columns of sandy loam soil that were leached with 20 inches of 0.01 N $CaCl_2$; ≥73.2% of the radioactivity applied to the soil columns (% TRR) remained in the surface 6 cm (Tables VII and VIII). The major degradates extracted from the soil were

(1RS)-cis,trans,-3(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (cis/trans-DCVA)

in soil columns treated with the cyclopropyl ring-labeled ^{14}C-cypermethrin residues, and

3-phenoxybenzoic acid (mPB acid) plus

3-phenoxyphenylmethanol (mPB alcohol)

in columns treated with the phenyl ring-labeled ^{14}C-cypermethrin residues.

Cyclopropyl ring-labeled ^{14}C-cypermethrin: Of the total radioactivity applied to duplicate soil columns, 43.73-64.36% remained in the treated soil layer, 11.36-26.84% was recovered from the 0- to 6-cm segment, 2.31-3.94% was distributed throughout the 12- to 30-cm segments, and 13.42-15.65% was recovered from the leachates (Tables VIII and IX). The recovery from the soil columns was 88.24-93.81% of the material applied to the column (Table X).

Based on reverse-phase HPLC analyses of methylene chloride extracts of the soil segments and leachates, cypermethrin comprised 24.2-36.5% of the applied in the treated layer, 5.0-15.4% in the 0- to 6-cm segment, and 0.3-0.4% in the leachates (Table XIII). DCVA was 2.8-4.8% of the applied in the treated layer, 1.3-2.2% in the 0- to 6-cm segment, and 10.1-13.2% in the leachates. Unidentified ("diffuse") ^{14}C-residues totaled 5.7-6.0% of the applied throughout the soil columns and in the leachates.

In the aged (30 days) soil prior to leaching, 47.1% of the ^{14}C-residues were cypermethrin, 19.9% were DCVA, 5.6% were unidentified extractable, and 24.0% were unextracted (Tables XI and XIII). Cumulative $^{14}CO_2$ totaled 21.84% of the applied (Table IV). The material balance during the 30-day aging period was 102.82% of the applied (Table V).

Phenyl ring-labeled ^{14}C-cypermethrin: Of the total radioactivity applied to duplicate soil columns, 20.83-23.96% remained in the treated soil layer, 68.46-72.32% was recovered from the 0- to 6-cm segment, 0.64-6.94% was distributed throughout the 6- to 30-cm segments, and 0.57-0.83% was recovered from the leachates (Tables VII and IX). The recovery from the soil columns was 94.31-101.53% of the material applied to the column (Table X).

Based on reverse-phase HPLC analyses of methylene chloride extracts of the soil segments and leachates, cypermethrin comprised 8.9-10.3% of applied in the treated layer, 28.6-34.2% in the 0- to 6-cm segment, and 2.2% in the 6- to 12-cm segment (Table XII). The degradates mPB acid and mPB alcohol were not differentiated and together comprised 1.2-1.4% of the applied in the treated layer, 3.6-4.3% in the 0- to 6-cm segment, and 0.5% in the 6- to 12-cm segment (one column). Unidentified ("diffuse") radioactivity comprised 4.2-5.0% of the applied throughout the soil columns.

In the aged (30 days) soil prior to leaching, 45.6% of the ^{14}C-residues were cypermethrin, 6.3% were mPB acid/mPB alcohol, 5.1% were unidentified extractable, and 38.6% were unextracted (Tables XI and XII). Cumulative $^{14}CO_2$ totaled 23.10% of the applied (Table III). The material balance during the 30-day aging period was 88.84% of the applied (Table V).

COMMENTS:

1. The treated soil was aged for slightly longer than one half-life; following the 30-day aging period, cypermethrin comprised 45.6-47.1% of the applied (Tables XII and XIII). The study author stated that the aerobic aging procedure was based on the results of an aerobic metabolism study in which a half-life of approximately 60 days was determined.

2. The study author stated that TLC analyses of extracts from the cyclopropyl ring-labeled samples were subject to severe matrix effects, resulting in sample R_f values for soil and leachate extracts that were considerably lower than the standards. Therefore, TLC regions were identified by matching patterns, instead of by direct comparison of the R_f values.

3. The material balance for the 1-month aerobic aging of the phenyl ring-labeled samples was 88.8% (Table V). The study author suggested that the missing radioactivity may have been $^{14}CO_2$ not adsorbed by an oversaturated KOH trapping solution during the first 5 days of aging.

4. The soil samples, leachates, and organic and aqueous fractions were frozen when not in use. The study author stated that no significant degradation of the parent compound occurred in treated, unaged soil that was stored frozen for 10 weeks.

5. The application rate of 0.55 ppm (0.1 lb ai/A) was reported to be the highest recommended rate for a single application of the test substance.

Cypermethrin Review

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Pages 162 through 182 are not included in this copy.

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DATA EVALUATION RECORD 8

CHEM 109702 Cypermethrin §164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 42459601
Leppert, B.C. 1992. Ammo 2.5 EC insecticide - terrestrial field dissipation. Study No. 191E4191E1. Unpublished study performed by FMC Corporation, Richmond CA, Pan-Agricultural Laboratories, Inc., Madera, CA, and Pest Management Enterprises, Inc., Cheneyville, LA; and submitted by FMC Corporation, Richmond, CA.

DIRECT REVIEW TIME = 17

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CONCLUSIONS:

Field Dissipation - Terrestrial

1. The terrestrial field dissipation study is upgradeable and does not satisfy the 164-1 data requirement at this time. The 164-1 data requirement for the 2.5 EC, 2E and 3E, and 40 WP formulations of cypermethrin may be satisfied if the registrant can identify the route of dissipation of cypermethrin in the field. While these studies demonstrate rapid dissipation of cypermethrin, there is no indication of degradation or mobility to account for this dissipation. The first half-life at both locations was 3 days for the 0-7 day and 0-14 day sampling intervals in California and Louisiana, respectively, which is far less than the total half-life in the aerobic soil metabolism study in this review (60 days). Degradate recoveries were low and cypermethrin does not appear to be mobile. The dissipation route must be identified.

2. Cypermethrin, at 0.2 lb ai/A, dissipated with registrant-calculated half-lives of 13 days in a bareground plot of silt loam soil located in California and 5 days in a bareground plot of loamy sand soil located in Louisiana. The cypermethrin degradates identified were 3-

phenoxybenzoic acid (MPBAcid) and trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (trans-DCVA; Louisiana site only). Cypermethrin was detected only once (0.01 ppm) in the 6-12 inch soil depth at 2 days after treatment in California, and was not detected below 3-6 inches of depth in Louisiana. Also, no degradates were detected below 3 inches of depth.

Ancillary Study - Freezer Storage Stability

1. Cypermethrin, cis-DCVA, and trans-DCVA were stable in soil stored frozen at -18 C for up to 240-295 days. MPBAcid appeared to be stable for up to 295 days in silt loam soil and up to 180 days in loamy sand soil.

2. Based on the information provided by this study, samples containing cypermethrin, cis-DCVA, and trans-DCVA can be stored frozen for up to 240-295 days. Samples containing MPBAcid can be stored frozen for up to 180 days.

3. No additional information is required on the freezer storage stability of cypermethrin, cis-DCVA, and trans-DCVA in soil samples stored for 240-295 days. Furthermore, no additional freezer storage stability data are required for MPBAcid in soil samples stored for up to 180 days. Additional storage stability information may be required if soil samples containing cypermethrin, cis-DCVA, and trans-DCVA are stored for more than 295 days, or if soil samples containing MPBAcid are stored for more than 180 days.

METHODOLOGY:

Field Dissipation - Terrestrial

Cypermethrin [(±)-alpha-cyano-(3-phenoxyphenyl)methyl (±)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate; Ammo 2.5 EC, 2.5 lb ai/gal EC, FMC] was applied in three broadcast applications at 0.2 lb ai/A/application (total 0.6 lb ai/A) to a bareground plots of silt loam soil located in Madera, California and loamy sand soil located in Cheneyville, Louisiana. In addition to normal rainfall, the plots were irrigated as necessary to equal the 10-year average precipitation.

Madera, California: A bareground plot (20 x 60 feet) of silt loam soil (78-82% sand, 14-20% silt, 2-4% clay, 0.2-0.6% organic matter, pH 6.5-7.2, CEC 5.9-27.9 meq/100 g) was treated with three applications of cypermethrin at 0.2 lb ai/A/application (total 0.6 lb ai/A) on June 14, 21, and 27, 1991. An untreated plot located 540 feet upslope from the treated plot served as a control. For sampling purposes, each plot was divided into 75 subplots (4 x 4 feet). Soil samples (five) were collected from both treated and untreated plots one day prior to the first cypermethrin application, immediately

after each cypermethrin application, and at 2, 4, 7, 14, 21, 28, 60, 90, 120, 150, and 180 days after the last application. A Concord excavator was used to collect the soil from the 0- to 6-inch soil depth. A tractor-mounted soil probe (2-inch diameter) equipped with an acetate liner was used to collect the soil from the 6- to 36-inch depth. The soil samples were frozen within 1 hour of collection. Prior to shipment to the analytical laboratory, the soil cores were divided in to 0- to 3-, 3- to 6-, 6- to 12-, 12- to 18-, 18- to 24-, 24- to 30-, and 30- to 36-inch segments. Segments from the same subplot, sampling interval, and soil depth were composited. Prior to analysis, the soil samples were stored at approximately -18 °C for up to 12 months.

Cheneyville, Louisiana: A bareground plot (70 x 250 feet) of loamy sand soil (30% sand, 64% silt, 6.0% clay, 0.7% organic matter, pH 7.0, CEC 8.2 meq/100 g) was treated with three applications of cypermethrin at 0.2 lb ai/A/application (total 0.6 lb ai/A) on July 24, 31, and August 7, 1991. An untreated plot located 100 feet upslope served as a control. For sampling purposes, the treated plot was divided into 70 subplots (6.6 X 10 feet) and the untreated plot was divided into 14 subplots (6.6 X 10 feet). Soil samples (five) were collected from both treated and untreated plots one day prior to the first cypermethrin application, immediately after each cypermethrin application, and at 2, 7, 14, 21, 28, 60, 90, 120, 150, and 180 days after the last application. The soil from the 0- to 3-inch and 3- to 6-inch depth was collected using hand-held samplers (5-inch and 4-inch diameters, respectively). The soil from the 6- to 36-inch depth was collected using a tractor-mounted soil probe (2-inch diameter) equipped with an acetate liner. All soil samples were placed on "blue ice" immediately after collection. The soil cores were divided into 6- to 12-, 12- to 18-, 18- to 24-, 24- to 30-, and 30- to 36-inch segments. The soil samples from the same plot, sampling interval, and soil depth were composited, then all soil samples were frozen. Prior to analysis, the soil samples were stored at approximately -18 °C for up to 9 months.

Analytical Methods: Subsamples (5 g) were extracted with methanol:water (4:1, v:v) for 3 minutes, then the slurries were filtered. To analyze for cypermethrin, an aliquot of the filtrate was diluted with water and extracted twice with hexane. The hexane extracts were combined, and an aliquot of the combined hexane extract was concentrated on a steam table. The concentrate was then cleaned-up using a Florisil column eluted with hexane:methyl-t-butyl ether (9:1, v:v). The eluate was concentrated on a steam table under nitrogen and an aliquot was analyzed by GC/MS. To analyze for acid degradates, an aliquot of aqueous phase was treated with 1.0 N NaOH, and the solution was concentrated under vacuum. The concentrated solution was acidified with concentrated HCl and refluxed for 1 hour. The solution was chromatographed on a C-18 cartridge that was eluted with methylene chloride. The eluate was concentrated, and the residues in the concentrate were derivatized with pentafluorobenzyl bromide. The solution was then cleaned-up on a Florisil column

eluted with hexane:methyl-t-butyl ether (9:1, v:v). The eluate was concentrated under nitrogen and aliquots of the concentrate were analyzed by GC/MS.

Ancillary Study - Freezer Storage Stability

Samples of silt loam soil (Madera site) and loamy sand soil (Cheneyville site) from the untreated plots at both study sites were fortified at 0.05 ppm with cypermethrin, cis-DCVA, trans-DCVA, or MPBAcid, and stored frozen at -18 °C for up to 295 days (silt loam soil) and 240 days (loamy sand soil). Fortified samples from the Madera site were removed from the freezer for analysis at 0, 7, 14, 30, 70, 90, 180, and 252 days posttreatment. Fortified samples from the Cheneyville site were removed from the freezer for analysis at 0, 7, 14, 30, 60, 150, 180, and 240 days posttreatment. The soil samples were analyzed as previously described.

DATA SUMMARY:

Field Dissipation - Terrestrial

Cypermethrin ([±]-alpha-cyano-(3-phenoxyphenyl)methyl (±)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate; Ammo 2.5 EC, 2.5 lb ai/gal EC, FMC], at 0.6 lb ai/A, dissipated with registrant-calculated half-lives of 5-13 days in bareground plots located in Madera, California and Cheneyville, Louisiana. The cypermethrin degradate,

3-phenoxybenzoic acid (meta-phenoxybenzoic acid, MPBAcid),

was detected in the soil at both sites. The degradate,

trans 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (trans-DCVA),

was detected only in the soil from the Louisiana site. Cypermethrin and its degradates were not detected below the 12-inch soil depth.

Madera, California: Cypermethrin dissipated with a registrant-calculated half-life of 13 days from the upper 12 inches of a plot of silt loam soil that was treated with three applications of cypermethrin at 0.2 lb ai/A/application (total 0.6 lb ai/A) on June 14, 21, and 27, 1991. Cypermethrin was detected to a soil depth of 12 inches; the degradate MPBAcid was detected only in the upper 3 inches of the soil. The degradate, cis-DCVA, was not detected at either site.

In the 0- to 3-inch soil depth, the average concentration of cypermethrin was 0.077 ppm immediately after the first application, 0.134 ppm immediately after the second application, 0.215 ppm

immediately after the third application, 0.145 ppm at 2 days after the third application, 0.112 ppm at 4 days, 0.046 ppm at 7-14 days, 0.056 ppm at 21 days, 0.031 ppm at 28 days, and was not detected (<0.007 ppm) at 60-180 days (Table 1). The average concentration of the degradate MPBAcid was <0.007 ppm immediately after the first application, 0.008 ppm immediately after the second application, 0.017 ppm immediately after the third application, 0.024-0.032 ppm at 2-14 days, 0.007-0.008 ppm at 21-28 days, and <0.007 ppm at 60-180 days.

In the 3- to 6-inch soil depth, the average concentration of cypermethrin was 0.018 ppm immediately after the first application, 0.008 ppm immediately after the second application, 0.033 ppm immediately after the third application, 0.020 ppm at 2 days after the third application, 0.029 ppm at 4 days, <0.007 ppm-0.013 ppm at 7-28 days, and <0.007 ppm at 60-180 days. In the 6- to 12-inch soil depth, cypermethrin was detected only at an average concentration of 0.010 ppm at 2 days after the final application. The degradate MPBAcid was not detected below the 3-inch soil depth at any sampling interval.

During the study period, air temperatures ranged from 24 to 109 F. Soil temperatures (2-inch depth) ranged from 30 to 123 F. During the study, total rainfall plus irrigation was approximately 0.68 inches at 0-13 days after the final application, 0.77 inches from 14-26 days, and 16.49 inches. The slope of the field was <1%, and the depth to the water table was 88-107 feet.

Cheneyville, Louisiana: Cypermethrin dissipated with a registrant-calculated half-life of 5 days from the upper 3 inches of loamy sand soil in a bareground plot that was treated with three applications of cypermethrin at 0.2 lb ai/A/application (total 0.6 lb ai/A) on July 24 and 31, and August 7, 1991. Cypermethrin and the degradates, trans-DCVA and MPBAcid, were not detected below the 3-inch soil depth.

In the 0- to 3-inch soil depth, the average concentration of cypermethrin was 0.148 ppm immediately after the first application, 0.187 ppm immediately after the second application, 0.301 ppm immediately after the third application, 0.231 ppm at 2 days after the third application, 0.029 ppm at 7 days, 0.017 ppm at 14 days, 0.016 ppm at 21 days, 0.007 ppm at 28 days, and <0.007 ppm at 60-180 days (Table 2). The average concentration of MPBAcid was 0.010 ppm immediately after the second treatment, 0.020 ppm immediately after the third treatment, 0.044 ppm at 2 days, and <0.007 ppm at all other sampling intervals. Trans-DCVA was only detected at average concentrations of 0.016 and 0.008 ppm at 2 and 7 days after the third application, respectively.

During the study period, air temperatures ranged from 23 to 101 °F; complete soil temperature data were not provided. Total rainfall and irrigation was 4.4 inches at 0-7 days after the final application,

1.45 inches at 8-14 days, and approximately 53.74 inches during the study period. The slope of the field was <1%, and the depth to the water table was 6 feet with a seasonal variation of 2-6 feet.

Ancillary Study - Freezer Storage Stability

Cypermethrin, cis-DCVA, and trans-DCVA were stable in silt loam soil (Madera, California site) and loamy sand soil (Cheneyville, Louisiana site) fortified at 0.05 ppm and stored frozen at -18 °C for up to 240 (loamy sand soil) and 295 days (silt loam soil).

Cypermethrin concentrations ranged from 0.039 to 0.066 ppm in the silt loam soil and from 0.036 to 0.067 ppm in the loamy sand soil, with no discernible pattern (Table 15).

Cis-DCVA concentrations ranged from 0.033 to 0.074 ppm in the silt loam soil and from 0.032 to 0.077 ppm in the loamy sand soil, with no discernible pattern (Table 16).

Trans-DCVA concentrations ranged from 0.039 to 0.069 ppm in the silt loam soil and from 0.036 to 0.081 ppm in the loamy sand soil, with no discernible pattern.

MPBAcid appeared to be stable in silt loam soil for up to 295 days; concentrations were 0.033-0.070 ppm, with no discernible pattern. MPBAcid appeared to be stable for up to 180 days in loamy sand soil; concentrations were 0.042-0.048 ppm immediately posttreatment, 0.038-0.048 ppm at 7-14 days, 0.051-0.084 ppm at 30 days, 0.037-0.058 ppm at 60-150 days, 0.039-0.059 ppm at 180 days, and 0.031-1.047 ppm at 240 days.

COMMENTS:

General

1. The analytical methods for detection of cypermethrin and its degradates in the field dissipation studies were very destructive and were not the methods used in the aerobic soil metabolism study. However, the destructive methods may have been necessary due to the low application rate, tight binding to soil, and the dilution that resulted from field application.

2. The degradate DCVA was produced in greater quantity and was more persistent than the MPBacid degradate in the aerobic soil metabolism study (MRID 42156601) in this review. However, DCVA was not detected in the California field dissipation study while the MPBacid degradate was detected as late as 62 days after treatment. Also, the DCVA degradate was mobile in the aged soil column leaching study (MRID 42029002) but showed no mobility in either the Louisiana or California field dissipation studies.

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3. The soil samples in this study were stored frozen (-18 °C) for up to 365 days for the silt loam soil (Madera site) and up to 270 days for the loamy sand soil (Cheneyville site). In stability experiments, cypermethrin, cis-DCVA, and trans-DCVA were determined to be stable in silt loam and loamy sand soils stored frozen (-18 °C) for up to 295 and 240 days, respectively. Since there was no evidence of degradation during the study, it is unlikely that cypermethrin, cis-DCVA, or trans-DCVA degraded during the additional storage period.

Madera, California

1. The prior use history of the test site was not reported. However, there were no apparent residues in the preapplication samples.

2. Weeds were controlled using paraquat dichloride.

Cheneyville, Louisiana

1. The study protocol called for additional samples to be collected at 4 days after the final cypermethrin application; however, this sampling could not be performed due to inclement weather (3.75 inches of rain at 2-5 days after the final application). The cypermethrin half-life of 5 days that was calculated by the study author is in good agreement with the half-life for the California site (13 days); half-lives of 7-30 days were calculated from field dissipation studies conducted in Arkansas and California and reviewed by Dynamac in November, 1985 (Sterns, J.W. 1985a. Dissipation of cyperamide and m-phenoxybenzaldehyde residues from soils treated with Ammo insecticide. RAN 0149. FMC Corporation, Philadelphia; and Sterns, J.W. 1985b. Dissipation of cypermethrin, dichlorovinyl acid, and m-phenoxybenzoic acid residues in soil. RAN 0148. FMC Corporation, Philadelphia.). The half-life of cypermethrin in an aerobic soil metabolism study (MRID 42156601, reviewed by Dynamac in a document dated September 30, 1992) was 60 days.

2. The test site had been fallow for 3 years prior to the study.

3. Weeds were controlled using pendimethalin, flumeturon, and paraquat.

Ancillary Study - Freezer Storage Stability

1. MPBAcid was stable for 295 days in the silt loam soil and 180 days in the loamy sand soil. However, the decrease in the concentration of MPBAcid in the loamy sand soil between 180 days and 240 days is unexplained. Since soil was not analyzed after 240 days, it could not be determined if the decrease was due to experimental variability or to degradation of MPBAcid. Based on the stability of MPBAcid in the silt loam soil for 295 days and the stability for 180 days in the loamy sand soil, it is unlikely that significant degradation occurred during storage. However, additional information on the stability of MPBAcid in loamy sand soil may be required for storage periods in

the silt loam soil for 295 days and the stability for 180 days in the loamy sand soil, it is unlikely that significant degradation occurred during storage. However, additional information on the stability of MPBAcid in loamy sand soil may be required for storage periods in excess of 180 days to confirm the apparent stability of MPBAcid in storage.

Cypermethrin Review

Page _____ is not included in this copy.

Pages 191 through 208 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.

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CYPERMETHRIN
Last Update on September 24, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer: JAB	Section Head:	Date:

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.

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

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Soil Partition Coefficient (Kd) (163-1)

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

	TEXTURE	OC	pH	CEC	KADS	KOC	KDES	KOC
[S]	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)

[ ]
[ ]

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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)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ]
[ ]
[ ]
[ ]

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

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

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

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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

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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

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