DP Barcode:168621,167607
181217,174669, 179844
PC Code:109701
Date Out: 24 AUG 93

TO: Linda Deluise
Product Manager PM #52
Special Review and Reregistration Division (H7508W)

FROM: Paul J. Mastradone, Ph.D., Section Chief
Environmental Chemistry Review Section #1
Environmental Fate & Ground Water Branch/EFED (H7507C)

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

Attached, please find the EFGWB review of...

Reg./File #L09701

Common Name:Permethrin

Product Name:Pounce

Company Name:FMC Corporation

Purpose:Review of 8 studies in response to Phase 4

Type Product:Insectici Action Code:627 EFGWB:910967,910869,920516
Review Time: 22 . 921100 921243

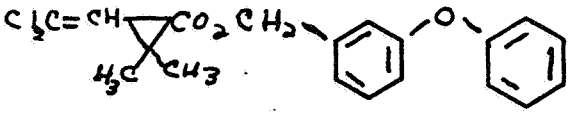
EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

161-1		162-4		164-4		166-1	
161-2		163-1	421967-01(P)	164-5		166-2	
161-3		163-2		165-1		166-3	
162-1	419706-02 (Y)	163-3		165-1		167-1	
162-1	424100-02 (Y)	164-1	42359109 (P)	165-4	413004-01 (Y)	167-2	
162-2	419706-01 (Y)	164-2		165-4	413004-02(Y)	201-1	
162-3		164-3		165-4	413004-03 (Y)	202-1	

Y = Acceptable (Study satisfied the Guideline)/Concur P = Partial (Study partially satisfied the Guideline, but additional information is still needed)
S = Supplemental (Study provided useful information, but Guideline was not satisfied) N = Unacceptable (Study was rejected)/Non-Concur

1.0 CHEMICAL:

chemical name: 3-(phenoxyphenyl)methyl(±)cis-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate
common name: permethrin
trade name: Pounce
structure:
chemical number: 109701



2.0 TEST MATERIAL: discussed in DER's

3.0 STUDY/ACTION TYPE: review of 8 Der's submitted in response to Phase 4 review

4.0 STUDY IDENTIFICATION;

424100-02 Hawkins, D.R., Kirkpatrick, D., Shaw, D., and J. Nicholson. May 1992. The Aerobic Soil Metabolism of ^{14}C-Permethrin. Laboratory Report No. HRc/ISn 251/911499. Unpublished study performed by ICI Agrochemicals, Huntingdon Research Center, Huntingdon, England.

419706-02 Hawkins, D., Kirkpatrick, D., Shaw, D., and J. Riseborough. June 1991. The Effects or Application Rate and Soil Moisture Content on the Rate of Degradation of ^{14}C-Permethrin. Laboratory Report No. HRC/ISN 247/91296. Unpublished study performed and submitted by ICI Agrochemicals, Inc., Huntingdon Research Center, Huntingdon, England.

419706-01 Hawkins, D., Kirkpatrick, D., Shaw, D., and J. Riseborough. July 1991. The Metabolism of ^{14}C-Permethrin in Sandy Loam Soil Under Anaerobic Conditions. Laboratory Report No. HRC/ISn 236/91107. Unpublished study performed and submitted by ICI Agrochemicals, Huntingdon Research Centre, Ltd., Huntingdon, England.

421967-01 Cranor, Walter. November 1991. Leaching Characteristics of Soil Incorporated Permethrin Following Aerobic Aging. Laboratory Report #39227. Performed by ABC Laboratories, Inc., Columbia, Mo. Submitted by FMC Corporation, Princeton, NJ.

42359109 Becker, J.M. Pounce 3.2 EC Insecticide - Terrestrial Field Dissipation. Vol. 3 of 8. May 1992. FMC Study #138E4191R1. Performed and submitted by FMC Corporation, Princeton, NJ.

413004-01 Burgess, David. October 1989. Uptake, Depuration and Bioconcentration of ^{14}C-Permethrin by Bluegill Sunfish (Lepomis macrochirus). Laboratory Report #PC-0117. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO. and submitted by FMC Corporation, Princeton, NJ.

413004-02 Tullman, Robert. November 1989. Accumulation Studies: Laboratory Studies of Pesticide Accumulation in Fish: Acid (Cyclopropyl)-^{14}C-Permethrin in the Bluegill Sunfish. Laboratory Report #138E5489E1-1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

413004-03 Singer, Sandra. October 1989. Accumulation Studies: Laboratory Studies of Pesticicide Accumulation in Fish: ^{14}C-Alchol (Phenyl)-Labelled Permethrin in the Bluegill Sunfish. Laboratory Report #138E5489E1-2. Unpublished study performed and submitted by FMC Corporatin, Princeton, NJ.

5.0 REVIEWED BY:

Patricia Ott, Chemist
Section #1, EFGWB/EFED

Signature: Patricia Ott
Date: 23 AUG 1993

6.0 APPROVED BY:

Paul Mastradone, Section Chief
Section #1, EFGWB/EFED

Signature: Paul J Mastradone
Date: 23 AUG 1993

7.0 CONCLUSIONS:

Aerobic Soil Metabolism

The 2 studies submitted are acceptable and fulfill the 162-1 data requirement by providing half-life and degradate information on the aerobic soil metabolism of permethrin in Frensham sandy loam (English soil). Permethrin appears to be subject to soil microbiological degradation, with a half-life of 37 days. The major degradate was $^{14}CO_2$ (after 6 months' incubation, it accounted for 34-40% of the applied (both radiolabelled compounds). For the cyclopropyl label, 2 other degradates were formed: trans-DCVA and 3-(2,2-dichlorovinyl)-2-methylcyclopropane-1,2-dicarboxylic acid. For the phenyl label, only 1 other major degradate was present (3-phenoxybenzoic acid).

The registrant did additional work to study the effects of application rate and soil moisture content on the rate of degradation of permethrin. Application rate had the greatest effect on degradation rate and may indicate permethrin microbial toxicity/inhibition occurred and/or the solubility was exceeded at the higher treatment rate (13 mg/kg versus 1 mg/kg). See DER for details.

Leaching and Adsorption/Desorption

The submitted study partially satisfies the leaching data requirement of 163-1 by providing an estimate of the leaching potential of parent and 1 degradate in a Nebraska sandy loam soil using soil columns. In order to completely satisfy the data requirement, leaching data for parent in 3 more soils, an estimate of the leaching potential in 4 soils of 3-phenoxybenzoic acid (one of

two major soil degradates, other than CO_2), and an estimate of the leaching potential in 3 more soils for trans-DCVA (the other major soil metabolite), should be provided. These data are needed because permethrin is registered for a great variety of food and non-food uses and is used on a great variety of soil types. Adsorption/desorption studies are preferred.

Parent did not appear to leach in a Nebraska sandy loam soil column study but a major soil degradate (cyclopropyl label), trans-DCVA, did appear to leach. However, an acceptable terrestrial field study conducted for terrestrial food uses at 0.4 lb ai/A in North Carolina (sandy loam) and Illinois (silty clay loam) showed no leaching pattern for both parent and permethrin's two principal soil metabolites, trans-DCVA and 3-phenoxybenzoic acid.

Anaerobic Soil Metabolism

The study submitted was acceptable and fulfills the 162-2 data requirement by providing information on half-life and degradates for permethrin in soil incubated under anaerobic conditions. Permethrin applied at 3.2 lb ai/A or 13 mg/kg had an anaerobic half-life of 204 days in an English soil (Frensham sandy loam). This rate is similar to the maximum application rate for the terrestrial non-food uses (4 lb ai/A). Only 1 major degradate was found for each label. For the cyclopropyl label, the major degradate was trans-DCVA. For the phenyl label, the major degradate was 3-phenoxybenzoic acid.

Terrestrial Field Dissipation

This study partially satisfies the 164-1 Terrestrial Field Dissipation data requirement for permethrin by providing mobility, degradation, and dissipation information for terrestrial food uses at 0.4 lb ai/A. To completely satisfy the data requirement, another field study, for terrestrial non-food uses at 4 lb ai/A, is still needed for two reasons: the terrestrial non-food uses' maximum application rate is significantly higher (8-10x) than for the terrestrial food uses; and the soil metabolism studies clearly show a markedly different half-life for the higher application rate (terrestrial non-food uses) compared to the lower application rate (terrestrial food uses).

Permethrin appears to degrade/dissipate in the field, with half-lives of 17 (North Carolina) and 43 (Illinois) days on bare-ground plots using five applications of Pounce 3.2 EC at 0.4 lb ai/A per application (ground sprayer). No pattern of leaching was observed for parent and permethrin's 2 principal soil metabolites, trans-DCVA and 3-phenoxybenzoic acid.

Laboratory Studies of Pesticide Accumulation in Fish

These 3 studies satisfy the 165-4 data requirement by providing information on the nature and quantity of pesticide residues which accumulated in bluegill sunfish exposed for 28 days

to 0.5 ug/l ^{14}C-Permethrin labelled in either the acid (cyclopropyl) or alcohol (phenyl) moiety. Up to 20% of the total radioactive residues (in the "oily fraction" of the fish tissues) could not be identified, though an exhaustive analytical scheme was tried. The registrant has hypothesized that these residues are phospholipid conjugates of permethrin metabolites.

The maximum bioconcentration of permethrin was observed in the viscera (950-1100x), followed by whole fish (570-610x) and fillet (180-230x). After 14 days of depuration, 73-83% depuration was observed (range for all 3 sample types), indicating significant depuration occurred. Only one metabolite was detected, trans-DCVA, present at 4-10% of the total radioactive residue. Parent accounted for most of the radioactive residue in the day 21 and 28 fish tissue (57-76% for the acid label and 76-90% for the alcohol label).

7.1 Status of Data Requirements:

Data Requirements	Review Status	MRID #
161-1 Hydrolysis	Satisfied	
161-2 Photolysis--Water	Satisfied	
161-3 Photolysis--Soil	Satisfied	
161-4 Photolysis--Air	Waived[1]	
162-1 Aerobic Soil Metabolism	Satisfied	424100-02 419706-02
162-2 Anaerobic Soil Metabolism	Satisfied	419706-01
162-3 Anaerobic Aquatic Metab.	Required	
162-4 Aerobic Aquatic Metabolism	Required	
163-1 Leaching and Ads./Des.	Partial[2]	421967-01
163-2 Laboratory Volatility	Waived[1]	
163-3 Field Volatility	Waived[1]	
164-1 Terrestrial Field Dissip.	Partial[3]	42359109
164-2 Aquatic Field Dissipation	Required	
164-5 Long-Term Terr. Dissipation	Reserved[4]	
164-5 Long-Term Aquatic Dissip.	Reserved[5]	
165-3 Irrigated Crop	Required	
165-4 Fish Bioaccumulation (Lab.)	Satisfied	3 MRID's
165-5 Aquatic Non-Target Org. (Field)	Reserved[6]	
166-1 Ground Water--Small Prospect.	Reserved[7]	
166-2 Ground Water--Small Retrospect.	Reserved[7]	
166-3 Ground Water--Large Retrospect.	Reserved[7]	
167-1 Field Runoff (Surface Water)	Reserved[6]	
167-2 Surface Water Monitoring	Reserved[6]	
201-1 Droplet Spectrum (Spray Drift)	Reserved[9]	
201-2 Field Spray Drift Evaluation	Reserved[9]	

1. Waived because of permethrin's very low vapor pressure.
2. Leaching data for permethrin and trans-DCVA in 3 more soils, and a leaching study for 3-phenoxybenzoic acid (4 soils) is still needed.
3. A terrestrial field dissipation study for terrestrial non-food uses at the highest application rate is still required.

4. The long-term terrestrial field dissipation study is reserved pending results of a terrestrial field dissipation study for terrestrial non-food uses at the highest application rate.
5. Long term aquatic field dissipation data requirement is reserved pending receipt of acceptable aquatic field dissipation data.
6. If projected aquatic residues, based on modeling scenarios, are of environmental concern, this study may be required.
7. Ground Water monitoring studies are reserved pending review of acceptable environmental fate studies.
8. Droplet size spectrum and drift field evaluation data are required. The registrant may elect to satisfy these data requirements through the Spray Drift Task Force, provided that neither EEB/EFED nor Tox/HED require these data in advance of the Task Force's final report (currently scheduled for December 1994). If the registrant wants to satisfy these data requirements in this manner, the procedure outlined in PR Notice 90-3 should be followed.

7.2 Environmental Fate Assessment (update of 6/24/91 Environmental Fate Assessment)

The major routes of dissipation for permethrin appear to be soil binding, followed by soil microbial degradation.

Based on an incomplete environmental fate data base, permethrin does not appear to degrade via hydrolysis or photolysis (acceptable hydrolysis, aqueous photolysis, and soil photolysis studies).

Based on an acceptable aerobic soil metabolism study, permethrin appears to be subject to microbial degradation, with a half-life of 37 days in an English soil, Frensham sandy loam (treatment rate 0.36 lb ai/A). The major degradate was $^{14}CO_2$ (34-40% of applied after 6 months' incubation), followed by trans-DCVA (peaking at 10% of applied on day 14), and 3-phenoxybenzoic acid (a maximum of 12-15% formed by day 30). The trans- isomer of permethrin degraded more rapidly than the cis- isomer (the ratio of cis to trans changed from 40/60 (day 0) to 50/50 (day 30) to 78/22 (day 365). Results from a supplemental aerobic study, which studied the effects of application rate and soil moisture on persistence, showed that the appliation rate had the greatest effect, with markedly different half-lives for the 1 mg/kg (t 1/2 19-23 days) versus the 13 mg/kg rate or 4 lbs ai/A (t 1/2 = 86-113 days). The cause could be microbial inhibition and/or exceeding pesticide solubility (the aqueous solubility of permethrin is estimated to be around 0.02 ppm).

Based on acceptable data, permethrin incubated anaerobically at 3.2 lbs ai/A (13 mg/kg) in an English soil (Frensham sandy loam) had a half-life of 204 days. Two major degradates were found: trans-DCVA (which reached a maximum of 13% after 60 days' anaerobic incubation) and 3-phenoxybenzoic acid (which reached a maximum of 12% after 60 days' anaerobic incubation).

Based on partially acceptable leaching data, permethrin does not appear to leach through soil columns of aged Nebraska sandy loam. A major soil metabolite, trans-DCVA, does appear to leach through soil columns (leachate contained 13.7%). In order to fully satisfy the data requirement, leaching data for parent and trans-DCVA in 3 more soils and leaching data for 3-phenoxybenzoic acid in 4 soils is still needed.

Based on partially acceptable terrestrial field dissipation data, permethrin had a half-life of 17 (Trial 1, North Carolina) and 43 (Trial 2, Illinois) days in a terrestrial field dissipation study for terrestrial food uses, where bareground control and treated plots were used (treated plots were treated with Pounce 3.2 EC Insecticide) at 0.4 lb ai/A (5 applications). Neither parent nor the 2 principal soil degradates (trans-DCVA and 3-phenoxybenzoic acid) were detected (limit of detection 0.025 ppm) below 6" at both the North Carolina and Illinois sites, indicating leaching was not occurring during this study.

At the North Carolina site, parent reached an average maximum of 0.233 ppm (5th application), trans-DCVA reached a maximum level of 0.035 ppm (5th application), and 3-phenoxybenzoic acid was only found below the limit of detection (0.025 ppm).

At the Illinois site, parent reached an average maximum of 0.654 ppm (5th application), trans-DCVA reached a maximum of 0.03 ppm (5th application), and 3-phenoxybenzoic acid reached a maximum of 0.054 ppm 1 day after the last (5th) application.

In order to fully satisfy the 164-1 Terrestrial Field Dissipation data requirement, a field study for terrestrial non-food uses, at the maximum (about 4 lb ai/A) rate is needed because the terrestrial nonfood use maximum rate is considerably higher than for the terrestrial food use rate (about 10x) and the aerobic soil metabolism study (MRID #410706-02) clearly showed a markedly different half-life for the highest application (terrestrial non-food) rate versus the lower rate (terrestrial food).

Acceptable fish bioaccumulation studies showed that the maximum bioconcentration of permethrin occurred in the viscera (950-1100x), followed by whole fish (570-610x) and fillet (180-230x). Depuration was significant and rapid--after 14 days' depuration, 73-83% depuration had occurred (range for all 3 sample types). Parent accounted for a significant amount of the radioactivity (57-76% of the total radioactivity for the acid label and 76-90% for the alcohol label). Only one metabolite was identified, trans-DCVA, and it accounted for 4-10% of the TRR (total radioactive residue) for the acid label. The "oily fraction" accounted for up to 20% of the TRR and, although the registrant tried an exhaustive analytical scheme to try to identify the residues, these efforts were unsuccessful. The registrant hypothesized that the residues are phospholipid conjugates of permethrin metabolites.

In summary, permethrin appears to dissipate via soil binding, followed by soil microbial degradation. It does not appear to degrade via hydrolysis or aqueous/soil photolysis, but does appear to degrade via aerobic soil metabolism and, to an appreciably lesser extent, via anaerobic soil metabolism (half-life about 7 months). Parent permethrin does not appear to leach through soil columns of aged Nebraska sandy loam, but a major soil metabolite, trans-DCVA, was found in the leachate (13.7%). The leaching behavior of the other principal soil metabolite (aside from CO_2), 3-phenoxybenzoic acid, is not clear at this point. Permethrin appears to degrade in the terrestrial field dissipation study (North Carolina and Illinois) conducted to satisfy terrestrial food uses and parent and the 2 major soil metabolites did not appear to be mobile.

8.0 RECOMMENDATIONS:

The routes of dissipation for permethrin, based on a nearly complete data base, appear to be aerobic soil metabolism (and to a significantly lesser, extent, anaerobic soil metabolism), and soil binding, which means permethrin may adsorb to soil and run off. Permethrin appears to bioconcentrate in bluegill sunfish viscera (950-1100x) but rapidly depurates. Permethrin does not appear to be subject to abiotic paths of degradation such as hydrolysis, and aqueous/soil photolysis. Based on an acceptable terrestrial field study, neither parent nor the 2 principal soil degradates (trans-DCVA and 3-phenoxybenzoic acid) appear to be mobile.

Since permethrin is registered for a great variety of food and non-food uses and is used on a great variety of soils, additional leaching data for parent and trans-DCVA in 3 more soils and for 3-phenoxybenzoic acid in 4 soils is still needed.

Also, another terrestrial field dissipation study is needed for two reasons: the terrestrial non-food uses' maximum application rate is significantly higher (8-10x) than for the terrestrial food uses; and the soil metabolism studies clearly show amarkedly different half-life for the highest application rate (terrestrial non-food uses) compared to the lower application rate (terrestrial food uses).

9.0 BACKGROUND:

These 8 DER's were submitted in response to the Phase 4 review.

10.0 DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: see DER's

11.0 COMPLETION OF ONE-LINER: attached

12.0 CBI-APPENDIX: n/a

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

SEP 29 1992

OFFICE OF PREVENTION,
PESTICIDES AND TOXIC
SUBSTANCES

EFGWB #: 92-0376 & 92-0754
Chemical Barcode #: 109701
DP Barcode #: D172646 & D176614
Case #: 819432

MEMORANDUM

SUBJECT: Request for Data Waiver (Anaerobic Aquatic--162-3 and Aerobic Aquatic--162-4 Metabolism and Aquatic Field Dissipation--164-2), Deferral Request (Field Accumulation in Rotational Crops--165-2) and Time Extension (Confined Accumulation in Rotational Crops--165-1) for Permethrin

FROM: Richard J. Mahler, Hydrologist
Environmental Chemistry Review Section #1
EFGWB/EFED

THRU: Henry Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division

Paul J. Mastradone, Chief
Environmental Chemistry Review Section #1
EFGWB/EFED

TO: Linda DeLuise, PM #52
Accelerated Reregistration Branch
Special Review and Reregistration Division (H7508W)

Conclusions:

1. Because permethrin can be used on banks and shorelines of bodies of water, and potentially can have an impact on aquatic systems, the requirement for anaerobic aquatic and aerobic aquatic metabolism and aquatic field dissipation studies cannot be waived.

2. Until EFGWB has received and reviewed an acceptable confined accumulation in rotational crops study for permethrin, the requirement for the field accumulation in rotational crops study can be deferred.

3. Environmental Fate and Ground Water Branch has no scientific objection to allowing a 10 month extension on the due date of the confined accumulation in rotational crops study (165-1) for permethrin.

Background:

1. ICI Americas Inc. and FMC Corporation are requesting a waiver from anaerobic aquatic and aerobic aquatic metabolism and aquatic field dissipation studies since the registrants indicate in their "CORRESPONDENCE FOR RESPONSE TO PHASE 4 FOR PERMITHERIN" that aquatic food uses (on watercress) will be cancelled; and permethrin is labeled as a mosquito adulticide, which is a terrestrial use. The Label Use Information System (LUIS) report, dated 3/1/91, indicates that permethrin can be used around swamps, marshes, wetlands, stagnant water, lakes, ponds and reservoirs. Although the label restricts direct application to water bodies, the use pattern indicates that permethrin can indirectly impact upon aquatic systems, therefore, the need for the data requirements. EFGWB notes that Subdivision N Guidelines N, Section 164-2 (b) states that aquatic field dissipation studies for aquatic impact uses are required when a pesticide is applied to ditchbanks and shorelines.

2. The registrants are also requesting a deferral for the requirement for the field accumulation in rotational crops study (165-2) until the results of the confined accumulation in rotational crops study (165-1) are known. Field accumulation studies in rotational crops are reserved and dependent upon the results of the confined accumulation in rotational crops study (165-1). If significant ^{14}C pesticide residues of concern to EPA are detected in the test crops analyzed in the confined accumulation study, then field accumulation studies in rotational crops may be required. Therefore, the field accumulation in rotational crops study can be deferred until the confined rotational crop study has been received, reviewed and assessed as having satisfied the data requirements.

3. ICI Americas Inc. and FMC Corporation are requesting a time extension of 10 months on the reporting commitment for the confined accumulation in rotational crops study. Because of the time needed to prepare protocols, initiate and conduct the study and to analyze plant and soil samples, it seems reasonable to allow a 10 month extension.

DATA EVALUATION RECORD

CHEM 109701 Permethrin 162-1

STUDY ID 419706-02
Hawkins, D., Kirkpatrick, D., Shaw, D., and J. Riseborough. June 1991. The Effects of Application Rate and Soil Moisture Content on the Rate of Degradation of ^{14}C-Permethrin. Laboratory Report No. HRC/ISN247/91296. Unpublished study performed and submitted by ICI Agrochemicals, Inc., Huntingdon Research Center, Huntingdon, England.

REVIEWED BY:

Patricia Ott, Chemist
Review Section #1, EFGWB/EFED
Signature: Patricia Ott
Date:

APPROVED BY:

Paul Mastradone, Section Chief
Review Section #1, EFGWB/EFED
Signature:
Date:

CONCLUSIONS:

This non-guideline study provides useful, supplemental information on the aerobic soil metabolism of permethrin.

Of the 3 parameters studied (soil moisture, application rate, and application volume/vehicle), application rate had the greatest effect on parent degradation and may indicate permethrin microbial toxicity/inhibition occurred at the higher treatment rate (13 mg/kg versus 1 mg/kg), which is similar to the maximum application rate for terrestrial non-food uses (13 mg/kg is equivalent to 3.2 lbs ai/A and the maximum terrestrial rate is 4 lbs ai/A).

The 5 different combinations of parameters studied were:

Group #	Applic. Rate	Soil Moisture	Application Vol./Vehicle
1	1 mg/kg	75% 0.33 bar	100 ul acetonitrile
2	13 mg/kg	75% 0.33 bar	100 ul acetonitrile
3	1 mg/kg	40% MHC	100 ul acetonitrile
4	13 mg/kg	40% MHC	100 ul acetonitrile
5	1 mg/kg	75% 0.33 bar	500 ul methanol/water

Calculated half-lives were: Group 5 (12 days); Group 3 (19 days); Group 1 (23 days); Group 4 (86 days); and Group 2 (113 days).

After 32 days of aerobic incubation, Group 5 favored the most rapid degradation of parent (about 28% of the applied radioactivity

11

was parent), followed by Group 3 (40% of the applied remained as parent). Group 1 was next, with parent accounting for 49% of the applied radioactivity (AR), followed by Group 4 and 2, both using the higher appication rate and resulting in 82 and 86% of the applied remaining as parent.

$^{14}CO_2$ production (volatile radioactivity) followed the same pattern. After 32 days of aerobic incubation, greatest production was observed for Group 5 (28% of applied), followed by Group 3 (26%), Group 1 (19%), Group 4 (7%) and Group 2 (5%).

MATERIALS AND METHODS:

The effects of application rate, application volume/vehicle, and soil moisture on the rate of permethrin degradation were studied under aerobic conditions. The 5 different soil treatment groups were:

Soil treatment groups

Group number	Application rate*	Soil moisture	Application vehicle#
1	1	75% 0.33 bar	100 µL acetonitrile
2	13	75% 0.33 bar	100 µL acetonitrile
3	1	40% MHC	100 µL acetonitrile
4	13	40% MHC	100 µL acetonitrile
5	1	75% 0.33 bar	500 µL methanol : water (1 : 4 v/v)

* mg permethrin/kg soil dry weight

\# Volumes shown were for application to each individual soil sample

^{14}C-Permethrin (labelled in the C-1 position of the cyclopropyl ring, 91-97% pure, s.a. 56.5 Ci/mol) was added to a sieved (2 mm) English soil, Frensham sandy loam (8% clay, 19% silt, 73% sand, 2.2% OM, pH 6.95, CEC 7.5 meq/100 gm, 10.25% water content (dry wt) at 75% of 0.33 bar), at 1 or 13 mg/kg soil dry weight. Following application, soil samples were incubated in darkness at 24.6 °C for up to 32 days prior to analysis.

Two traps (polyurethane foam plugs and ethylene glycol) were used to trap neutral volatile organics and $^{14}CO_2$ was trapped via KOH and ethanolamine/2-ethoxyethanol.

Spiking solutions of radiolabelled and nonradiolabelled parent were prepared and evenly applied to the soil surface. Duplicate soil dishes were sampled at day 14 and 32 postapplication. Foam plugs and trapping solutions were analyzed on day 7, 14, 22, and 32. Trapping solutions were radioassayed directly and foam plugs were extracted once with acetone and radioassayed.

Soil samples were extracted 3x with acetonitrile, centrifuged, and extracts were radioassayed. Soil solids were combusted and radioassayed (LSC). Analytical methodology consisted of TLC, HPLC,

and MS (electron impact). TLC analyses involved 3 different normal phase solvent systems; radiochromatograms were obtained via a TLC-Linear Analyser linked to a computer and autoradiographs were obtained using X-ray film.

HPLC analyses were completed using 2 detectors: a Ramona-5 radioactivity detector and a UV detector. The 3 acetonitrile extracts for each soil sample were combined and radioassayed. A portion of the extracts was concentrated and analyzed by HPLC.

Mass spectrometry (direct probe electron impact) was used to confirm the identifies of the test substances.

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS:

Total radioactivity recoveries were 96-104% of the applied. Almost all the volatile radioactivity was associated with $^{14}CO_2$ and there were significant differences in levels produced between treatment groups. The greatest amount of $^{14}CO_2$ (19-28% AR during 32 days) evolved from soil treatment at the lower rate (1 mg/kg). At this rate, both the soil mositure content and application volume/vehicle influenced $^{14}CO_2$ production. For soil samples incubated at 75% of 0.33 bar moisture after application of ^{14}C-permethrin in 0.1 ml acetonitrile, $^{14}CO_2$ production was 18.5% AR. Increasing the soil water content to 40% MHC or applying ^{14}C-permethrin in 0.5 ml/methanol:water (1:4,v/v) increased production to 26-28% AR.

The higher treatment rate of 13 mg/kg resulted in relatively low amounts of $^{14}CO_2$ (5-7% AR). In absolute terms, these amounts were higher than from soil treated at 1 mg/kg but $^{14}CO_2$ did not increase proportionately with application rate.

The objective of the extraction procedure was to extract parent, rather than exhaustively extract degradates. Half-lives were calculated assuming first order kinetics (plots appeared to be reasonably linear, based on 3 data points). Rate of degradation varied considerably--it was shortest for the 1 mg/kg rate. For soils incubated at 75% of 0.33 bar at the 1 mg/kg rate in 0.1 ml acetonitrile, the half-life was 23 days. Increasing water content to 40% MHC only decreased the half-life to 19 days, while applying parent in 0.5 ml methanol:water (1:4, v/v) reduced half-life to 12 days.

For the higher application rate (13 mg/kg), the half-life was 86 (estimated) and 113 days (estimated) for soil samples incubated at 40% MHC and 75% of 0.33 bar, respectively.

As expected from the aerobic and anaerobic soil metabolism studsies, the trans-isomer degraded more rapidly than the cis-isomer.

REVIEWER'S COMMENTS:

1. An English soil was used (Frensham sandy loam) from the same source as was used in the aerobic and anaerobic soil metabolism studies.

RIN - 7063-93 EFGWB Review for Permethrin

Page_____ is not included in this copy.

Pages 15 through 22 are not included.

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.

____ 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.

DATA EVALUATION RECORD

CHEM 109701 Permethrin 162-1

STUDY ID 424100-02
Hawkins, D.R., Kirkpatrick, D., Shaw, D., and J. Nicholson. May 1992. The Aerobic Soil Metabolism of ^{14}C-Permethrin. Laboratory Report No. HRC/ISN 251/911499. Unpublished study performed by ICI Agrochemicals, Huntingdon Research Center, Huntingdon, England.

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Date: 23 AUG 1993

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CONCLUSIONS

This study satisfies the 162-1 Aerobic Soil Metabolism data requirement by providing half-life and degradate information on the soil metabolism of permethrin in Frensham sandy loam (English soil).

Permethrin appears to be subject to soil microbiological degradation, with a half-life of 37 days (in sterile soil, 79% parent remained at 90 days).

The major degradate was $^{14}CO_2$; after 6 months incubation, it accounted for 34-40% of the applied (both labels). For the cyclopropyl label, 2 other degradates were formed: trans DCVA (trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid, peaking at 10% of the applied on day 14 and ICIA0597/06/03 (3-(2,2-dichlorovinyl)-2-methylcyclopropane-1,2-dicarboxylic acid), reaching a maximum of 8% on day 60. For the phenyl label, only 1 other major degradate was present, 3-phenoxybenzoic acid, with a maximum of 12-15% formed by day 30 and steadily declining to 2-3% at 1 year.

The trans isomer degraded more rapidly than the cis isomer. At day 0, the ratio was 40%cis/60%trans; at day 30, the ratio was 50:50 and by day 365, the ratio was about 78%cis/22%trans. The degradative pathway for permethrin appears to be biphasic and involve ester cleavage and CO_2 production.

MATERIALS AND METHODS:

An aerobic soil metabolism study was conducted on a 2 mm sieved sandy loam soil (5% clay, 19% silt, 76% sand, 2.1% OM, pH

6.63, CEC 6.7 meq/100 gm) from Frensham, Surrey, England under aerobic or aerobic/sterile conditions. ^{14}C-Permethrin labelled either on the Cl position of the cyclopropyl ring (98% radiopurity, specific activity 52.9 CI/mol) or uniformly on the phenyl ring (98% radiopurity, specific activity 53.5 Ci/Mol), was applied at about 1.6 mg/kg or 0.36 lbs ai/A.

Soil samples were incubated aerobically under sterile conditions up to 90 days or under nonsterile conditions for up to 1 year, maintained in darkness at 25°C in flow-through systems designed to trap radiolabelled volatiles (4 traps: polyethylene foam plugs, ethylene glycol, potassium hydroxide, and ethanolamine/2-ethoxyethanol). The soil water content was held at 75% of 0.33 bar.

Non-sterile soil samples were taken on day 0, 1, 3, 7, 14, 30, 60, 90, 120, 181, 275, and 365; sterile soil samples were taken on day 7, 30 and 90. Foam plugs and trapping solutions for non-sterile experiments were analyzed after 1, 3, and 7 days, then weekly up to 60 days and biweekly up to 365 days; for the sterile samples, analyses were done at weekly intervals up to 60 days and then after 76 and 90 days.

Foam plugs were extracted with acetonitrile once and radioassayed; trapping solutions were directly radioassayed. Soil samples were shaken with acetonitrile and extracts separated from solids by centrifugation. Extracts were radioassayed or further extracted by heat refluxing with acetonitrile/water (7/3 v/v) for 3 hours, then radioassayed. Solids were combusted and radioassayed (LSC) or heat refluxed with ethanolamine for ca. 16 hours, then radioassayed by combustion/LSC.

Analytical methodology consisted of TLC, HPLC and MS. TLC analyses (4 solvent systems) used X-ray film radioautography; reference compounds were detected by the UV fluorescent indicator on the TLC plate. Refluxed soil extract samples were further cleaned up (C8 or C18 Bond Elut column) and eluted with acetonitrile, followed by radioassay and TLC.

HPLC analyses were done (variable wavelength detector and a radioactivity detector) and MS (electron impact) was done to confirm identities of test substances.

Acceptable recoveries (91-105% for 0-30 day samples and 80-85% for soil sampled after 30 days) were obtained for non-sterile soil samples; for sterile samples, recoveries ranged from 89-105%.

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS:

The proportion of unchanged permethrin in non-sterile soil declined biphasically to about 16% of the applied amount after 90 days' incubation and to about 4% after 1 year. The initial half-

life was 37 days. The trans- isomer degraded more rapidly (from a day 0 level of 60% to 50% on day 30 to 22% on day 365) than the cis- isomer. In sterile soil, parent declined to about 79% by day 90 and was equivalent for both isomers, indicated permethrin degradation in soil was predominantly by microbiological activity.

The major degradate for both radiolabels was $^{14}CO_2$. After 1 year's incubation, $^{14}CO_2$ accounted for 49% of applied radioactivity (cyclopropyl label) and 45% (phenyl label). Volatile radioactivity for sterile soils was minimal (<0.3%). For the cyclopropyl label, 2 other major degradates were formed: trans-DCVA or trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (maximum of 10% of applied after 14 days) and 3-(2,2-dichlorovinyl)-2-methylcyclopropane-1,2-dicarboxylic acid (maximum of 7% after 30 days). The phenyl label yielded one major degradate, in addition to CO_2, 3-phenoxybenzoic acid (13% after 30 days)

In sterile soil, trans-DCVA and 3-phenoxybenzoic acid were found (12% and 8% maximum of applied radioactivity after 90 days).

REVIEWER'S COMMENTS:

1. The degradation pattern is biphasic (Fig. 19); however, a half-life was only given for the first phase.

2. Study was done on an English soil.

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DATA EVALUATION RECORD

CHEM 109701 Permethrin 162-2

STUDY ID 419706-01
Hawkins, D., Kirkpatrick, D., Shaw, D., and J. Riseborough. July 1991. The Metabolism of ^{14}C-Permethrin in Sandy Loam Soil Under Anaerobic Conditions. Laboratory Report No. HRC/ISN236/91107. Unpublished study performed and submitted by ICI Agrochemicals, Huntingdon Research Centre, Ltd., Huntingdon, England.

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CONCLUSIONS:

This study satisfies the 162-2 Anaerobic Soil Metabolism data requirement by providing information on half-life and degradates for permethrin in soil incubated under anaerobic condtions.

Permethrin applied at 3.2 lb ai/A or 13 mg/kg had an anaerobic soil half-life of 204 days in an English soil (Frensham sandy loam). This rate is similar to the maximum application rate for the terrestrial non-food uses (4 lb ai/A). Only 1 major degradate was found for each label. For the cyclopropyl label (Cl position), the major degradate was trans-DCVA (trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid), which steadily increased to a maximum of 13% after 60 days' anaerobic incubation (65-68% was parent at the end of the experiment). For the phenyl label (uniformly labelled), the major degradate was 3-phenoxybenzoic acid, which steadily increased to a maximum of 12% after 60 days' anaerobic incubation (parent accounted for 70-72% of applied radioactivity at end of study).

$^{14}CO_2$ production occurred mainly during the 30 days of aerobic incubation (about 4%).

MATERIALS AND METHODS:

Permethrin was radiolabelled (95% pure for both labels, s.a. 56.5 Ci/mol for the cyclopropyl label and 53.5 Ci/mol for the phenyl label) in either of 2 positions (Cl position on the cyclopropyl ring and uniformly labelled on one phenyl ring) and applied to an English sandy loam (10% clay, 15% silt, 75% sand,

3.3% OM, pH 6.6, CEC 8.0 meq/100 gm, and 11.1% (dry wt) water at 75% of 0.33 bar). Soil was passed through a 2 mm sieve. Application rate was 3.2 lb ai/A or 13 mg/kg and the soil was maintained under aerobic conditions for 30 days, then flooded and kept under nitrogen for 60 days in darkness at 25 °C. The test vessels were connected to 4 traps: polyurethane foam plugs, ethylene glycol, KOH, and ethanolamine/2-ethoxyethanol. The first 2 traps captured neutral volatile organic compounds, including parent, and the last two trapped CO_2.

A total of 14 soil beakers were treated with cyclopropyl-labelled parent and 20 (including 6 for the pilot study, for monitoring when the half-life was achieved) for the phenyl-labelled permethrin. Permethrin was applied to the soil surface with no subsequent mixing. Single "pilot" study samples were taken on days 7, 14, and 21 after application. Duplicate "main" study soil samples were taken (for each label) on day 0, after 30 days' aerobic incubation, and on days 14, 30, 46, and 60 of the anaerobic incubation.

In the "main " study, foam plugs and trapping solutions were analyzed after 7, 14, 21, and 30 days of aerobic incubation and after 14, 30, 46, and 60 days' anaerobic incubation. Trapping solutions were radioassayed directly; foam plugs were extracted with acetonitrile. For the pilot study, foam plugs and trapping solutions were analyzed on day 7, 14, and 21 after application.

For the flooded soil samples, the redox potential was measured and the supernatant water removed before soil extracction. Soil samples were shaken 2x with acetonitrile, then heat refluxed with acetonitrile/water (7:3, v/v). Time zero samples were extracted 3x with aceonitrile. Soil solids remaining after extraction were combusted and radioassayed by LSC. Refluxed extracts were adjusted to pH 2 and further cleaned up on a C18 Bond Elut column and eluted with acetonitrile. $^{14}CO_2$ was measured by precipitating the carbonate formed in the KOH trap with barium chloride.

Analytical methodology consisted of TLC, HPLC, and MS (electron impact). TLC analyses involved 4 normal phase solvent systems and 1 reverse phase system, with reference compound detection by UV quenching (fluorescent indicator on the TLC plate) and radioactivity detection of monitored compounds by X-ray film (autoradiogrphs).

HPLC analyses were done with both UV and radioactivity detectors and mass spectrometry was used to confirm the identities of test substances.

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS:

Half-life of permethrin during anaerobic incubation was 204 days (about 68% parent remained after 60 days' anaerobic incuba-

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tion). The trans-isomer degraded more rapidly than the cis-isomer (from 55-60% at time zero to about 50% after 60 days' anaerobic incubation). After 30 days of aerobic incubation, trans-DCVA and 3-phenoxybenzoic acid accounted for 3% of the applied radioactivity (AR). The cyclopropyl label gave 1 major degradate, trans-DCVA (trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid), reaching 13% at 60 days' anaerobic incubation. The phenyl label yielded 1 major degradate, 3-phenoxybenzoic acid, yielding 12% AR after 60 days' anaerobic incubation.

Polar material represented 2% AR (cyclopropyl label) after 30 days' aerobic incubation, then increased to 6% AR after 30 days' anaerobic incubation, declining to 2% after 60 days. For the phenyl label, polar material represented <1% after 30 days' aerobic incubation, increased to 3% AR after 30 days' anaerobic incubation, but declined to 1% AR afater 60 days.

$^{14}CO_2$ production occurred mainly during the 30 days of aerobic incubation (3-4% for both labels).

Material balance (total radioactivity) ranged from 96-102% throughout the study.

REVIEWER'S COMMENTS:

1. In this study, the half-life for permethrin during the 30 day aerobic period was considerably longer (175 days versus 37 days) than the half-life reported in the aerobic soil metabolism study due to the higher application rate (3.2 lbs ai/A in this study versus 0.36 lb ai/A in the aerobic soil metabolism study).

2. An English soil was used (Frensham sandy loam).

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DATA EVALUATION RECORD

CHEM 109701 Permethrin 163-1

STUDY ID 421967-01
Cranor, Walter. November 1991. Leaching Characteristics of Soil Incorporated Permethrin Following Aerobic Aging. Laboratory Report #39227. Performed by ABC Laboratories, Inc., Columbia, Mo. Submitted by FMC Corporation, Princeton, NJ.

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CONCLUSIONS:

This study partially satisfies the aged leaching data requirement (aged portion of 163-1, Leaching and Adsorption/Desorption) by providing an estimate of the leaching potential of parent and 1 degradate in a Nebraska sandy loam soil using soil columns. In order to completely satisfy the data requirement, leaching data for parent in 3 more soils, an estimate of the leaching potential in 4 soils of 3-phenoxybenzoic acid, one of two major degradates (other than $^{14}CO_2$) found in the aerobic and anaerobic soil metabolism studies, and an estimate of the leaching potential in 3 more soils for trans-DCVA, should be provided.

Parent does not appear to leach but one of the 2 major degradates (cyclopropyl label), aside from $^{14}CO_2$, found in the aerobic and anaerobic soil metabolism studies, transDCVA, does appear to leach through the soil columns (leachate contained 13.7%) and has a potential to leach through soil.

MATERIALS AND METHODS:

^{14}C-Permethrin (labelled in the Cl position of the cyclopropyl ring[1] or uniformly labelled in one phenyl ring[2]) was added at 3 ppm to a 2 mm sieved Nebraska sandy loam soil (56% sand, 26% silt, 18% clay, pH 6.8, 1.6% OM, CEC 11.6 meq/100 gm) and aged in the dark aerobically for 30 days. The soil was then sieved (1 mm) and used for the soil column leaching phase of the experiment.

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1. Radiochemical purity was 99% (HPLC) and 96% (TLC).
2. Radiochemical purity was 94% (HPLC) and 96% (TLC).

During the 30 day aerobic incubation, the soil samples were attached to 4 traps (ethylene glycol, 1N H_2SO_4, and 2 KOH traps (1N). For the column leaching glass columns (12"long and 4.7 cm i.d.) were used and the soil was leached with 881 ml (20 acre-inches) of 0.01 N $CaCl_2$. The bottom of the column was hooked to a 1N KOH trap.

Soil was refluxed with methanol (3x), centrifuged, and the extracts were analyzed by LSC and HPLC. However, day 30 samples were extracted (3x) with 70:30 aceonitrile:water, extracts were adjusted to a pH of 2, and re-extracted (3x) with methylene chloride and both fractions (aqueous and organic) were analyzed by LSC. The solid residue was combusted and analyzed by LSC. During the 30 day aerobic aging, soil was sampled on day 7, 14, and 30. Mass spectrometry was used to analyzed the 30 day soil extracts. Trapping solutions were analyzed by LSC.

Soi columns (control and treated) were prepared by filling the column with 12" of sieved sandy loam, then 26 gm of treated, aged soil, and topped with 10 gm of non-treated soil. After leaching, the columns were frozen and segmented into 13-1" parts. Each segment was extracted like the aerobic soil samples, analyzed by HPLC and MS, combusted and radioassayed. The leachate was analyzed by LSC, HPLC, MS, and TLC.

Three replicate columns (#2, 3, and 4) were dosed with cyclopropyl-^{14}C-labelled permethrin and 2 replicate columns (#5 and 6) were dosed with phenyl-^{14}C-permethrin; the remaining two columns were undosed.

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS:

30 Day Aerobic Aging

After 30 days of aerobic aging, 85% was parent, 11% was trans-DCVA (cyclopropyl label) and 20% was bound. For the phenyl label, 87% was parent, 11% was 3-phenoxybenzoic acid and 5% of the applied radioactivity was bound. Half-lives were 133 days (cyclopropyl label) and 207 days for the phenyl label. Insignificant $^{14}CO_2$ and other volatiles was produced (less than 1%).

Column Leaching

For the cylopropyl label, an average of 78% of the applied radioactivity (AR) was in the top 1". About 91% of this was parent. Around 14% was in the leachate and 98% of this was trans-DCVA.

For the phenyl label, an average of 74% of the AR was in the top 1" and 93% of this was parent. Around 5% of the AR was in the leachate, but this was not identified, apparently.

REVIEWER'S COMMENTS:

1. The aged leaching study was done on a U.S. sandy loam soil but the aerobic and anaerobic soil metabolism studies (and a non-guideline aerobic soil study) were all done on an English sandy loam.

2. The columns were leached for 17-18 days at a slow rate (33-58 ml/day for the cylcopropyl-labelled permethrin and 33-36 ml/day for the phenyl-labelled permethrin column.

3. The registrant used a higher dosing rate to ensure adequate amounts of degradtes but higher fortification rates of permethrin appeared to cause microbial inhibition and slow parent degradation, as shown in the non-guideline aerobic soil study.

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DATA EVALUATION RECORD

CHEM 109701 Permethrin 164-1

STUDY ID 42359109
Becker, J. M. Pounce 3.2 EC Insecticide - Terrestrial Field Dissipation. Vol. 3 of 8. May 1992. FMC Study #138E4191R1. Performed and submitted by FMC Corporation, Princeton, NJ.

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CONCLUSIONS:

This study partially satisfies the 164-1 Terrestrial Field Dissipation data requirement for permethrin by providing mobility, degradation, and dissipation information for terrestrial food uses at 0.4 lb ai/A. To complete the data requirement, another field study, for terrestrial non-food uses at 4 lb ai/A is still needed for two reasons: the terrestrial non-food uses' maximum application rate is significantly higher (8-10x) than for the terrestrial food uses; and the soil metabolism studies clearly show a markedly different half-life for the higher application rate (terrestrial non-food uses) compared to the lower application rate (terrestrial food uses).

A terrestrial field dissipation study (control and treated bareground plots) was conducted using Pounce 3.2 EC at Halifax County, NC (Trial 1, sandy loam) and Champaign County, Illinois (Trial 2, silty clay loam) at 0.4 lb ai/A. Five applications by ground sprayer were made at 5-7 day intervals beginning 5/31/91. Soil samples (to a depth of 3 ft) were taken at least 6 months after the last application and analyzed for cis- and trans-permethrin and the two major soil metabolites found in the aerobic and anerobic soil metabolism studies (other than carbon dioxide), cis- and trans-DCVA, and 3-phenoxybenzoic acid.

The half-life was 17 (North Carolina) and 43 (Illinois) days. Neither parent nor the 2 principal soil degradates (aside from carbon dioxide), trans-DCVA and 3-phenoxybenzoic acid, were detected (LOD 0.025 ppm) below 6 inches at both the NC and IL sites, indicating leaching was not occurring during this study.

At the NC site, permethrin levels reached an average maximum of 0.233 ppm on 6/15/91 (fifth application), while one of 2 prin-

cipal soil metabolites (aside from carbon dioxide), trans-DCVA, reached a maximum level of 0.035 ppm (5th application); the other principal soil metabolite, 3-phenoxybenzoic acid, was only found below the limit of detection (0.025 ppm).

At the IL site, permethrin reached an average maximum of 0.654 ppm (5th application), while one of two major soil metabolites, trans-DCVA, reached a maximum of 0.03 ppm (5th application). The other major soil metabolite, 3-phenoxybenzoic acid, attained a maximum of 0.054 ppm 1 day after the 5th (last) application.

MATERIALS AND METHODS:

Terrestrial field dissipation studies (bareground plots) were conducted at 2 sites: Trial 1 in Halifax County, NC (Goldsboro fine sandy loam, 0-12" depth, 67% sand, 22% silt, 11% clay, CEC 5.2 meq/100 gm, 1% OM, pH 6.2, 17% moisture at 1/3 bar) and Trial 2 in Champaign, IL (silty clay loam, 0-12" depth, 22% sand, 52% silt, 26% clay, CEC 22 meq/100 gm, 3% OM, pH 6.2, 31.6% moisture at 1/3 bar). Test sites in North Carolina had <1% slope and the Illinois site was described as "nearly level".

For the NC site, a control (10 x 20 m) and treated plot (16 x 24 m), separated by 15 m, were studied. Plots were divided into 5 blocks and each block wasa subdivided into 1 x 1 m subplots and each subplot was randomly sampled once. At each sampling interval, 15 subplots (3 from each of the 5 blocks) were sampled. The 15 soil cores taken at each sampling interval were composited into 3 samples per depth, except at day 1. Pretreatment samples were taken on 5/31/91. Using a backpack sprayer, 5 applications of Pounce 3.2 EC, at 0.4 lb ai/A, were made at 5 to 7 day intervals beginning 5/31/91. Plots were irrigated when rainfall fell below the 30 year average. Soil cores were collected to a depth of 36" from both plots pretreatment (day 0), immediately following each of the 5 applications, and 1, 3, 7, 14, 21, 29, 60, 90, 120 and 180 days after the last (5th) application (treated plot) and on days 0, after each application and on days 12, 29, 90 and 180 post-treatment (control plot). Cores (0-6") were first taken with a golf green cup cutter (4.25" diameter), then a 1" steel soil probe with acetate liner was used to collect the 6-36" segment, which was divided into 6" segments.

For the IL site, the field trial began 5/31/91 and continued through 4/92. The control plot was 50 x 100 ft; the treated plot was 70 x 100 ft.^{2} Each plot was divided into 5 sections and subdivided into 1 m^2 subplots. Pretreatment soil cores were composited into 1 sample for each depth. For the 1 day posttreatment (treated plot), each 6" core sample was analyzed with no compositing. For all other sampling intervals, soil cores were composited to give 3 composite samples per depth. Five applications fo Pounce 3.2 EC Insecticide were made at 0.4 lb ai/A by broadcast spray over bare soil. Irrigation was provided to maintain rainfall equivalent to the 10 year average. Soil cores were taken for both control and treated plots preapplication and

immediately postapplication. After the last (5th) treatment, samples from the treated plot were taken on days 1, 3, 7, 21, 31, 61, 90, 139, 208, and 270. The control plot was sampled on days 17, 31, 90, and 208.

At each sampling interval, 15 soil cores were collected from each plot to a depth of 36" (6" segments).

Soil samples were extracted with acetonitrile:water (7:3, v/v) and the extract made alkaline to a pH of 8.5, which was then partitioned with hexane. The hexane fraction was cleaned up on a silica gel column and analyzed by GC-ECD. The remaining alkaline aqueous fraction (which contained the 2 principal degradates, DCVA and m-PB acid) was made acidic and partitioned with methylene chloride. The 2 degradates were derivatized using pentafluoro-benzyl bromide, hexane was added, and the hexane/methylene chloride fraction was clenaed up on a silica gel column and analyzed by GC-MSD. The limit of detection for parent, DCVA, and m-PB acid was 0.025 ppm.

Average method recoveries were 85%, 96%, 90%, 87%, and 94% for cis-permethrin, trans-permethrin, cis-DCVA, trans-DCVA, and m-PB acid, respectively.

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS:

All 5 analytes (cis- and trans-permethrin, cis- and trans-DCVA, and m-phenoxybenzoic acid) were found only in th top 6" of soil. At the NC site, permethrin decreased from 0.233 ppm to <0.005 ppm within 90 days. At the IL site, permethrin decreased from 0.654 ppm (after 5th application) to about 0.014 ppm within 90 days. Dissipation of trans-permethrin was more rapid than the cis-isomer. The half-life of permethrin (both isomers combined) was 17 and 43 days, respectively, for the NC and IL sites (first-order linear regression), though the data suggests that permethrin dissipation kinetics more closely follows a biphasic pattern, with a rapid initial rate and slow secondary rate.

The 2 major soil metabolites, trans-DCVA and 3-phenoxybenzoic acid, were detected only in the top 6" and only during the first 2 months of the study.

REVIEWER'S COMMENTS:

1. The storage stability data (Table 13) indicates soil samples spiked with parent were analyzed up to 7 months and the soil samples spiked with 2 degradates (trans-DCVA and 3-phenoxybenzoic acid) up to 6 months, showing no degradation. However, some field samples were not analyzed until stored for 9 months.

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DATA EVALUATION RECORD

CHEM 109701 Permethrin 165-4

STUDY ID 413004-01
Burgess, David. October 1989. Uptake, Depuration and Bioconcentration of ^{14}C-Permethrin by Bluegill Sunfish (Lepomis macrochirus) Laboratory Report #PC-0117. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, Mo. and submitted by FMC Corporation, Princeton, NJ.

STUDY ID 413004-02
Tullman, Robert. November 1989. Accumulation Studies: Laboratory Studies of Pesticide Accumulation in Fish: Acid (Cyclopropyl)-^{14}C-Labelled Permethrin in the Bluegill Sunfish. Laboratory Report # 138E5489E1-1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

STUDY ID 413004-03
Singer, Sandra. October 1989. Accumulation Studies: Laboratory Studies of Pesticide Accumulation in Fish: ^{14}C-Alcohol (Phenyl)-Labelled Permethrin in the Bluegill Sunfish. Laboratory Report # 138E5489E1-2. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

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Date: 23 AUG 1993

CONCLUSIONS:

These 3 studies satisfy the 165-4 Laboratory Studies of Pesticide Accumulation in Fish data requirement by providing information on the nature and quantity of pesticide residues which accumulated in fish exposed for 28 days to 0.5 ug/l ^{14}C-Permethrin labelled in either the acid (cyclopropyl) or alcohol (phenyl) moiety. Up to 20% of the total radioactivity was not identified, but based on an exhaustive analytical scheme, the registrant hypothesizes that the residues are phospholipid conjugates of permethrin metabolites.

1. <u>Acid Label</u>

a. Bioconcentration

Maximum bioconcentration factors (day 28) for fish tissues

Maximum bioconcentration factors (day 28) for fish tissues exposed to 28 days of acid-labelled ^{14}C-Permethrin were: 230x (fillet); 610x (whole fish); and 1100x (viscera).

b. Depuration

After 14 days of depuration, the percent depuration (expressed as a percentage of the day 28 ^{14}C-Permethrin concentrations) were: 82% (fillet); 79% (whole fish); and 83% (viscera).

c. Fish Tissue Residues

Table XXI (MRID 4130041-02) indicates that parent accounted for most of the radioactive residue in the day 21 and day 28 fish tissues, ranging from 57-76% TRR. Only one metabolite was identified (DCVA) and it was present from 4-10% TRR. The "oily fraction" acccounted for 7-20% of the TRR but the substantial effort the registrant made to identify the residues did not succeed.

2. Alcohol Label

a. Bioconcentration

Maximum bioconcentration facctors (day 28) for fish tissues exposed to 28 days of alcohol-labelled ^{14}C-Permethrin were: 180x (fillet); and 950x (viscera). The maximum bioconcentration factor for whole fish was reached on day 21 (570x).

b. Depuration

After 14 days of depuration, the percent depuration (expressed as a percentage of the day 28 ^{14}C-Permethrin concentrations were: 81% (fillet); 73% (whole fish) and 83% (viscera).

c. Fish Tissue Residues

Table X (MRID 4130041-03) indicates that parent accounted for most of the radioactive residue in the day 21 and 28 fish tissue, ranging from 76-90% of the TRR. Only a trace amount (<1%) of PB-acid (3-phenoxybenzoic acid) was detected. The "oily fraction" contained 5-12% of the TRR but substantial efforts to identify the radioactive residues did not succeed.

MATERIALS AND METHODS:

In-Life Portion of Study

Bluegill sunfish were continuously exposed to 0.5 ppb (0.5 ug/l) ^{14}C-Permethrin (labelled either on the "acid" or "alcohol" moiety). Five aquaria (2 per label plus 1 control tank) each containing 120 fish were sampled on days 0, 1, 3, 7, 14, 21, and 28 (treatment period) and on days 1, 3, 7, 10, and 14 (depuration period). Fish were sectioned to include fillet (muscle, skin, and

skeleton) and viscera (fins, head, internal organs); whole fish were also analyzed. On each sampling date, 3 fish from each tank were sectioned into edible and visceral portions and pooled for radioanalysis. In addition, 3 more fish were pooled for whole fish analysis. Additional fish were collected for metabolite identification (days 21 and 28): 20 fish from the treated radioanalysis tank and 60 fish from the treated metabolite tank, which were divided into 20 whole fish and 40 fish dissected into edible and nonedible portions.

The ^{14}-C activity in whole fish, fillet and viscera was determined by sample combustion followed by LSC. Recoveries using control fish spiked with ^{14}C-Permethrin (both labels) were 95-101%.

In order to ascertain the correct treatment (exposure) rate, a preliminary study (10 day flow-through) was done to determine the acute toxicity and 0.5 ug/l was selected as the correct exposure level. Prior to addition of the test fish for the bioconcentration study, a 4 day equilibration and calibration study was done to check diluter accuracy. Water concentrations in the test aquaria ranged from 0.29 ug/l-0.44 ug/l (av = 0.36 ug/l) for the acid label and 0.25-0.70 ug/l (av = 0.41 ug/l) for the alcohol label.

Limits of detection (LSC) were: 0.02 ppb (water and 1 ppb for fish tissues. Mean recovery for ^{14}C-Permethrin in tissue sample oxidations were 98% for all tissue types.

Water samples were received from ABC, acidified and extracted with hexane (3x) and analyzed by TLC and HPLC. The radioactivity in the aqueous phase was further removed via a C_{18} Sep-Pak column and eluted with methanol and/or acetonitrile, concentrated and analyzed by TLC>

Metabolite Identification (Fish Tissue from Day 21 and 28)

1. Acid Label (95% pure, s.a. 23.7 mCi/mmol)

Control fish tissue samples were used to obtain recovery data (200 ppb) and storage stability data (5-6 weeks).

Replicate samples of viscera, fillet, or whole fish were extracted with acetone/hexane (3x), filtered and combined extracts were assayed by LSC. The dried filter cake was combusted. The combined extracts were taken to dryness and re-dissolved with hexane, partitioned with hexane-saturated acetonitrile (5x) and assayed by LSC. Fractions containing significant radioactivity were further purified by gel permeation chromatography, and eluted with cyclohexane/methylene chloride. Fractions containing the bulk of the radioactivity and little or no oil were analyzed by TLC or transferred to acetonitrile and analyzed by HPLC. Oil fractions were taken to dryness and subjected to 1 of 5 procedures: (1) dissolved with MeCN (2) dissolved with hexane and cleaned up on florisil (3) reverse phase (C_{18}) solid phase extraction (4) acid hydrolysis (5) enzyme hydrolysis with phospholipase C.

2. Alcohol Label

The "non-oily" fraction contained parent (77-90% of the TRR), with only trace amounts of other components. The "oily" fraction contained 0-9% of the TRR. The PES (post extraction solids) only contained 3-7% of the TRR and was not analyzed further. The oil fraction was further subjected to a variety of cleanup columns, acid extraction, refluxing with acid or ethanolic KOH, enzyme hydrolysis, followed by LSC/TLC/HPLC analysis, but all attempts to analyze the polar, fat soluble radioactive residues were unsuccessful. It is hypothesized by the registrant that the unidentified radioactive residues are phospholipid conjugates.

Analytical Methodology

Radioactivity in solution was determined initially by LSC. The HPLC system used was a Waters 840 HPLC system with dual (UV and radioactivity) detectors. For TLC, silica gel plates (eluted with 90% hexane/10% ethyl acetate plus 1% acetic acid) was used and, when sufficient material allowed, samples were also chromatographed via reverse phase. Standard spots were visualized by a UV lamp and detection of radioactive zones was done by a Bicscan Analyzer or exposure of the plate to film.

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS:

1. Bioconcentration Factors and Depuration (both labels)

Tissue residues after 28 days of exposure to acid-labelled ^{14}C-Permethrin were 83 ug/kg (ppb) for fillet, 220 ug/kg for whole fish and 390 ug/kg for viscera. Bioconcentration factors were 230x, 610x, and 1100x, respectively. Tissue residues (alcohol label) after 28 days were 72 ug/kg, 210 ug/kg, and 390 ug/kg for fillet, whole fish and viscera, respectively. Bioconcentration factors were 180x, 510x, and 950 x, respectively.

By day 14 during the depuration phase, 82, 79, and 83% depuration (acid label) had occurred in fillet, whole fish, and viscera, respectively. The alcohol label showed 81, 73, and 83% depuration.

The uptake rate constant (K_1), depuration rate constant (K_2), time to 50% clearance, and steady state BCF for whole fish were determined (using a BIOFAC computer program) for both labels and determined to be:

	Acid Label	Alcohol Label
Uptake Rate Constant (K_1) ug/kg fish/ug/l water/day	83	76
Depuration Rate Constant (K_2) per day	0.15	0.15
Time (50%) for depuration (days)	4.7	4.6

Bioconeentration Factor (BCF) average	570	500
Time to reach 90% of steady-state (days)	16	15

2. Aquarium Water (0.5 ppb exposure level)

Two interesting observations were made by the registrant. The concentrations in the mixing box were consistent with the desired exposure level (on days 1, 14, 21, and 28, levels were 0.54, 0.50, 0.48, and 0.51 ppb, respectively). By contrast, the aquarium water samples for the same days contained 0.63, 0.23, 0.28, and 0.27 ppb, respectively, caused by the presence of fish absorbing the permethrin.

Also, the aquarium water from Day 1-28 contained metabolites, while water from the equilibration period contained only parent; metabolites were apparently excreted into the water by the fish. The percentage of material remaining in the water after partitioning decreased from day 21 to day 28, probably caused by the fact that half the fish (60/120) were removed on day 21.

3. Tissue Analysis (Day 21 and 28)

a. Acid Label

Fish samples were taken from the metabolite aquarium and combusted to determine total radioactivity. Day 21 and 28 values ranged from 47-58 ppb (fillet), 268-322 ppb (viscera) and 166-184 ppb for whole fish.

Permethrin accounted for 57-76% of the total radioactivity and DCVA accounted for 4-10%. Some polar yet oily material was present at 7-20% fo the total radioadtivity. Partial characterization of the material as phospholipid conjugates of permethrin degradates was made by phospholipase C enzymatic hydrolysis and TLC.

b. Alcohol Label

Only small amounts of metabolites were found in fish tissue, the maximum being 0.9% TRR (total radioactive residue) of an unidentified metabolite found in the 28 viscera sample. Some metabolites appeared to be phospholipid conjugates and remained in the GPC (gel permeation chromatography) lipid (oily) fraction. The latter accounted for up to 12% TRR (whole fish 21 day). These conjugates were not cleaved readily by acid or base and only to a limited extent with enzyme. Hexane and PES (post extraction solids) fractions also contained unidentified residues, ranging from 0-9% TRR.

REVIEWER'S COMMENTS

1. Storage stability studies were done for both aquarium water and fish tissues and demonstrated a quantitative recovery of parent in stored samples.

RIN 7063-93 EFGWB Review for Permethrin

Page_____ is not included in this copy.

Pages 110 through 148 are not included.

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.

__✓__ 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
PERMETHRIN
Last Update on August 27, 1993
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer:	Section Head:	Date:

Common Name:PERMETHRIN
Smiles Code:ClC(Cl)=CC(C1(C)C)C1C(=O)OC-c(ccc2)cc2O-c(ccc3)cc3
PC Code # :109701 CAS #:52645-53-1 Caswell #:

Chem. Name :3-(PHENOXYPHENYL)METHYL (+/-)-cis,trans-3-(2,2-DICHLORO-ETHENYL)-2,2-DIMETHYLCYCLOPROPANECARBOXYLATE
Action Type:Insecticide (a synthetic pyrethroid)

Trade Names: AMBUSH; BW-21-Z; ECTIBAN; EKSMIN; POUNCE
(Formul'tn): 3.2EC; 25%WP
Physical State:

Use Patterns (% Usage) :FOLIAR APPL. GENERAL. TO BE APPLIED WHEN INSECTS APPEAR OR :FEEDING IS NOTICED.

Empirical Form: $C_{21}H_{20}O_3Cl_2$
Molecular Wgt.: 391.29 Vapor Pressure: 2.15E -8 Torr
Melting Point : VARIES °C Boiling Point: °C
Log Kow : 6.1 pKa: @ °C
Henry's : E Atm. M3/Mol (Measured) 5.53E -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)
[V] pH 5.0:>30 DAYS
[V] pH 7.0:>30 DAYS
[V] pH 9.0:>30 DAYS
[ ] pH :
[ ] pH :
[ ] pH :

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Photolysis (161-2, -3, -4)
[V] Water:79.7 DAYS
[ ] :
[ ] :
[ ] :

[V] Soil :>30 DAYS ON LOAM; Xe ARC
[ ] Air :

Aerobic Soil Metabolism (162-1)
[ ] <10 WK IN THREE SdClLm AND A LmSd SOILS.
[V] 37 days in Frensham sandy loam (English soil)
[ ]
[U] 30 days
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[ ] >14 WK (ONLY 15% OF APPLIED EVOLVED AS CO2 IN 14 WEEKS)
[V] 204 days in Frensham sandy loam (English soil)
[ ]
[ ]
[ ]
[ ]
[ ]

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

Aerobic Aquatic Metabolism (162-4)
[ ]
[ ]
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[ ]

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Soil Partition Coefficient (Kd) (163-1)
[ ] FINE SAND, 1.7% OM; (Kd = 0.386)
[ ] CLAY LOAM, 5.2% OM: (Kd = 633)
[V] parent did not leach in soil columns of Nebraska sandy loam
[ ] but trans-DCVA was found in leachate
[ ]
[ ]

Soil Rf Factors (163-1)
[ ] IMMOBILE IN AGED AND UNAGED
[ ] FINE SAND, SdLm, SiLm, AND
[ ] ClLm.
[ ]
[ ]
[ ]

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[ ] CYPERMETHRIN (WHICH HAS DEGRADATES IN COMMON WITH PERMETH-
[ ] RIN) DISSIPATED WITH T1/2 OF 7-30 DAYS IN UPPER 6" OF LOAM
[ ] SOILS IN CALIFORNIA AND ARKANSAS. APPLICATION HAD BEEN AT
[ ] 2 LBS AI/A. CYPERMETHRIN WAS <0.15 PPM IN 6-12" DEPTH AND
[ ] DID NOT APPEAR TO LEACH. DICHLOROVINYL ACID AND 3-PHENOXY
[ ] BENZOIC ACID WERE <0.04 PPM AT ALL SAMPLING LEVELS.
[V] 17 days (NC) and 43 days (IL) at 0.4 lb ai/A bareground, 5
[ ] applications; no pattern of leaching for parent or two major
[ ] soil metabolites (trans-DCVA and 3-phenoxybenzoic acid).
[ ]

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)
[ ] AFTER FOUR MONTHS, RESIDUES WERE STILL PRESENT IN COTTON,
[ ] LETTUCE, SUGAR BEETS AND WHEAT.

Accumulation in Rotational Crops, Field (165-2)
[ ] NO RESIDUES ARE EXPECTED IN CROPS PLANTED 60 DAYS
[ ] OR MORE AFTER APPL. OF 1 LB AI/ACRE/YEAR

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

Bioaccumulation in Fish (165-4)
[ ] BLUEFISH BCF: EDIBLE 21X; VISCERA 715X
[ ] CATFISH BCF: EDIBLE 91X: VISCERA 703 X; also valid study below

Bioaccumulation in Non-Target Organisms (165-5)
[V] 165-4 bluegill study:Viscera (950-1100x);whole fish (570-610x);
[ ] fillet (180-230x); depuration rapid--73-83% (range for all 3

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-phenoxybenzylalcohol (major degradate in soil), further degrades to 3-phenoxybenzoic acid, 3-phenoxybenzaldehyde, and dichlorovinyl-methylcyclopropanecarboxylic acid (cis and trans).

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Comments

Field monitoring (cotton) - permethrin will runoff
Permethrin strongly sorbed in soils with high %OM, and less in soils with low %OM. Degradates more mobile but do not appear to be a problem. There are data which show hydrolysis at pH 9 to be rapid, with T1/2 = 2.9 to 4.6 days (at 45 C).

Soil microorganisms degrade permethrin.
Soil Koc = 10,600.

EFGWB has recommended that the registrant be notified that the environmental fate of both the cis and trans isomers of permethrin and degradates should be elucidated, or acceptable evidence should be presented that shows there is little, if any, difference in the environmental fate of the two isomers.

References: EAB FILES
Writer : PJH and RJM