US EPA ARCHIVE DOCUMENT

Date Out EFB: APR 29 1982

To: Product Manager 17 GEE
TS-767

From: Dr. Willa Garner III
Chief, Review Section No. 1
Environmental Fate Branch

FILE COPY

Attached please find the environmental fate review of:

Reg./File No.: 10182 - AL, 10182 - AU

Chemical: Cypermethrin

Type Product: Insecticide

Product Name: Cymbush

Company Name: ICI

Submission Purpose: Registration of New Insecticide Chemical for use on cotton

ZBB Code: 3(c)(5)

ACTION CODE: 105

Date in: 2/17/82

EFB # 130, 131

Date Completed 4/29/82

TAIS (level II) 61

Days 29

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

Crop	Pests	Rates: lb ai/acre	Rates: Fl. oz./acre	Remarks
Tomatoes	Tomato Fruitworm Cabbage Looper Potato Aphid	0.025-0.1	1.3 to 5	Apply as necessary for insect control using a minimum of 15 gallons of finished spray per acre with ground equipment or 3 gallons of finished spray per acre when applied by aircraft.
	Beet Armyworm Southern Armyworm Tomato Pinworm Fall Armyworm Colorado Potato Beetle	0.04-0.1	2-5	Lower rates of Ammo 2.5 EC should be used under light to moderate insect pressure. Higher rates should be used to control heavy insect populations. Do not make more than 12 applications per season. Do not plant rotational crops within 30 days of the last application. Do not use Ammo 2.5 EC on small fruited varieties (less than 1.0 inch in diameter) such as red cherry, small fry tomatoes. Ammo 2.5 EC may be used up to 3 days before harvest.

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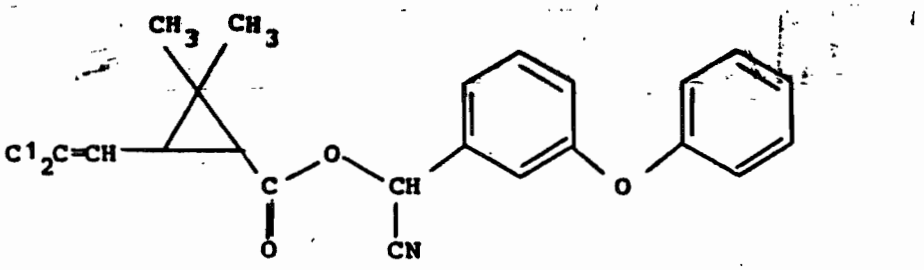
1.0 INTRODUCTION

1.1 Purpose

ICI Americas, Inc. is requesting full registration of Cymbush 2E and 3E, a new insecticide, under Sec. 3(c)(5) of FIFRA (PM #17, EFB #130,131). Cymbush 2E and 3E is intended for use as an insecticide on cotton at a maximum dosage of 1.875 lb ai/A/season

1.2 Chemical

Trade Name: "CYMBUSH" Pyrethroid Insecticide
Common chemical name: cypermethrin
Code numbers: PP383, NRDC 149, WL 43467
Systematic chemical name: (±) L-cyano-(phenoxyphenyl) (±)- cis, trans-3-(2,2-dichloroethenyl-2,2-dimethylcyclopropanecarboxylate - 22.8% (2 lbs ai./gal), 35.6% (3 lbs ai/gal)
Type: Insecticide
Molecular weight: 416
Molecular formula: C22 H19 03 N12
Structural Formula:



cypermethrin

(RS)-α-cyano-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
or
(RS)α-cyano-3-(phenoxyphenyl)methyl (1RS)cis:trans 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate

Isomer Ratio:
45 ± 10% Cis
55 ± 10% Trans

Physical and Chemical Properties of Technical Grade Material:

Appearance	:Dark brown viscuous liquid
Specific gravity	:1.24
Flash point	:Not below 44°C. Not explosive
Solubility	:Miscible with alcohols, ketones, chlorinated hydrocarbons and substituted aromatic hydrocarbons (Xylene). Sparingly soluble in aliphatic hydrocarbons

Corrosivity :Not corrosive

Physical and Chemical Properties of Formulated Material:

Formulation	GFU 034B	GFU 061	JF 6670
Description (lbs ai/gal)	3	3	2
Specific gravity	1.00	1.01	1.05
Weight lb/gal	8.35	8.43	8.76
Viscosity (centistokes)	7	7	-
Vapor pressure (mm Hg at 25°C)	22	10	-
Boiling Point °C	157	160	-
Flash point (Seta Flash °F)	93	110	118
Explosion Hazards	none	none	none
Flammability	not fl.	not fl.	not fl.

1.3 Previous Reviews

10182-EUP-19 5/8/80
10182-EUP-19 5/4/81

1.4 Background

Cymbush 2E and 3E has been under experimental use permit to test its effectiveness as an insecticide in cotton since 1981. In the initial experimental use permit reviewed on 5/8/80 no environmental chemistry data were submitted therefore EFB did not concur with issuance of the permit request. On 12/29/80 ICI Americas Inc requested an EUP extension and expansion allowing the 1981 and 1982 continued testing of cymbush for insect control in cotton. The following environmental chemistry data submitted in 10182-EUP-19 were found to be acceptable in the 5/4/81 review of that submission:

(a) Hydrolysis
(b) Aerobic soil metabolism
(c) Anaerobic soil metabolism
(d) Leaching
(e) Field dissipation

The 5/4/81 review also recommended:

(1) Against issuance of an EUP until "Rotational Crop Studies" are met. Alternatively a statement must be added to the label which denies the rotation of crops.

(2) At the time of registration, the following studies for a Field-vegetable crop will need to be submitted:

(a) Photodegradation
(b) Effects of microbes on cypermethrin
(c) Effects of cypermethrin on microbes
(d) Adsorption/desorption
(e) Fish Accumulation studies

2.0 Proposed Uses

Cymbush 2E and 3E Insecticide should be applied to cotton as a foliar multiple application at 5-7 day intervals. Proposed dosage for Cymbush 2E is 0.24 to 0.48 pints/Acre/ Application (0.06 to 0.12 lbs ai/A/Application) and for Cymbush 3E is 0.16 to 0.32 Pints/Acre/ Application). (0.06 to 0.12 lbs ai/A/Application). All applications are to be applied in a minimum spray volume of 1.5 gallons of water /A by aerial equipment or 5 gallons of water /A by ground equipment. Apply Cymbush insecticide using sufficient water to obtain full coverage of foliage. Apply every 5 to 7 days or as needed. Timing and frequency of applications should be based on insect populations reaching locally determined economic thresholds.

2.1 Use Precautions

(a) Do not apply more than 7.5 pints/A/Season Cymbush 2E (1.875 lbs ai/A/Season) or 5.0 pints/A/Season Cymbush 3E (1.875 lbs ai/A/Season).

(b) Do not graze livestock in treated areas. Do not apply within 14 days of harvest.

(c) This pesticide is extremely toxic to fish. Use with care when applying to areas adjacent to any body of water. Keep out of lakes, streams, ponds, tidal marshes or estuaries. Do not contaminate water by cleaning of equipment or disposal of wastes.

(d) Do not apply when weather conditions favor drift from treated areas.

(e) This product is highly toxic to bees exposed to direct treatment or residues on crops or weeds. Do not apply AMBUSH (sic) or allow it to drift to crops or weeds on which bees are actively foraging.

(f) Do not use or store near heat or open flame or near food or feed.

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(g) Do not reuse container. Triple rinse residue from empty container and add rinse to mixture in spray tank. Dispose of container in sanitary landfill in accordance with State and local regulations.

3.0 Discussion of Data

Data previously submitted for cypermethrin were filed under EPA No. 10182-EUP-19 accession No. 244018, dated 12/29/80. The following is a list of the studies submitted at that time and reviewed on 5/4/81 by EFB.

1J Rapley, J.H., Arnold, D.J., Vincent J. and Moore, D., "Cypermethrin: Degradation in River Water and Sediments" ICI Plant Protection Division Report No. RJ0119B [March 1980].

2J Hill, I.R., Harvey, B.R. and Weissler, M.S., "Permethrin" Degradation in River Sediments, River Water and In Flooded Soils" ICI Plant Protection Division Report No. R, J0008A [January 1979].

3J Leahey, J.P., Richardson, K., Woods, T.M. and Bewick, D.W. "Hydrolysis of Cypermethrin" ICI Plant Protection Division Report No. RJ0117B [January 1980].

4J Allsup, T.L. "Hydrolysis of FMC 33297 Insecticide" FMC Corporation Report No. W-0103 [April 1976].

5J Standen, M.E. "The Degradation of the Insecticide WL43467 In Soil Under Laboratory conditions" Shell Research Ltd. Report No. WKGR 0094.76 [September 1976].

6J Standen, M.E. "Further Studies of The Degradation Of the Insecticide WL43467 (Cypermethrin) in Soil Under Laboratory Conditions" Shell Research Ltd. Report No. BLGR 0034.78 [March 1978].

7J Roberts, T.R. and Standen, M.E. "Degradation of the Pyrethroid Cypermethrin (NRDC 149, (±)-α-cyano-3-phenoxybenzyl (±)-cis, trans-3-(2,2 dichlorovinyl)-2,2-dimethyl-cyclopropanecarboxylate) and the Respective cis(NRDC 160) and trans-(NRDC 159) Isomers in Soil" Pestic. Sci. 8, 305-319 [1977].

8J Swaine, H. and Hayward, G.J. "CYPERMETHRIN: Laboratory Degradation On Two Standard Soils. Part I" ICI Plant Protection Division Report No. Rj00115B [December 1979].

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9J Arnold, D.J., Cleverley, B.A. and Hill, I.R. PERMETHRIN: Laboratory Studies Of The Degradation Of The Pesticide In Soil" ICI Plant Protection Division Report No. TMJ1287B [February 1976].

10J Arnold, D.J., Cleverley, B.A. and Hill, I.R. "PERMETRIN: The Degradation Of The Pesticide In Soil Under Laboratory Conditions. III" ICI Plant Protection Division Report No. TMJ1512B [June 1977].

11J Arnold, D.J., Cleverley, B.A. and Hill, I.R. "PERMETHRIN: Degradation In Soil Under Laboratory Conditions (II)" ICI Plant Protection Division Report No. TMJ1427B [November 1976].

12J Gowman, M. and Riley, D. "Determination Of The Physical And Chemical Properties Of Soils. Methods In Use At Jealott's Hill Research Station" ICI Plant Protection Division Report No. TMJ1190A.

13J Prashad, S. and Newby, S.E. "PP383: Leaching on Thick-Layer Soil Chromatograms" ICI Plant Protection Division Report No. TMJ1525B [August 1977].

14J Stevens, J.E. and Riley, D. "Pesticide Mobility In Soil: Determination By Soil Thick-Layer Chromatography" ICI Plant Protection Division Report No. TMJ1080A [November 1974].

15J Ussary, J.P. "Cypermethrin Dissipation In Soils" ICI Americas Inc Report No. TMU0511/B [July 1980].

16J Fitzpatrick, R.D. "A Gas-Liquid Chromatographic Method For The Determination Of Cypermethrin (PP383) In Soils". ICI Americas Inc Report No. GRAM-7 [September 1980].

The current submission was compiled under Section J Environmental Chemistry containing 40 studies (Numbered 17J - 56J). Studies Numbered 41J - 46J inclusive will not be reviewed in this submission in that they describe residue uptake of permethrin and/or cypermethrin in the rat, mallard duck, quail or dairy cattle, subjects more appropriately dealt with in other reviews. Data were filed under accession numbers 070558, 070559 and 070560, PP Nos. 2F2623 and 2H5334 on 12/30/81.

3.1 CYPERMETHRIN: Degradation in River and Pond Waters and Sediments. Rapley, J.H., Arnold, D.J. and Vincent, J. [ICI Plant Protection Division Report No. RJ0175B, March 1981]. Experimental

The distribution and fate of radiolabeled cypermethrin was studied in aquatic model systems in the United Kingdom. Three river water and one pond water samples and their associated sediments were collected from sites within the United Kingdom and transferred to laboratory aquatic incubation units maintained in the dark at 16°C under both aerated and static conditions for periods of up to 26 or 63 weeks. At zero time, samples were spiked with either cis, trans-^{14}C-benzyl labeled cypermethrin or cis, trans-^{14}C-cyclopropane labeled cypermethrin at rates equivalent to 0.14 kg/ha (0.125 ppm).

Results

Degradation rates and products formed from cypermethrin were similar in all treatments; more than 50% of the parent compound was degraded in under 2 weeks and 90% in 2 to 9 weeks. Less than 4% of the pesticide was present in the water after two weeks in all but one treatment. After approximately one year 40 to 70% of the applied radioactivity was evolved as $^{14}CO_2$ from ^{14}C-benzyl labeled treatments and approximately 8% from the cyclopropane label.

The major degradative route was by hydrolysis of the ester link leading to the formation of cis and trans cyclopropane carboxylic acids, 3-phenoxybenzaldehyde and 3-phenoxybenzoic acid. All but the cyclopropane carboxylic acids were further degraded.

The structures of all cypermethrin degradation products identified on plants in animals and in the environment throughout this submission are presented in tabular form in Section 4.91 of this review.

The major ^{14}C-benzyl labeled degradation product present in the sediments was 3-phenoxybenzaldehyde (compound III) which accounted for up to 28% of recovered radioactivity. Compound IV (3-phenoxybenzoic acid) was also present in amounts up to 9% of recovered radioactivity in sediments. Compounds III and IV were further degraded with time. Compound VI 4'hydroxy-3-phenoxybenzoic acid was present in amounts less than 2% of recovered radioactivity and Compound V 3-phenoxybenzyl alcohol was detected in trace amounts.

The major ^{14}C-cyclopropane labeled products formed in sediment were (1RS) cis and trans -3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acids (compounds Ia and Ib). These accounted for up to 34% and 14% of recovered radioactivity in the aerated and static units, respectively. Also present in the sediment extracts was the methyl ester of cis, trans dichlorovinyl

cyclopropane acid (compound XII) accounting for up to 14% of the recovered radioactivity. The major ^{14}C-benzyl labeled degradation product in river and pond waters was 3-phenoxybenzoic acid (IV) which was present in amounts up to 21% of the recovered radioactivity. The dichlorovinyl acids accounted for the majority of the recovered ^{14}C-cyclopropane label (34% and 54% respectively in aerated and static units after 26 weeks incubation) and remained at this level in aerated units for over a year.

Up to 23% and 31% of the recovered radioactivity remained unextracted from the sediments of ^{14}C-cyclopropane and ^{14}C-benzyl labeled treatments respectively.

Conclusions

Cypermethrin was rapidly degraded in natural pond and river water in contact with its underlying sediment with 50% of the parent compound lost in under 2 weeks and 90% in 2 to 9 weeks. Unextracted radioactivity in all sediments however rapidly increased during the first 5 to 12 weeks following treatment and gradually declined to levels of 6 to 27 ppb after 26 weeks in some sediments or to 17 to 30 ppb after 63 weeks in other sediments.

Comments

This study which describes the degradation of cypermethrin in natural river and pond waters including sediments does not fulfill environmental chemistry data requirements for the proposed use of this insecticide on a field-vegetable crop (cotton). However this study which is adequately performed satisfies the guidelines requirements under 162-3 (Anaerobic Aquatic) and 162-4 (Aerobic Aquatic Metabolism) studies. This study should be resubmitted by the registrant at such time that an aquatic use of cypermethrin is contemplated.

3.2 ^{14}C-CYPERMETHRIN: Aqueous Photodegradation in Sunlight" Day, S.R. and Leahey, J.P. [ICI Plant Protection Division Report No. R10154B, November 1980].

EXPERIMENTAL

This study was designed to establish the fate of ^{14}C-cypermethrin in sterile aqueous solutions irradiated with natural sunlight for periods of up to 32 days.

Autoclaved glass distilled water was added to each of 18, 250 cm^{-3} quartz flasks which were tightly plugged with non-adsorbent cotton wool. ^{14}C-benzyl labeled cypermethrin was added to half of the flasks and ^{14}C-cyclopropyl labeled cypermethrin (both in 30% acetonitrile/water (V/V) stock solutions) was added to the remainder of the flasks to give

a final solution concentration of the radiolabeled chemicals at 1 ppm. Three flasks of each radiochemical solution were covered with aluminum foil to act as controls. All eighteen flasks were placed outside in a position affording maximum direct sunlight. Local weather records including the intensity of incident sunlight were reported during the 32 day exposure period of the experiment. The pH of test solutions averaged 5.3 at 26°C.

At intervals of 1,2,4,8,16 and 32 days a flask of each radiochemical was removed and radioassayed immediately by LSC. At 32 days dark controls were also radioassayed. At these same time intervals the percentage of cypermethrin in all samples was measured by reverse phase HPLC.

A more detailed analysis was carried out on the day 32 samples in order to characterize, where possible, the photoproducts formed. HPLC analysis was carried out using gradient elution and the characterization of photoproducts was established by comparison of retention data with that of reference compounds.

Portions of the day 32 solutions were also analyzed qualitatively by TLC (solvent systems A and B) after evaporation to dryness and dissolution into acetonitrile.

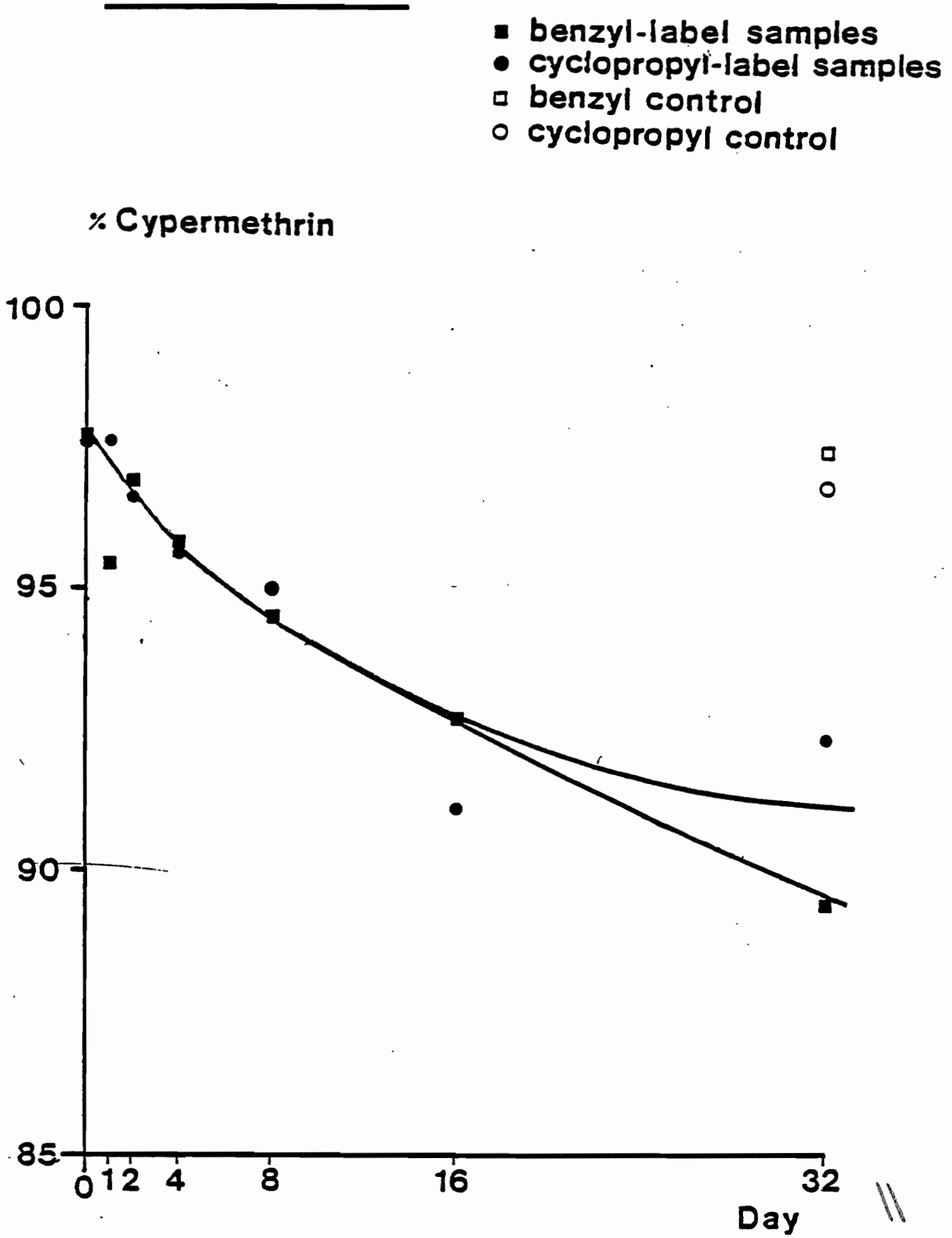
Silica gel plates (0.25mm, Keiselgel 60 F^{254}, Merck) were used for TLC. The solvent systems used were as follows:

A cyclohexane (saturated with formic acid/diethyl ether, 3:2
B toluene (saturated with formic acid)/diethyl ether, 10:1

Reference compounds were located on developed chromatograms by their quenching of gel fluorescence under uv light.

Autoradiograms were prepared from developed plates to facilitate the location of radioactive products. Characterization was deduced by the co-chromatography of products with admixed reference compounds.

Fig. 1 Photodegradation Rate of Cypermethrin in Aqueous Solution



RESULTS

[A] Rate of Degradation of Cypermethrin
After 32 days of exposure to natural sunlight cypermethrin accounted for 89.4% of the activity in the ^{14}C-benzyl labeled sample and 92.37% in the ^{14}C-cyclopropyl labeled sample. Dark controls contained 97.4% and 96.8% cypermethrin respectively at day 32. A graphical representation of the rate of photo-degradation of cypermethrin is given in Figure 1.

RESULTS

[B] Identification of Photoproducts

At least eight photoproducts were formed from each radiochemical illustrated by the autoradiograms of thin layer chromatograms of the day 32 samples. Two of the photoproducts in the ^{14}C-benzyl labeled sample co-chromatographed with Compounds III and IV in both solvent systems A and B.

The photoproducts formed after 32 days were quantified by HPLC analysis. Radiotraces were obtained from these analyses and the fractions were collected for radiocounting.

CONCLUSIONS

Solutions of cypermethrin in sterile distilled water are degraded very slowly in sunlight, so that only 10% degradation occurs after 32 days irradiation. A large number of photoproducts result from the irradiation (8 or more radioactive compounds were formed from both acid and alcohol-labeled cypermethrin). Three of the photoproducts formed were characterized as compounds I (a and b), III and IV and these accounted for 0.9%, 1.4% and 2.6% respectively of the activity in the irradiated solutions. No uncharacterized photoproduct was formed at a level greater than 2.6% (0.026 ppm).

Loss of cypermethrin from solution by absorption, in the later stages of the study, prevented calculation of the photodegradation rate constant.

COMMENTS

Due to experimental difficulties the photolytic half-life or rate constant could not be provided by the registrant. However, based on an extrapolation of the data presented we estimate the T 1/2 of cypermethrin in sterile distilled water to exceed 100 days at environmentally expected temperatures and pH values.

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This study satisfies guidelines requirements under 161-2 (Photodegradation Studies in Water) and demonstrates that Cypermethrin is stable to photolysis in sterile aqueous solutions.

3.3 "CYPERMETHRIN: Photodegradation on a Soil Surface". Hall, J.S., Leahey, V.P. and Curl, E.A. [ICI Plant Protection Division Report No. RJ0192B, May 1981]

EXPERIMENTAL

The purpose of this study was to investigate the photodegradation of cypermethrin on a soil surface.

[A] Soil Treatment

The soil utilized for this study was obtained from a field in the United Kingdom and was classified as a coarse sandy loam with a pH 7.25, organic matter content of 4.27% and a Cation Exchange Capacity of 19.0 mEq/100 g dry soil. The soil was air dried, sieved to 0.5 mm for preparation of a slurry in water and poured onto (20 x 20 cm) glass plates. A total of 18 plates were prepared. Nine of the plates were treated with 14C-cyclopropane labeled cypermethrin and the remainder with 14C- benzyl labeled cypermethrin both at a rate equivalent to treating the soil surface at 210 g/ha^{-1}. Two of the plates, deep frozen at -15°C served as zero time samples and one-half of the remaining 16 plates wrapped in aluminum foil served as dark controls. The 16 soil plates were placed outside and exposed to sunlight for an equivalent of 32 days (May 15 to June 20) at a location near Berkshire, England. Weather records and the intensity of incident sunlight were recorded during the exposure period.

[B] Sample Analysis

Four plates each were sampled for analysis after 4, 8, 16 and 32 days of exposure. Soil was scraped away from the glass plate and extracted (2x) by heating under reflux for 1.5 hrs with 50% aqueous acetonitrile. The second extract was filtered and combined with the first before taking subsamples for LSC. The soil residue and filter papers were air-dried before measuring the unextracted radioactivity by combustion and LSC.

The percentage of cypermethrin present in the soil extracts at each time interval was measured by reverse phase HPLC and normal phase TLC. Normal phase TLC was carried out using Merck plates (silica gel 60 F - 254, 0.25 mm). Whatman KC18 plates (0.2 mm) were used for reverse phase TLC. The soil extracts from 14C- benzyl labeled cypermethrin
treated plates were also analyzed by reverse phase TLC in (2) acetonitrile/water 80:20 and by normal phase TLC in (3) toluene saturated with formic acid/ether 10:1. The percentage of radioactivity on the chromatograms which cochromatographed with cypermethrin was then quantified using the Berthold TLC Linear Analyzer. Additional analyses were carried out on the extracts of the 16 and 32 day plates to characterize the photodegradation products. Reverse phase HPLC was used to characterize and quantify compounds Ia, Ib and XIV. These extracts were also analyzed by normal phase TLC using the following solvent systems: (3) toluene saturated with formic acid/ether 10:1; (4) cyclohexane saturated with formic acid/ether 3:2; (5) chloroform/methanol/acetic acid 95:4:1; and (7) chloroform/methanol/acetic acid 95:5.

RESULTS

[A] Photodegradation of Cypermethrin

The percentage of radioactivity extracted from the soil plates which was due to ^{14}-C cyclopropane labeled cypermethrin was measured by reverse phase HPLC and normal phase TLC. The results, given in Table 1 indicate that the half-life of cypermethrin on a soil surface was between 8 and 16 days. The percentage of radioactivity extracted from soil plates which was due to ^{14}C benzyl labeled cypermethrin was analyzed by normal phase and reverse phase TLC and the extracts quantified by linear scanning. The results of Table 1 show that the half life of cypermethrin to be approximately 16 days.

[B] Characterization of Metabolites

The relative amounts and characterization of the degradation products in the soil extracts from ^{14}C- cyclopropane labeled cypermethrin treated plates exposed for 16 and 32 days were determined by reverse phase HPLC and normal phase TLC with 2 different solvent systems.

Table 1

The % Radioactivity in the Soil Extracts (Cyclopropane and Benzyl-labeled Treatments) Characterized as Cypermethrin

Plates	Exposure Time (Days)	% Cypermethrin Irradiated Plates HPLC[1]	Normal Phase TLC	Reverse Phase TLC	% Cypermethrin Dark Control Plates[2] HPLC[1]	Normal Phase TLC	Reverse Phase TLC
14C-Cyclo-propane							
1	0				91	94	
2 and 3	4	71	74		88	88	
4 and 5	8	48	55		85	90	
6 and 7	16	54	59		81	81	
8 and 9	32	22	21		68	60	
14C-Benzyl							
10	0					92	89
11 and 12	4		66	60		84	82
13 and 14	8		66	55		81	75
15 and 16	16		59	53		74	73
1 7	32		38	40			

1 The total recovery of injected radioactivity ranged from 87-102%

2 The recovery of applied radioactivity from all of the control plates was >93%

[B]

After 16 days irradiation no unindentified compounds were detected which individually represented more than 10% of the extracted residue. However after 32 days the unindentified polar material represented 32% of the extracted radioactivity. Additional analysis showed this polar fraction to be two major components, representing 12 and 13% of the radioactive extract, and three minor components. Total unidentified radioactivity represented 61% of the total extractable radioactivity after 32 days exposure. Metabolites identified after 32 days exposure included compounds la, lb and XIV which accounted for 5.0 and 3.3% respectively of extractable radioactivity. Twelve percent of the radioactivity extracted from the 32 day plates treated with 14-C cyclopropane labeled cypermethrin was lost by volatilization during analysis indicating that cypermethrin photodegrades, at least in part to volatile fragments.

Normal phase TLC using a combination of solvent systems (3), (5) and (7) and reverse phase TLC using solvent system (2) were used to characterize and quantify the radioactive degradation products in soil extracts from plates irradiated for 16 or 32 days following treatment with 14C - benzyl labeled cypermethrin. The degradation products containing the alcohol moiety of cypermethrin were characterized as compounds III, IV, V, XIV and XV. These compounds accounted for (6-8), 16, 5, (19-20) and (3-4%) respectively of the total percentage of radioactivity found in each area of the TLC plate when extracts from the 32 day irradiated soil plate were analyzed. Only a small percentage (6-7%) of products containing the alcohol moiety were uncharacterized.

CONCLUSIONS

Cypermethrin is rapidly degraded on soil plates irradiated in sunlight on which it has a half-life of 8-16 days. A complex mixture of degradation products mostly derived from ester cleavage is formed.

The major degradation products formed on soil after 32 days irradiation were compounds XIV and IV at 0.036 ppm (20%) and 0.029 ppm (16%) respectively of the original application rate of 0.18 ppm. The study is adequately performed and satisfies the guidelines requirements under 161-3 (Photodegradation Studies on Soil).

3.4 "CYPERMETHRIN: Degradation in Soil in the Laboratory", Harvey, B.R., Zinner, C.K.J., White, R.D. and Hill, I.R. [ICI Plant Protection Division Report No. 0162B, February 1981]

EXPERIMENTAL

[A] Soil Treatment

This study describes the fate of ^{14}C-benzyl labeled cypermethrin in three soil types and both in "natural' and in 'sterilized' soil.

The soils used in this study were obtained in the United
Kingdom and consisted of a clay loam pH 7.5, 12.2% OM, CEC 47 meq/100g, loamy coarse sand pH 6.1, 1.8% OM, CEC, 7meq/100g and a fen peat soil pH 7.4, 72.7% OM, CEC 55 meq/100g.

The soils used for the sterile treatments were irradiated with a 2.5 Mrad dose on each of two consecutive days. Soil moisture was adjusted to 40-48% of moisture holding capacity at zero suction. Prior to pesticide application the sieved soils were dispersed into glass pots (4 cm diameter x 3 cm high). After addition of the cypermethrin solution and distilled water the pots were assembled into glass columns supported on PFTE coated wire racks. ^{14}C-labeled cis and trans cypermethrin uniformly labeled in the benzyl ring was applied to the surface of soil contained in the glass pots at application rates of 0.2 and 2.0 Kg/ha. Application to sterile soils was carried out under aseptic conditions. Evaluation of radioactivity from the soil was monitored throughout the period of incubation. In two treatments sodium hydroxide traps were used in place ethanolamine traps to enable the identification of any $14CO_2$ evolved.

All soil containing glass pots were incubated at 15, 25 or 35°C under either sterile or non-sterile conditions for up to 25 weeks.

[B] Sample Analysis

Complete pots of soil were removed for analysis at zerotime and after 1, 3, 10 and 25 weeks. At zerotime, 1 and 3 weeks the soils were extracted with n hexane: acetone (3:2, 18 hr reflux) followed by methanol (18 hr soxhlet). At week 10 the soils were extracted twice with n hexane: acetone (18 hr reflux) then methanol (18 hr. soxhlet) followed by distilled water (6 hr. reflux). Radioactivity remaining in the soil after extraction was quantified by combustion and subsequent scintillation counting of the evolved $14CO_2$.

At zerotime, 1 and 3 weeks, the soil extracts were dried with anhydrous Na_2SO_4 and concentrated by rotary evaporation under vacuum prior to chromatographic analysis. Duplicate samples of the concentrated extracts were applied to TLC plates (silica gel, 0.25 mm, $60F_{254}$, E. Merck) one sample being admixed with authentic standards of cypermethrin (I) and potential degradation products III, IV and V.

Autoradiographs of the developed TLC's were prepared using Kodak Industrex 'C' x-ray film (Kodak UK Ltd.) The positions of the admixed cypermethrin and degradation product standards were marked on the silica after visualization under UV, 254 nm.

The amounts of ^{14}C labeled cypermethrin and degradation products on the TLC plates were determined by removing the appropriate areas of silica from the plate. The silica fractions were combusted (Packard Sample Oxidizer, Model 306) and evolved $14CO_2$ trapped in 2-methoxyethylamine, scintillator added and scintillation counted.

RESULTS

The amounts of $14CO_2$ evolved (Table 3) from all the nonsterile soils during the 25 weeks incubation period were very similar (60-70% of the recovered radioactivity). In sterile soils 8% or less of the recovered radioactivity was evolved as CO_2 by week 25 (Table 4).

The amount of unextractable radioactivity in the nonsterile soils increased from <1% at zerotime to between 21 and 39% after 10 weeks. The amount of unextracted material did not increase appreciably between the 10 and 25 week period and in some cases fell.

In the sterile soils extractability remained high throughout the period of incubation. Over 85% of the radioactivity in the soil was extracted on all occasions. Amounts of extractable ^{14}C-cypermethrin decreased rapidly in all non-sterile soils (see Tables 2 and 3). Less than 50% of cypermethrin remained after 3 weeks incubation and 90% loss occurred in less than 25 weeks (Table 2). The rate of degradation was much slower under sterile conditions with 38 and 57% remaining in the two soils after 25 weeks incubation.

In non-sterile soils the amounts of extractable radioactivity other than cypermethrin increased up to week 3 then decreased (Tables 2 and 3). Three degradation products were present in all three soils, as characterized by cochromatography on TLC; 3-phenoxybenzaldehyde (III), 3-phenoxybenzoic acid (IV) and (RS)-α-cyano-4'-hydroxy-3-phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (IX). 3-phenoxybenzylalcohol was not detected in any extract of soil. Of these compounds IV was the major product accounting for up to 15% of the recovered radioactivity by week 3. However, after 25 weeks incubation less than 1% IV remained.

In sterile soils compound IV was the major identified product accounting for up to 41% of recovered radioactivity during the 25 weeks incubation.

Extractable radioactivity, not characterized, ('remainder' on Tables 3 and 4) generally accounted for less than 10% of the recovered radioactivity (except in sterile soils, week 25).

CONCLUSIONS

In all non-sterile treatments the 'half-life' of cypermethrin was less than 3 weeks and over 90% of the parent had degraded by 25 weeks incubation. Under sterile conditions 38 and 58% of the cypermethrin remained in clay loam and loamy coarse sand soil respectively compared to <3.9 and 6.9% in the same soils under non-sterile conditions after 25 weeks incubation. This suggests that microbes play a significant role in the degradation of cypermethrin in soil. The major products detected from ester hydrolysis of ^{14}C-benzyl cypermethrin in soil were 3-phenoxybenzaldehyde (III) and 3-phenoxybenzoic acid (IV), reaching a maximum of 6.4 and 15.2% of the recovered radioactivity, 0.01 and 0.03 ppm, respectively in non-sterile soils. Further degradation of the ester hydrolysis products containing the

benzyl moiety was evidenced by the fairly rapid evolution of $14CO_2$ from the benzyl ring; 50-70% of the radiolabel during the 25 weeks incubation period. Unextractable (bound) ^{14}C residues increased rapidly over the first few weeks incubation of non-sterile soils, but in most soil types had reached a peak of between 20 and 40% of the recovered radioactivity, .036 and .072 ppm respectively, by week 10.

This study is adequately performed and satisfies guidelines requirements under 162-1 (Aerobic soil metabolism studies).

Table 2.

Rate of loss of extractable cypermethrin from soil

Soil Type	Kg ai/ha	°C	Time for loss of cypermethrin 50% (weeks)	90% (weeks)
Clay Loam	0.2	25	1	5
Loamy Coarse Sand	0.2	25	2	20
Fen Peat	0.2	25	3	20
Clay Loam	0.2	15	2	15
Clay Loam	0.2	35	1	8
Clay Loam	2.0	25	3	15
Clay Loam (sterile)	0.2	25	7	>25
Loamy coarse sand (sterile)	0.2	25	>25	>25

3.5 "PERMETHRIN: Extraction and Identification of the 'Bound' Residues of the Pesticide in Soil", Arnold, D.J. and Hill, I.R. [ICI Plant Protection Division Report No. 1513B, July 1977].

Reviewers note

[Extensive previously submitted data exists on the environmental fate of permethrin, including data generated with "acid" labeled material. Thus, in the radiolabeled studies on the fate of cypermethrin emphasis has been placed on the use of radiolabeling in the "alcohol" part of the molecule. This provides information on degradates and metabolites derived

Table 3 Distribution of radioactivity in ^{14}C-cypermetrin treated soils.

	Radioactivity as a percent of total recovered														
	Treatment AT 0.2 Kg/ha INCUBATION @ 25°C (0.18 ppm)														
	CLAY LOAM SOIL					LOAMY COARSE SAND SOIL					FEN PEAT SOIL				
	Weeks incubation (a)														
	0	1	3	10	25	0	1	3	10	25	0	1	3	10	25
$^{14}CO_2$	ND	14.0	38.0	56.5	69.3	ND	8.9	25.8	44.9	60.3	ND	4.8	19.7	44.3	62.1
in ex- acts of il I	91.4	43.9	15.7	3.9	ND	85.9	64.5	42.2	23.3	6.9	91.1	68.8	47.8	24.9	6.6
III	(b)	2.9	(b)	(b)		6.4	2.6	0.4	(b)	(b)	(b)	(b)	(b)	(b)	(b)
IV	1.9	9.0	2.5	0.3		2.2	4.6	2.1	1.8	(b)	(b)	12.3	8.4	2.0	0.8
IX	(b)	1.5	1.6	0.5		(b)	(b)	3.2	1.2	(b)	(b)	4.5	3.4	2.7	0.8
remainder	3.2	6.8	2.9	1.4		5.2	7.8	5.7	2.5	6.3	6.9	2.7	2.6	2.5	4.8
C evolved during xtractions	(b)	1.7	1.6	0.4	0.1	(b)	(b)	(b)	0.2	(b)	(b)	0.2	0.2	0.3	0.1
ıer extractions	3.2	(c)	4.2	5.5	8.5	(b)	(b)	(b)	4.5	5.1	1.9	2.4	3.1	2.9	2.2
nextracted adioactivity	0.3	20.3	33.4	31.6	22.0	0.4	11.6	20.5	21.6	20.9	0.1	4.2	13.7	20.5	22.6

(a) zerotime analyses carried out 2hr after application of the pesticide
(b) radioactivity less than 0.1% of recovered or not detected on TLC.
(c) extracts were chromatographed and results included above

ND not done

Table 4. Distribution of Radioactivity in ^{14}C-cypermethrin treated sterile soils

	Radioactivity as a percent of total recovered					
	Treatment At 0.2 Kg/ha (0.18 ppm) Incubation @ 25°C					
	Clay Loam Soil			Loamy Coarse Sand Soil		
	weeks incubation					
	0	10	25	0	10	25
$^{14}CO_2$	ND	<0.1	1.6	ND	<0.1	8.0
in extracts of soil I	87.5	43.7	37.7	89.4	76.4	57.3
in extracts of soil III	(c)	3.7	(c)	(b)	3.5	(b)
in extracts of soil IV	6.1	40.5	29.5	1.4	10.2	8.4
in extracts of soil IX	(b)	(b)	(b)	(b)	(b)	(b)
in extracts of soil remainder	2.4	3.7	15.7	3.0	8.1	9.9
^{14}C evolved during extraction	(b)	(b)	(b)	(b)	(b)	(b)
Other extractions	3.9	(c)	5.3	6.1	(c)	8.3
Unextracted radioactivity	0.1	2.7	12.6	<0.1	1.2	7.9

For notes see Table .

from the "alcohol" part of the molecule. However, commencing with this study and throughout the remainder of this review data generated with the analog of cypermethrin (permethrin) have been included to demonstrate the environmental fate of the "acid" part of cypermethrin after ester cleavage.]

Previous studies of the degradation of radiolabeled permethrin in soil showed that a considerable amount of the pesticide or its products was not extracted by refluxing in n-hexane: acetone and methanol: water. The radioactivity remaining in the soil was considered to be 'bound.'

In this study attempts were made to extract and characterize these 'bound' residues from the extracted freeze-dried soils.

The majority of 'bound' radioactivity in all soils (aerobic and flooded) was solubilized by reflux with 0.5 M NaOH. From 48-85% of the 'bound' radioactivity was associated with the fulvic acid fraction of the soil organic matter. Extraction of the freeze-dried soils with hexane: acetone and methanol: water, removed up to 67% of the 'bound' radioactivity from flooded soils and up to 13% from aerobic soils. In most soils, the majority of this radioactivity was shown to be permethrin and its previously identified degradation products cis, trans - 3(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid, 3-phenoxybenzoic acid and 3-phenoxybenzyl alcohol.

3.6 "CYPERMETHRIN: Laboratory degradation on two standard soils Part II." Swaine, H. and Hayward, G.J. [ICI Plant Protection Division Report No. RJ 01788 January 1981].

EXPERIMENTAL

The degradation of cypermethrin in two standard soils was studied over a 52 week period. The degradation over the first 16 week period was reported as Part I of this study. "Cypermethrin: Laboratory degradation on two standard soils, Part I". H. Swaine and G.J. Hayward, RJ 0115B Issued 12/20/1979 and reviewed by S. Malak, EFB on 5/4/81 as part of submission 10182-EUP-19.

Two German soils, one Speyer 2/2 (5.6% OM, pH 6.4 and CEC 11.9 meq/100 g and the other Speyer 2/3 (1.2% OM, pH 7.7 and CEC 6.0 meq/100 g with moisture retention capacities of 50 and 30% respectively were fortified with cypermethrin at 1 ppm and incubated at 22°C for 52 weeks.

Soils were extracted with 50% v/v acetone: hexane and cypermethrin residues were cleaned-up by adsorption chromatography prior to final quantitative determination by GLC using electron capture detection. Recovery experiments were carried out by fortifying untreated soil samples with a known amount of cypermethrin prior to extraction.

RESULTS

Recovery of cypermethrin from fortified soils ranged from 81-120% with a mean of 101% at fortification levels of 0.05-1.0 ppm. Test results showed that cypermethrin degraded on both soils used in the study (Fig 2). The time taken for half of the initial residue to decay was 2-3 weeks for the Speyer 2/3 soil and approximately 8 weeks for the Speyer 2/2 soil. The initial rate of degradation slowed after the first 8 weeks; between 3 and 4% of the initial residue remained in the Speyer 2/3 soil after 52 weeks. The corresponding amounts remaining on the Speyer 2/2 soil being 15 to 17%.

CONCLUSIONS

Cypermethrin, under laboratory conditions, tends to persist longer in soils that are higher in Organic Matter Content and Cation Exchange Capacity (half-life 8 weeks) vs. 2-3 weeks for soils lower in Organic Matter content and Cation Exchange Capacity.

3.7 "Persistence of Five Pyrethroid Insecticides in Sterile and Natural Mineral and Organic Soil." Chapman, R.A., Tu, C.M. Harris, C.R. and Cole , C. Bull. Environ. Contam. Toxicol. 26, 513-519 (1981)

EXPERIMENTAL

Five pyrethroid insecticides (permethrin, cypermethrin, decamethrin, fenpropanate and fenvalerate were added to an oven dry 'mineral' or 'organic' soil pH ranges 7.7-8.1 and 6.5-7.2 respectively at 1 ppm each and aerobically incubated for 16 weeks. Treated soils following incubation were extracted with acetone which in turn was extracted with hexane. The concentrated hexane extracts were analyzed by GLC. The soils used were a sandy loam (2.9% organic

Figure 1 Degradation of Cypermethrin on Speyer 2/2 Soil

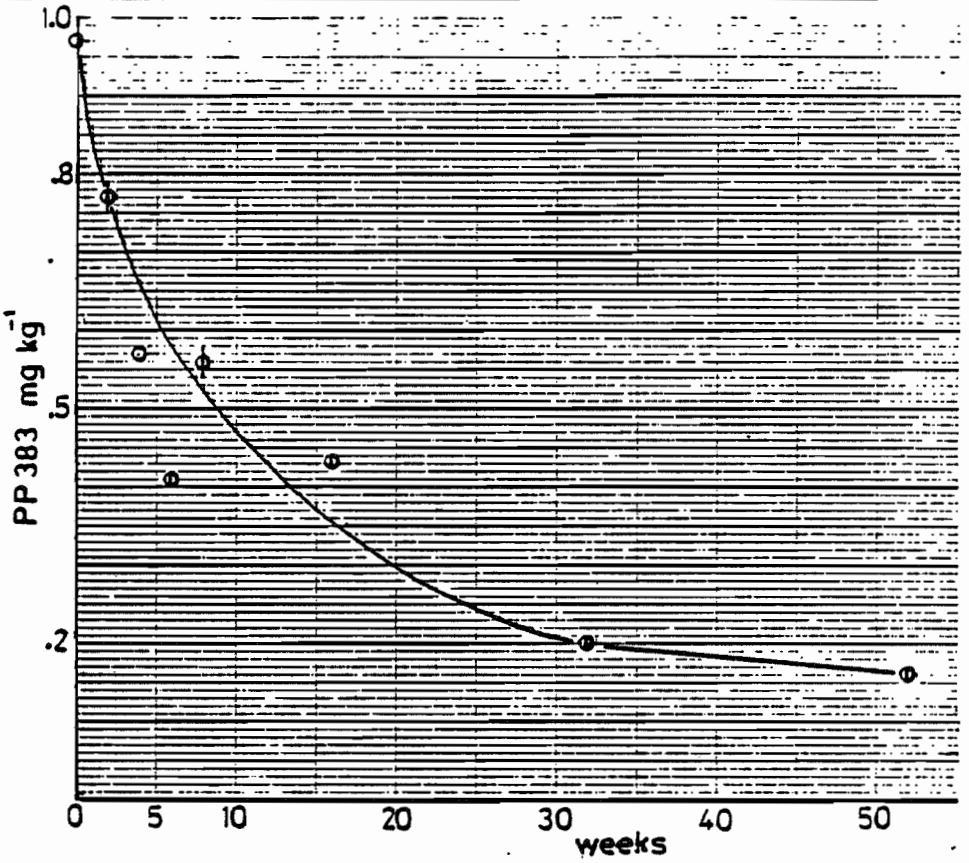
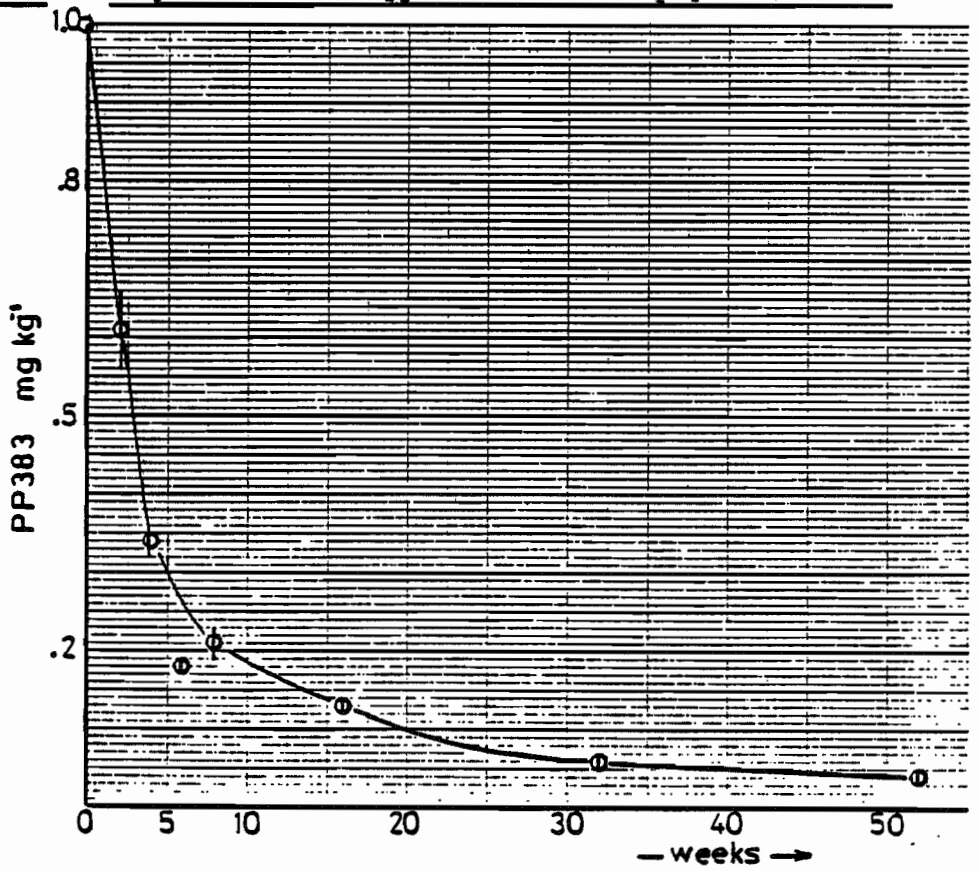


Figure 2 Degradation of Cypermethrin on Speyer 2/3 Soil



matter, 46% MHC, pH 8.0) and in organic soil (48.7% OM, 166% MHC, pH 7.6) Seventy grams of oven dried soil was treated with insecticide placed in 280 ml glass milk bottles and incubated in the darkness at 28°C. Soil moisture was maintained at 60% MHC. Samples were removed for determination of microbial activity and insecticide residues 0, 1, 2, 4, 8, 12 and 16 weeks after treatment.

RESULTS

All of the insecticides degraded more slowly in the sterilized soils then in the natural soils (see Table 5) indicating that heat labile agents such as microorganisms are much more inportant then purely physical on chemical processes in the disappearance of these materials. There is a considerable range in the susceptibility of the insecticides to degradation in soil. Decamethrin and fenvalerate were the least susceptible particularly in the organic soil. Permethrin and cypermethrin were both degraded much more rapidly. In the Authors earlier experiments it was demonstrated that permethrin was less persistent than cypermethrin when incorporated into soil. Cypermethrin might be expected to be less susceptible to degradation than permethrin because of the alpha-cyano substitution in the alcohol component.

CONCLUSIONS

Heat labile factors, assumed to be microorganisms, play a major role in the degradation of pyrethroid insecticides in soil. Degradation rates in soil are, in part, dependent on the structure of the pyrethroid insecticide but also on as yet undetermined variables. The results of isomer ratio measurements suggest that both oxidative and hydrolytic processes are operative.

COMMENT

The quantitative aspects of soil residue data reported in this study are somewhat suspect since no GLC recovery data from soil were reported or cited for the pyrethroid insecticides tested. The study does have some value from the standpoint of providing comparative data for the degradation of pyrethroid insecticides in soil.

Table 5

Persistence of Pyrethroid Insecticides in Sterilized and Natural Soils

% of initial application (1 ppm) remaining 8 weeks after treatment

	Mineral		Organic	
Insecticide	Sterilized	Natural	Sterilized	Natural
Parathion	80	<2	95	6
Fenpropanate	94	2	83	8
Permethrin	101	6	100	16
Cypermethrin	93	4	92	16
Fenvalerate	91	12	100	58
Decamethrin	97	52	106	74
DDT	92	89	100	76

The following studies 3.10 through 3.18 that deal with effects studies of Cypermethrin and/or Permethrin on soil microorganisms, microarthropods, earthworms, sewage treatment processes and effects of activated sludge on cypermethrin degradation were not reviewed but briefly summarized since these data requirements are not now required by the current Environmental Fate Guidelines.

3.8 "CYPERMETHRIN: Effects on Soil Microbial Processes." Castle, D.L., Drew, E.A., Singer, J.M., Askew, P.D., Greaves, R.W. and N.J. Rovle [ICI Plant Protection Division, Report No. RJ 0165B, December 1980].

This report details an investigation into the effects of cypermethrin on the degradation of organic matter, on ammonification, and nitrification and on microbial populations reflected by adenosine triphosphate (ATP) concentrations and by direct total counts.

These studies were carried out on two soils obtained from sites within the United Kingdom. One soil was classified as a loam with a pH 7.3 and % O.M. 4.3, the other soil a loamy sand with a pH 6.0 and % O.M. 3.9. Both soils were incubated in the laboratory at 20°C and with a moisture content of 40% of their moisture holding capacity (MHC) at zero suction. Cypermethrin was applied as an emulsifiable concentrate to each soil at rates equivalent to 50 g a.i./ha (1X) and 500 g a.i./ha (10X). Further applications of cypermethrin at field rate took place at days 7, 14, 23 and 46 following the initial application.

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Effects on the microbial community (determined by direct count and ATP measurements), on the carbon cycle (CO_2 release from unamended soils and soils amended with glucose or maize) and on the nitrogen cycle (ammonification and nitrification) were examined. The effects of cypermethrin on microorganisms under stress were also determined on dry soil i.e. at a soil moisture of 15% of MHC at zero suction. The effects of multi-applications of cypermethrin on the release of CO_2 from unamended soils was also studied.

The results of these studies indicate that cypermethrin did not effect the rate of CO_2 evolution from the unamended soils at any time after treatment. Similarly, when used in multiple applications to unamended soils there was no noticeable treatment effect even following a period of drying. Degradation of plant material was unaffected by cypermethrin at either rate in these experiments indicating that the carbon cycle should not be affected by the normal use of cypermethrin. And finally, in neither soil was either the degradation of organic matter to ammonium (ammonification) or the subsequent transformation of ammonium to nitrate (nitrification) significantly affected for more than one sampling period.

3.9 "Evaluation of the effects of agrochemicals on soil microorganisms and their activities - Methods currently in use at Jealott's Hill Research Station" Johnen, B.G., Drew, E.A., and Davis, P.I. [ICI Plant Protection Division, Report No. AR 2660A, March 1977].

Methods currently in use at Jealott's Hill Research Station for evaluating the effects of pesticides on soil microbial populations and their activities are described. Numbers of organisms are determined for major groups, such as bacteria, fungi, and actinomycetes by dilution agar plate tests. Algal populations are enumerated by direct microscopy and survival of algal inocula added to soil is monitored in the same way. Estimations of the microbial 'biomass' without specifying major groups is carried out by direct microscopy and/or ATP extraction, the latter also giving some indication of microbial activity. Activities of soil microorganisms are measured by monitoring carbohydrate turnover. This includes soil organic matter and plant material decomposition as well as the microbial utilization of a range of organic substances e.g. glucose, urea, starch, protein, cellulose, phenol, tripalmitin, and vanillin. Nitrogen transformation, another major microbial process is studied using both plant material (ammonification and nitrification) and ammonium sulphate (nitrification only) as nitrogen sources.

The specific enzymes or enzyme systems, phosphatase and dehydrogenase are also investigated.

All tests are confined to the aerobic microflora and the tests are carried out under laboratory conditions. The soils used have been processed and treated with pesticides in the laboratory, the general techniques of which are also presented.

3.10 "Permethrin: The degradation of the pesticide incubated for 51 weeks in soil under laboratory conditions (Addendum to TMJ 1512B)" Cleverly, B.A., Arnold, D.J. and Hill, I.R. [ICI Plant Protection Division Report No. 1112B October 1978].

This study is a continuation of one previously reported (Arnold, D.J., Clevery, B.A. and Hill, I.R.) and reviewed by EFB on 5/4/81 as part of the environmental fate review of Cypermethrin, Request for extension of EUP (10182-EUP-19).

In this study the degradation of cis and trans permethrin, ^{14}C-labeled separately, in the dichlorovinyl group, the cyclopropane ring, the methylene group and the terminal phenyl ring was determined in four soils, incubated under laboratory conditions. Soils were incubated for up to 51 weeks following application of the pesticide. Permethrin continued to degrade in all soils tested throughout the 51 week period, under both aerobic and flooded conditions.

During the 51 weeks incubation, between 29% and 63% of the applied radioactivity was evolved as $^{14}CO_2$ from all ^{14}C-labeled permethrin treated aerobic soils. Less $^{14}CO_2$ was evolved from comparable soils kept flooded throughout the study (11-39% of the applied radioactivity).

Products of permethrin degradation which were identified in soil extracts were, cis and trans 3-(2,2 dichlorovinyl) -2,2-dimethylcyclopropanecarboxylic acids, 3-phenoxybenzoic acid and 3-phenoxybenzyl alcohol. Other uncharacterized radioactive products were also present in soil.

During the initial 20 weeks incubation, up to 50% of the recovered radioactivity was bound (unextractable with the solvents used), although in some soils a decrease was observed between 10 and 20 weeks.

From 20 to 51 weeks incubation of permethrin, the amounts of 'bound' radioactivity had decreased in most aerobically incubated soils and also in flooded soils treated with ^{14}C-phenyl and ^{14}C-methylene labeled permethrin. In flooded soils, treated with ^{14}Cvinyl and ^{14}C-cyclopropane labeled permethrin, the amount of bound radioactivity had increased over the same period.

3.11 "PP557: Effect on the Soil Microbial Population and its Enzymic Activities" Johnen, B.G., Drew, E.A. and Davis, P.I. [ICI Plant Protection Division Report No. AR 27343 May 1977].

The effects of permethrin (PP557) formulated as the 10% e.c. on the microbial population and its enzymic activities were investigated in two soils (coarse sand and sandy loam) at normal (0.5 kg ai/ha) (IX) and (20X) (10 kg ai/ha) rates of application. Results in both soils showed no effects of PP557 treatment on ATP content, on bacteria, fungi and actinomycetes counted on agar plates, or on propagules and algae counted directly. Activity of dehydrogenases and phosphatase in the soils was transiently inhibited or stimulated. The effects on dehydrogenase activity disappeared after 7 days but effects on phosphatase activity lasted longer. The magnitude of the effects (5% inhibition) was unlikely to be important in practice. It was concluded that PP557 is very unlikely to have an adverse effect on the size and composition of the soil microbial population or its enzymic activities.

3.12 "PP557: Effect on Carbon and Nitrogen Turnover by Soil Microorganisms" Johnen, B.G., Singer, J.M. and Bridgman, P.A. [ICI Plant Protection Division Report No. AR 2659B May 1977].

The effects of permethrin formulated as the 10% e.c., on soil microorganisms and their activities were studied in two soils (coarse sand and sandy loam) at normal (1X) (0.5 kg a.i./ha) and (20X) (10 kg a.i./ha) rates of application.

These treatments did not adversely affect ammonification and nitrification in the two soils amended with lucerne, wheat straw or ammonium sulphate. Slight stimulatory or inhibitory effects (generally less than 10%) observed in the nitrogen transformation studies were only transient.

The permethrin treatments also had no adverse effects on soil organic matter turnover and the decomposition of the following substrates in soil: uniformally ^{14}C-labeled glucose, sucrose, urea, starch and phenol; unlabeled pectin, cellulose, vanillin and tripalmitin.

Treatment of uniformally ^{14}C-labeled wheat straw with permethrin at rates equivalent to the soil treatments and applied as the 10% e.c. and the 25% e.c. did not have any influence on the decomposition of the straw. It was therefore concluded that permethrin is very unlikely to cause adverse effects on nitrogen and carbon turnover and probably other functional processes of the microbial population in soil.

3.13 "Cypermethrin (PP383): Effects on Earthworms, Lumbricidae" Brown, S.M. and Edwards, P.J. [ICI Plant Protection Division Report No. RJ0151B October 1980].

Cypermethrin applied at a rate of 0.1 kg a.i./ha (1X) to 6m x 6m plots on permanent grassland in the United Kingdom, had no appreciable effect on numbers or on the weight of earthworms sampled from untreated control, toxic standard and treated plots 1 week before and 1, 6 and 12 months after treatment. The higher rate of 1.0 k g a.i./ha (10X) also had no effect except for a small reduction, after 1 month, in numbers of Lumbricus terrestris immatures and small reductions after 12 months in members of Allolobophora caliginosa and A. chlorotica adults.

It was concluded that normal use of cypermethrin is unlikely to adversely affect earthworm populations.

3.14 "Cypermethrin (PP383): Effects on Soil Microarthropods" Cole, J.F. and Wilkinson, W. [ICI Plant Protection Division Report No. RJ0150B October 1980].

Cypermethrin was applied at a rate of 0.1 (1X) and 1.0 kg (10X) a.i./ha to 6m x 6 m plots on permanent grassland in the United Kingdom.

Microarthropods were sampled from control and treated plots 1 day before treatment and approximately 3 weeks, 4 months, 7 months and 1 year after treatment.

The microarthropod populations on the treated plots were, in general, not significantly different (P=5%) from those on untreated controls. The only clear effect was a reduction in the numbers of thrips by the 'normal' and high rate treatments at 3 weeks. There were only a few other significant differences, which were apparently unrelated to insecticide rates, time after application or other arthropod groups, and were probably due to chance.

The results indicate that cypermethrin is unlikely to cause a disturbance of soil microarthropod populations.

3.15 "Assessment of The Effect of Cypermethrin On The Activated Sludge Sewage Treatment Process Using A Semi-Continuous Laboratory System" Street, J.R. and Hill, R.W. [ICI Brixham Laboratory Report No. BL/B/2062 April 1981]

Cypermethrin was dosed on a daily basis, at concentrations of 1, 3.2, 10 and 32 ppm., to semi-continuous activated sludge units for a period of two weeks at each concentration. Further S.C.A.S. units were dosed once weekly with 100 ppm. cypermethrin for four weeks.

Continuous dosing

No adverse effects were observed on either biochemical oxygen demand (BOD) removal or nitrification at the concentrations tested. Slightly lower total organic carbon (TOC) removals were observed at dose rates of 10 and 32 ppm. cypermethrin compared with the control.

At least 93% of the added cypermethrin was removed during sewage treatment, the bulk being adsorbed onto the sludge solids. If effluents were centrifuged to further decrease suspended solids, removal of the cypermethrin increased to >98% of that added.

'Shock' dosing

Once weekly dosing of 100 ppm. cypermethrin affected both BOD and TOC removal, the former being reduced from 97% to 94% during the first week after addition. During the subsequent weeks of dosing recovery was observed and a further week without dosing resulted in a return to control levels.

Nitrification was completely inhibited after one dose of 100 ppm. cypermethrin. After three further doses the nitrification process began to show recovery and running for an additional week without cypermethrin permitted a return to control levels. During the first week after dosing, 47% of the added cypermethrin was removed and this decreased during the second week to 35%. However, cypermethrin removal increased after the 3rd and 4th doses to 67% and 79% respectively, indicating recovery of the system.

The Author's concluded that cypermethrin is unlikely to affect sewage treatment processes when continuously dosed at concentrations up to 32 ppm. Shock doses of cypermethrin may cause inhibition, principally of nitrification, but the process should recover in 7-10 days.

3.16 "Cypermethrin: Degradation by Activated Sludge" Leahey, J.P., Stapleton, A.P., Milner, S.D. and Curl, E.A. [ICI Plant Protection Division Report No. RJ0179B, February 1981].

^{14}C-cypermethrin, radiolabeled in the acid and alcohol parts of the molecule was added to shake flasks, containing activated sludge, at rates of 1, 3.2, 10, 32 and 100mg l^{-1}. After 23 hours incubation, up to 25% degradation occurred in the flasks treated at 1.0mg l^{-1}. However, the percentage degradation decreased with increasing concentration of cypermethrin, so that with an addition rate of 100mg l^{-1} only 3% degradation occurred. The main route of degradation was via ester hydrolysis to give cis- and trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid and α-cyano-3-phenoxybenzyl alcohol. The latter compound being rapidly further degraded to 3-phenoxybenzaldehyde and then to 3-phenoxybenzoic acid. The degradation products formed were almost exclusively in solution in the aqueous phase of the sludge suspension, whereas the cypermethrin was almost completely absorbed onto the sludge solids.

The Authors also observed that the rate of degradation of cypermethrin by sewage sludges which have not been pretreated with cypermethrin was not significantly different from that of sludges that were treated with cypermethrin at various rates for up to 4 weeks. They concluded that induction of microbes capable of degrading cypermethrin was not a prerequisite for cypermethrin degradation.

3.17 "Movement of Cypermethrin, Decamethrin, Permethrin, and Their Degradation Products in Soil". Kaufman, D.D., Russell, B.A., Helling, C.S. and A.J. Kayser. J. Agric. Food Chem 29, 239-245, 1981.

EXPERIMENTAL

The purpose of this investigation was to examine the movement of several synthetic pyrethroid insecticides and their degradation products in soil columns and on soil thin-layer chromatographic plates and to compare the results obtained by both methods.

The soils used in this study were a Hagerstown silty clay (pH 5.5, O.M. 4.31%, CEC 12.5 meq/100g and 29.1% moisture at 0.33 bar), Hagerstown silty clay loam (pH 7.5, O.M. 2.26%, CEC 8.8 meq/100g and 21.1% moisture at 0.33 bar), and a Tifton loamy sand (pH 4.9, O.M. 0.98%, CEC 2.4 meq/100g and 6.0% moisture at 0.33 bar).

Soil Columns

The columns were made from 2.5 cm segments of 7.6 cm (3 in.) (i.d.) machined aluminum tubing and uniformly packed with either the air dried Hagerstown silty clay or Tifton loamy sand to a depth of 30.5 cm. The mean volumetric water content for columns of Hagerstown silty clay was 545.8 ml and for Tifton loamy sand 373.8 ml.

^{14}C chemical adsorbed to a 50g sample of air dried soil was added to the top of each column and each column then slowly leached with one V of distilled water. The leachate from each column was collected in uniform volumes and subsampled for ^{14}C activity by LSC. The leached columns were segmented, extracted with methanol and the extracts counted by LSC. The product concentration present in any individual segment was then calculated as a percentage of total ^{14}C activity extracted from all segments of the columns and its leachate.

The residual extract from the methanol extractions was acidified to pH2 with conc. HCL and partitioned with ether. The ether extracts were concentrated and applied to silica gel F254 chromatoplates with appropriate standards. The plates were developed with benzene saturated with formic acid-diethyl ether (10:3 v/v). After development the plates were exposed to (UV 254 nm) light to locate UV absorbing spots and to X-ray film for 3-4 weeks. After autoradiography all radioactive spots were removed and analyzed for their ^{14}C content by LSC.

Soil Thin-Layer Chromatography (TLC)

Air-dried soil was sieved to 250 um, moistened and then applied to clean glass TLC plates with a commercial TLC spreader. The soil layer thickness was 500um.

The ^{14}C-labeled compounds to be tested were spotted 1.5 cm above the base of the plate and immersed in 0.5 cm of water in a closed glass chamber. The ^{14}C-labeled compound was leached over a distance of 10 cm by ascending chromatography. After development the plates were air-dried then autoradiographed for 3 days. The resultant autoradiograph was considered indicative of pesticide movement which was measured is the frontal R_f of the spot or streak. Center R_f values were also determined for comparisons of the two soil leaching methods.

RESULTS

Soil Columns

When decamethrin is adsorbed to soils and added directly to moist soil columns and immediately leached, there is essentially no movement down through the soil column with 96-97% of the ^{14}C activity remaining in the 0-2.5 cm layer of both the Hagerstown silty clay and Tifton loamy sand columns. DCVA (cis, trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-carboxylic acid) is a degradation product of both cypermethrin and permethrin in soil and PBAc (3-phenoxybenzoic acid) is a degradation product of cypermethrin, decamethrin, permethrin and PBAl (3-phenoxybenzyl alcohol) in soil. In this study both DCVA and PBAc were mobile in both soils used in column leaching studies with DCVA remaining in both soil columns, yet ca 20% and <4% appearing in the leachates from the silty clay and loamy sand respectively. PbAc leached more readily in both soils but was more mobile in the Hagerstown silty clay then in the Tifton loamy sand: PBAI, a soil degradation product of permethrin was only slightly more mobile then decamethrin in soil columns with >96% of the ^{14}C activity present in the upper 13-cm zone in the silty clay soil and in the upper 15 cm of the loamy sand soil.

Table 5

Soil TLC of Synthetic Pyrethroid Insecticides and Their Degradation Products

compound	soil type	R_f values frontal	central
decamethrin	silty clay loam	0.04	0.02
	silty clay	0.05	0.03
	loamy sand	0.04	0.02
cis-cypermethrin	silty clay loam	0.13	0.06
	silty clay	0.08	0.04
	loamy sand	0.12	0.06
trans-cypermethrin	silty clay loam	0.13	0.07
	silty clay	0.10	0.05
	loamy sand	0.16	0.08
cis-permethrin	silty clay loam	0.10	0.05
	silty clay	0.04	0.02
	loamy sand	0.08	0.04
trans-permethrin	silty clay loam	0.08	0.04
	silty clay	0.05	0.02
	loamy sand	0.09	0.05
DCVA	silty clay loam	0.87	0.72
	silty clay	0.45[a]	0.31[a]
		0.61[b]	0.54[b]
	loamy sand	0.51	0.29
PBAc	silty clay loam	0.73	0.53
	silty clay	0.39	0.22
	loamy sand	0.36	0.18
PBAl	silty clay loam	0.26	0.13
	silty clay	0.21	0.10
	loamy sand	0.35	0.19

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[a] Cis isomer of DCVA. [b] Trans isomer of DCVA.

Soil TLC

Decamenthrin, cis and trans-cypermethrin, and cis and trans permethrin were classified as low mobility to immobile compounds in the soils examined (Table 5). On the basis of frontal R_f values measured, both cis-cypermethrin and trans-cypermethrin appear to be slightly more mobile than cis-permethrin, trans-permethrin, or decamethrin. These results indicate that very little movement of any intact synthetic pyrethroid would occur through soil.

In the soils examined, the pyrethroid degradation products DCVA, PBAl, and PBAc were all more mobile in the soils examined than any of the parent materials. Soil pH seemed to be the primary factor affecting mobility of the organic acids PBAc and DCVA in the three soils tested with differing pH values. The results suggest that DCVA and PBAc would be fairly mobile in agricultural soils having a neutral to alkaline pH.

CONCLUSIONS

The synthetic pyrethroid insecticides decamenthrin, permethrin and cypermethrin are relatively immobile in soil and do not readily leach through the soil profile. PBAl a direct hydrolysis product of permethrin degradation, and a metabolite of PBAc produced during degradation of decamethrin and cypermethrin, is of low mobility in soil. PBAc is a degradation product of all three synthetic pyrethroid insecticides studied and is produced during microbial metabolism of PBAl in soil. As organic acids both PBAc and DCVA could be expected to be somewhat mobile through soil, the extent of their mobility determined by the soil pH, as well as by the rate of their degradation in soil.

3.18 "CYPERMETHRIN: Mobility of Cypermethrin and its Degradation Products in Soil Columns" Stevens, J.E.B., and I.R. Hill [ICI Plant Protection Division, Report No. RJ0166B, December 1980].

EXPERIMENTAL

This report describes laboratory experiments designed to study the leaching of ^{14}C-benzyl labeled 55:45 cis/trans cypermethrin and its degradation products in clay loam, loamy sand and fen peat soil columns. This study can be considered an aged leaching study in that cypermethrin treated soils were aerobically incubated for 3 weeks before they were applied to the top of soil leaching columns.

The four soils utilized in this study were obtained from sites within the United Kingdom and had the following physical and chemical characteristics: 'Gore Hill' a clay loam (pH 7.8, 13.9% OM, CEC 47.5 meq/100g and MHC 42% at 1/3 bar), 'Frensham' a loamy sand (pH 6.3, 1.9% OM, CEC 7.1 meq/100g and MHC 10% at 1/3 bar), 'Lilyfield' a coarse sand (pH 5.9, 1.0% OM, CEC 2.8 meq/100g and MHC 4% at 1/3 bar) and 'Rosedean' a fen peat (pH 7.4, 72.7% OM, CEC 55 meq/100g and MHC 103% at 1/3 bar).

Table 15 Cypermethrin and its Degradation Products in 'Gore Hill', 'Frensham' and 'Rosedean' Soils after 3 Weeks Aerobic Incubation*+

	% of Total Radioactivity Recovered		
	'Gore Hill'	'Frensham'	'Rosedean'
$^{14}CO_2$ evolved during incubation	38.0	25.8	19.7
extracts of soil: cypermethrin	15.7	42.2	47.8
extracts of soil: III	-	0.4	-
extracts of soil: IV	2.5	2.1	8.4
extracts of soil: IX	1.6	3.2	3.4
extracts of soil: Unidentified	7.1	5.7	6.7
Unextracted (bound)	33.4	20.5	13.7
$^{14}CO_2$ evolved during extraction	1.6	-	0.2

- radioactivity less than 0.1% of recovered.

+ 'Lilyfield' soil was not analysed at this time. However, during the three week incubation period 1.7% of the applied radioactivity was evolved from the treated soil.

Table 17 Summary of Residues of Cypermethrin Equivalents in Soil Leaching Columns

Distance from top of soil column (cm)	'Gore Hill' Mean of Column Nos.2,3 & 4		'Frensham' Mean of Column Nos.6,7 & 8		'Lilyfield' Mean of Column Nos. 10,11 & 12		'Rosedean' Mean of Column Nos.14,15 & 16	
	cypermethrin equivalents in soil (µg/g soil)	% of applied radioactivity in soil segment	cypermethrin equivalents in soil (µg/g soil)	% of applied radioactivity in soil segment	cypermethrin equivalents in soil (µg/g soil)	% of applied radioactivity in soil segment	cypermethrin equivalents in soil (µg/g soil)	% of applied radioactivity in soil segment
Sand	<0.0006	<0.2	<0.0005	<0.2	<0.0004	<0.1	0.001	0.2
0-5*	0.113	78.6	0.072	68.1	0.115	85.8	0.224	73.1
5-10	<0.0005	<0.3	<0.0004	<0.3	0.001	0.4	0.001	0.3
10-15	<0.0005	<0.3	<0.0004	<0.3	<0.0004	<0.3	<0.0006	<0.1
15-20	<0.0005	<0.3	<0.0004	<0.3	<0.0004	<0.3	<0.0004	<0.1
20-25	<0.0005	<0.3	<0.0004	<0.3	<0.0004	<0.3	<0.0004	<0.1
25-30	<0.0005	<0.3	<0.0004	<0.3	<0.0004	<0.3	<0.0004	<0.1
Leachate	<0.0002+	<1.5	<0.0002+	<1.2	<0.0002+	<0.9	<0.0002+	<1.1
Total	-	78.6	-	68.1	-	86.2	-	73.6

* Pesticide treated incubated soil placed on top of this soil segment; segment soil depth after treatment therefore 6-7cm.

\+ µg/ml

Soil preparation

Thirty gram aliquots of each of the mineral soils and 20g aliquots of the fen peat were dispersed into 4cm diameter glass pots and surface treated with 0.2 kg ^{14}C-benzyllabeled cypermethrin/ha. The soils were adjusted to 40% MHC and incubated at 25°C in an atmosphere of CO_2 free air under aerobic conditions for 3 weeks. Replicate pots were extracted at this time and the extracts analyzed by chromatography. Non-extracted radioactivity was also determined. During incubation volatile compounds were trapped and analyzed by LSC of aliquots at intervals. Degradation products of cypermethrin identified and quantified after 3 weeks soil incubation are presented in Table 6.

Soil Columns

Four soil leaching columns were prepared for each soil type. Each column consisted of seven, 5.0 cm joined segments of aluminum tubing to form a hollow column 35 cm in length. Individual 5 cm segments were packed with a predetermined weight of soil until six segments were filled. In each segment the moist weights of soil used were 'Gore Hill' 115g, 'Frensham' - 160g, 'Lilyfield' - 168 g and Rosedean 88g. To the seventh segment of 3 columns of each soil type was added the appropriate incubated soil containing ^{14}Clabeled cypermethrin plus degradation products. To the fourth column was added untreated soil.

Leaching columns were kept at 20 $\pm$ 2°C with 30 ml portions of 0.01M $CaCL_2$ solution added to each column daily for a total volume of 1380 ml applied to each column over a period of 9 weeks. Since the column had a cross sectional area of 20.43 cm^2, 1380 ml 0.1M $CaCL_2$ is equivalent to 67.5 cm 'rain'.

Radioactivity in the column leachate was determined by "Instagel' scintillator and scintillation counting. After leaching the columns were sectioned into six 5cm segments, the soil segments dried and combusted in a Packard Tri-Carb Sample Oxidizer. Evolved $14CO_2$ was trapped and subjected to LSC.

RESULTS

Recoveries of radioactivity applied to the leaching columns provided recoveries of 68 to 86% indicating that cypermethrin underwent further degradation to volatile products probably CO_2 during the 10 weeks leaching period.

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The distribution in soil columns of ^{14}C-benzyl labeled cis/trans (55:45 mixture) cypermethrin plus its degradation products is summarized in Table 7. The data indicate that more than 99% of the ^{14}C-residue in the soil columns remained within the top (0-5 cm) treated soil segment after leaching with 67.5 cm 'rain'. Leaching below 5cm occured only in 'Lily-field' (coarse sand) and 'Rosedean' (fen peat) soils and was, respectively, 0.4, and 0.3% of applied radioactivity.

CONCLUSIONS

^{14}C-benzyl labeled cypermethrin including its soil degradation products arising from 3 weeks aerobic incubation in 4 different soil types have a low mobility in these same soils as measured by elution through soil columns.

^{14}C-cyclopropane labeled cypermethrin which would metabolize to DCVA (IRS)-cis, trans-3- (2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid as a major metabolite in soil following aerobic incubation and has also been shown to be somewhat mobile in soil (see Study 3.17 above) was not used in this study. However, in a study by Prashad, S. et al (1977) "Permethrin: Mobility of Permethrin and its Degradation Products in Soil," ICI Plant Protection Division, Report No AR2716B less than 6% of the cyclopropane radiolabeled residues of permethrin were leached below 5cm by 75 cm 'rain'. Therefore, it can be concluded that very little leaching of the cyclopropane moiety-containing ester hydrolysis products of cypermethrin (which are also common to permethrin) will occur under the conditions of Study 3.18. This study satisfies the guidelines requirements for an aged leaching study under 163-1 (Leaching and Adsorption/desorption studies).

3.19 "Permethrin: Mobility of Permethrin and its Degradation Products in Soil." Prashad, S. Stevens, V.E. and S.E. Newby [ICI Plant Protection Division, Report No. AR 2716B, February 1977].

EXPERIMENTAL

Soil Thick-Layer Chromatograms

The mobility of a 40:60 mixture of ^{14}C cyclopropane labeled cis/trans permethrin was determined by soil thick-layerchromatography using four soils - a coarse sandy loam (Pear Tree), a coarse sand (Lily Field), a calcareous clay loam (Gore Hill) and a

TABLE 8

^{14}C permethrin equivalent in chromatogram segments after leaching with 80 ml 0.01 M $CaCl_2$ (32 cm 'rain') in 4 soils.

Distance from top of chromatogram (cm)	Pear Tree		Lily Field		Gore Hill		Blackborough	
	µg/g soil (or µg/ml)	% of applied	µg/g soil (or µg/ml)	% of applied	µg/g soil (or µg/ml)	% of applied	µg/g soil (or µg/ml)	% pf applied
0–2	0.01	0.4	0.004	0.2	0.027	1.1	0.030	0.3
2–4	1.261	91.1	0.554	70.2	1.659	87.4	5.253	85.8
4–6	0.008	0.5	0.143	16.7	0.008	0.5	0.004	0.6
6–8	0.002	0.1	0.020	2.0	0.002	0.1	0.003	<0.1
8–10	0.002	0.1	<0.001	0.1	0.002	0.1	0.009	0.1
10–15	<0.001	0.1	<0.001	0.1	<0.001	0.1	0.001	<0.1
15–20	<0.001	0.1	<0.001	<0.1	<0.001	0.1	<0.001	<0.1
20–25	<0.001	0.1	0.004	1.0	<0.001	0.1	<0.001	<0.1
25–30	<0.001	0.1	<0.001	0.1	<0.001	<0.1	0.002	0.1
Leachate	$11x10^{-5}$	<0.1	$50x10^{-5}$	<0.1	$7x10^{-5}$	<0.1	$2x10^{-5}$	<0.1
Total recovered		93		91		90		87

TABLE 9 Leaching of ^{14}C labelled permethrin plus its degradation products present in incubated soils, by 74.9 cm (1530 ml) 0.01 M $CaCl_2$ in 4 soils.

Results expressed as a percentage of total initially applied to soil (before incubation).

Distance from top of soil column (cm)	Lily Field			Pear Tree			Gore Hill			Blackborough		
	1. cis/trans	2. cis	2. trans	1. cis/trans	2. cis	2. trans	1. cis/trans	2. cis	2. trans	1. cis/trans	2. cis	2. trans
sand	1.2	1.7	1.5	1.6	0.1	2.1	0.7	1.2	0.6	0.2	1.0	0.2
0-5	58.1	81.1	36.8	48.1	51.0	36.5	45.8	45.0	41.2	45.3	69.7	35.9
5-10	0.4	1.6	3.9	0.2	0.1	0.3	0.4	0.6	0.6	0.8	0.8	0.3
10-15	0.1	0.3	0.6	0.2	0.1	<0.1	<0.1	<0.1	0.1	0.2	0.2	0.1
15-20	0.1	0.2	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1
20-25	<0.1	0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
25-30	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
30-35	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Leachate	<0.1	0.2	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
Total % recovered	60.0	85.3	44.0	50.1	51.3	38.9	46.9	46.8	42.5	46.6	71.9	36.8

1) ^{14}C phenyl labelled.

2) ^{14}C cyclopropane labelled.

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peat (Blackborough). The properties and characteristics of the soils used and the experimental procedures employed were the same as those previously described in Section 3.13 ("Leaching of Cypermethrin in Thick-Layer Soil Chromatograms," Prashad, S. and S.E. Newby, 1977) of the S. Malak 5/4/81 review of Submission 10182-EUP-19.

Soil Columns

Lily Field, Pear Tree, Gore Hill and Blackborough soils were incubated with a 40:60 mixture of ^{14}C phenyl labeled cis/trans permethrin; ^{14}C cyclopropane labeled cis permethrin, and ^{14}C cyclopropane labeled trans permethrin for two weeks under aerobic conditions.

Each labeled compound was applied to each soil at a rate of 0.2 kg/ha prior to incubation at 25°C. Soil column preparation, leaching techniques and sample collection and analysis are described in detail in Section 3.19 of this review.

RESULTS

Soil Thick-Layer Chromatograms

Less than 1.5% permethrin equivalent was leached more than 2cm in Pear Tree, Gore Hill and Blackbourough soils while less than 4% was leached lower than 4cm in Lily Field soil by 32 cm 'rain". The results are summarized in Table 8.

Soil Columns

In Gore, Pear Tree and Blackborough soils 50% degradation of ^{14}C permethrin was observed in 1/2 to 1 1/2 weeks and 90% in 1 1/2 to 10 weeks. For Lily Field soil, 50% degradation took place after 5 1/2 weeks. From an application of 0.12 - 0.13 kg/ha permethrin the amounts leached below 5 cm ranged from 0.4 - 1.1% for cis/trans treatments; from 0.2 to 2.5% for cis treatments; and from 0.3 to 5.7% for trans treatments. The amounts of ^{14}C permethrin equivalent found in leachates were less than 0.1, 0.2 and 0.5% respectively. The maximum concentration of permethrin equivalent in the leachates was 0.0003 ug/ml and was generally less than 0.0001 ug/ml. Loss of volatile ^{14}C products from the columns was greater with the trans than with the cis/trans or cis isomers.

The results of the soil column leaching study are summarized in Table 9. In an additional experiment when formulated permethrin (emulsifiable concentrates, JF 5346 and JF 5855) was applied at 0.5 kg ai/ha, the concentration of permethrin in the leachates from 30 cm long coarse sand and loamy coarse sand soil columns, following an application of 19.2 cm 'rain', was below the limit of detection (0.005 ug/ml).

CONCLUSIONS

Both cyclopropane and benzyl moiety containing degradation products of permethrin arising from 2 weeks aerobic incubation in 4 different soil types have a low mobility in these same soils (generally less than 5cm) when measured by soil thick-layer chromatography or by elution through soil columns.

3.20 "CYPERMETHRIN: Adsorption and Desorption in Soil", Stevens, J.E.B. and N.V. Poole [ICI Plant Protection Division, Report No. RJ0184B, March 1981].

EXPERIMENTAL

Author's notes

The normal method for conducting an adsorption/desorption study was modified in this study to account for the short persistence of cypermethrin in soil and its expected high K_d values. For example, to minimize the formation of degradation products with different K_d values the experiment was performed at 4°C and in addition since low cypermethrin concentrations in the water phase could be expected, a high soil:water ratio of 1:50 was used to minimize analytical errors.

Cypermethrin Adsorption

A loamy sand soil (Frensham, pH 5.4, 2.1% OM, CEC 5.9 meq/100 g and MHC 9.3% at 1/3 bar) obtained from a site in the United Kingdom was selected for this study. Moist (adjusted to field capacity) soil samples (0.61 g) equivalent to 0.50 g dry soil, were maintained for one hour in aqueous calcium chloride (25 ml 0.01 Molar stored at 4°C) in 40 ml glass centrifuge tubes before treatment with C^{14} labeled cypermethrin. The soil/aqueous calcium chloride ratio was therefore 1:50.

^{14}C-cyclopropane labeled cypermethrin was added to the soil solution at 0.01, 0.025, 0.04, and 0.10 ug cypermethrin/ml aqueous 0.01M Ca Cl_2. Each treatment was duplicated. After treatment samples were mixed at (4 ± 1°C) in the dark for 1, 4 or 24 hours. At the end of each time period slurries were centrifuged (400 g) for 15 minutes and aliquots of supernatant (1.0 ml) were withdrawn for scintillation counting of radioactivity.

Cypermethrin Desorption

^{14}C-cyclopropane labeled cypermethrin was added to the soil solutions described above at 0.01, 0.04 and 0.10 ug cypermethrin/ml aqueous 0.01M$CaCl_2$. Each treatment was duplicated. After treatment samples were mixed at (4 ± 1°C) in the dark for a total of 54 hours. During the total re-distribution time (54 hours), portions of supernatant (10ml) were removed at time intervals of 24, 29, 48 and 54 hours. Fresh aqueous 0.01M $CaCl_2$ was added each time to restore the slurry to its initial volume. At the end of each re-distribution period, the residual cypermethrin concentration remaining in soil solution was determined from the radioactivity associated with aliquots (1.0 ml) of supernatant.

For both adsorption and desorption determinations the soil/water phases were separated by centrifugation, the supernatant decanted and the soil in the tube freeze-dried for 16 hours. The soil was recovered from the tube, weighed, mixed with 0.25 g glucose and combusted in a Packard Tri-Carb Sample Oxidizer Model 306. $^{14}CO_2$ was trapped in 2-methoxyethylamine and radioactivity determined by LSC using a Tri-Carb Liquid Scintillation Spectrometry Model 3390, with Model 544, Absolute Activity Analyzer (AAA) and Data Dynamics 390 Teleprinter. Standard deviation of the counts was always 7.5% or better and the count time ranged from 0.1 to 10 minutes.

RESULTS

Adsorption of Cypermethrin to Soil

The starting concentrations of 0.01, 0.025, 0.04 and 0.10 ug cypermethrin/ml are equivalent to 15, 37.5, 60 and 150 g/ha mixed with water to a depth of 15 cm, and after adsorption the equilibrium concentration was respectively 0.00027, 0.00064, 0.00102 and 0.00257 ug/ml.

Table 10 Adsorption and Desorption Equilibration Constant (Kd) Values of Cypermethrin in Frensham Loamy Sand Slurries

Initial Application		Adsorption Equilibration Time Period (Hours)			Desorption Equilibration Time Period (Hours)
µg	µg/ml	1	4	24	54
0.27	0.011	995	1674	1955	1828
0.65	0.026	1058	1714	1937	ND
1.04	0.042	1014	1382	2005	2564
2.57	0.103	990	1195	1745	2666

ND Not Determined

Table 1 shows the progressive adsorption of cypermethrin in an agitated solution with Frensham loamy sand soil. Total recoveries of cypermethrin equivalents (solution plus soil) ranged from 62 to 100% (average 81.5%) of applied cypermethrin. Maximum K_d values observed were in the region of 2000 and partitioning approached equilibrium after 24 hours.

Desorption of Cypermethrin from Soil

Calculated K_d values for the progressive desorption of cypermethrin in an agitated solution with Frensham loamy sand soil are given in Table 10. The total recoveries of cypermethrin equivalent (solution plus soil) ranged from 74 to 106% (average 96.1%) of applied cypermethrin. The results confirm the conclusions derived from the adsorption study that cypermethrin is strongly adsorbed to the soil, and only very small amounts of cypermethrin will be found in the water phase of a soil/water system.

CONCLUSIONS

Cypermethrin per se is strongly adsorbed to soil particles and, therefore, only very low concentrations will occur in the water phase of a soil/water system. However, since this experiment was conducted under conditions that minimized the breakdown of cypermethrin to its degradation products in soil during aerobic incubation, no information was obtained (although not required in the October 3, 1980 Subpart N Guidelines) on the K_d values of these degradation products that would occur following the proposed use of the chemical. In all likelihood, these degradation products would have lower K_d values than the parent compound. This study satisfies the intent of the guidelines requirements for a batch equilibrium study under 163-1 (Leaching and adsorption/desorption studies).

3.21 "Adsorption of PP557 and its Hydrolysis Products, R11074 and R79406 by Soil" Clarke, G.E. and R.S. Morrod [ICI Plant Protection Division, Report No. TMJ1472B March 1977].

EXPERIMENTAL

The adsorption coefficients of ^{14}C cyclopropane permethrin and its two hydrolysis products, 3-phenoxybenzyl alcohol (R79406) and dichlorovinyldimethylcyclopropane-carboxylic acid (R11074) by one soil were determined. The one soil is a coarse sandy loam of the following characteristics: coarse sand

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41.8%, fine sand 23.5%, silt 14.5%, clay 20.2%, organic matter content 4.9%, pH 6.2, CEC 13.0, and 1/3 bar 33.2%.

Results:

There were very high losses of permethrin radioactivity from solution phase to the glass container in the absence of soil. This adsorbed radioactivity was not resolubilized from glass surfaces by washing dichloromethane, hexane or acetone.

Due to the high adsorption onto glass, the adsorption coefficient for the soil was determined by counting of the radioactivity in solution phase and by combustion of the residual soil radioactivity, and thereby subtract out the effects of the glass adsorption. This method is satisfactory. Permethrin has a K_d of between 340 and 440 after 3 to 7 hours, on a coarse sandy loam with organic matter content of about 5%. This Kd indicates a high degree of adsorption.

The experiment was repeated but without agitation of the soil slurry, to simulate a pond with stagnant flow. The soil was centifuged down and represents the bottom of the pond. When permethrin in solution is added to container without agitation, very little adsorption of permethrin occurs, with a Kd of about 2.2. Interpretation of this information is that permethrin will not adsorb out of aqueous solution onto bottom sediments; however, permethrin would adsorb onto suspended solids in the solution phase. That is, permethrin will adsorb onto suspended soil particles or suspended organic matter in water much faster than it will adsorb onto bottom soil, if undisturbed. The degradates of permethrin showed adsorption coefficients of less than 2.0 for the dichlorovinyldimethylcyclopropane carboxylic acid and about 10 for 3-phenoxybenzyl alcohol. This data indicates that these degradates would not be highly absorbed in a pond situation and may be available for leaching in certain soils. The low adsorptivity of DCVA is estimated to be due to its ionization at the soil pH of 6.

Conclusions:

Permethrin is strongly absorbed by soil with adequate amount of organic matter. Adsorption by soil will decrease in direct relation to the decrease in organic matter content. The degradates of permethrin are much less adsorbed by soil, to the extent that they may be available for leaching in very low organic soils. The adsorption of permethrin and its degradates from soil is not investigated.

Table 11

Treatment and Sampling Schedule
July-September 1980

Day	July	August	September
1			
2			R
3			
4			ICI(13)
5		ICI(7)	
6	ICI-F(1)		
7			
8			
9			FMC(14)
10		FMC(8)	
11	FMC(2)		
12			
13			
14			F,CS-ICI-F(15)
15		ICI(9)	
16	ICI(3)		
17			
18			
19			FMC(16)
20		F,CS-FMC-F(10)	
21	FMC-R(4)		F,CS
22			
23			
24			
25		ICI(11)	
26	F,CS-ICI-F(5)		
27	R		
28			
29			
30		FMC(12)	
31	FMC(6)		

FMC: Cypermethrin Treatment
ICI: Cypermethrin Treatment
F: Foliar Sample
CS: Cotton Soil Sample
R: Runoff Collected

3.22 "Cypermethrin Residues in Samples from a 1980 Alabama Run-Off Study" Ussary, J.P. [ICI Americas Inc. Report No. TMU 0541/B (Revised) February 1981].

This study was conducted to monitor the fate of cypermethrin in the hydrologic cycle after aerial applications to a cotton field located near a stream.

EXPERIMENTAL

A 30 acre cotton field with a 2 to 5% slope and loamy sand soil located approximately 20 miles east of Selma, Alabama was treated 16 times with 0.125 lb/A cypermethrin in spray volumes of 2 gal/A. The applications were made 5 days apart beginning on July 6, 1980. The applications were made alternately with CYMBUSH (ICI Americas Inc.) and FMC cypermethrin (FMC 45806). See Table 11 for treatment and sampling schedule.

Sampling

Immediately before each application filter paper disks (125 or 150 mm diameter) were placed in triplicate on the soil surface under a cotton plant at each of 3 well separated sampling sites in the field. These samples were collected immediately after each application. Samples of the entire aerial portions of cotton plants were collected from the three sampling sites after first application, immediately before and after the 5th, 10th and 15th applications, then 2 and 7 days after the 16th application.

Soil samples from areas not protected by the crop were collected from three sites in the cotton field immediately prior to the 5th and 15th applications. The samples were collected by carefully scooping the top three inches from a 6"x6" area.

Water and sediment samples were collected from designated stations on days of sufficient rainfall to cause significant runoff from the cotton field. Water samples were collected from a rivulet running out of the field towards the stream. Two sites (S1 and S2) were in two small streams that run parallel to the lower site of the cotton fields. Site S3 was at the confluence of these streams with Little Mulberry Creek. Site S4 was approximately two miles further down the stream. Site 5 was approximately eight miles down the stream from the cotton field and which was approximately 1 mile after the creek merged

with the Alabama River. The collection of the samples from the stream was timed to allow the runoff from the cotton field to reach the sampling sites. Figure 1 in study 3.24 "Monitoring The Fate of Cypermethrin After Aerial Application on Cotton" illustrates the locations of all sampling stations used in this study.

Analytical Procedure

Filter Papers

Each disk was extracted in a blender with 40% acetone in hexanes, filtered through Whitman GF/A paper, evaporated to dryness, redissolved in isooctane and analyzed by GLC/EC.

Cotton Foliage and Soil

Samples were extracted according to a modification of ICI Plant Protection Division method PPRAM-42, cleaned up by gel permeation chromatography followed by Florisil column chromatography, then analyzed by GLC/EC.

Water and Sediment

Procedure same is above for cotton foliage and soil except for the low limits of detection desired it was necessary to use a 5% diethyl ether in hexanes for the Florisil column elution rather than the 10% diethyl ether in hexanes and then to re-Florisil the samples. These modifications lowered the limits of determination to 2 ppb for sediment and 1 ppb for water.

RESULTS

Cotton Plants

Mean residues on cotton plants collected before the 5th, 10th and 15th application ranged from 1.59 to 3.22 ppm. Residues after the 1st, 5th, 10th and 15th applications ranged from 3.71 to 15.3 ppm. Two and seven days after the 16th application the mean residues were 8-32 ppm and 5.5 ppm, respectively.

Filter Papers

Whitman 42 filter paper disks placed under the leaf canopy of cotton plants immediately before each application and collected immediately after the application contained cypermethrin residues ranging from 0.0002 lb/A to 0.0409 lb/A with a mean of 0.0088 lb A. If it is assumed that exactly 0.125 lb of cypermethrin were applied per acre, then only 7% of the spray penetrated the foliage and reached the soil.

Soil Samples

The mean residues from the 6"x6"x3" samples collected immediately prior to the 5th, 10th and 15th applications were 0.12, 0.12 and 0.15 ppm respectively. Three soil samples collected two days after the 16th application had a mean residue of 0.33 ppm cypermethrin.

Runoff Water

Runoff water including the suspended solids, collected from the rivulet running towards the test streams contained residues ranging from 1.17 to 12.7 ppb.

Sediment Samples

Sediment samples collected at the point the runoff entered the stream on 2 of 3 sampling dates each contained 2 ppb cypermethrin. The other samples contained no detectable residues at a limit of determination of 2 ppb. One sample collected 165 meters from the point of runoff had 2 ppb cypermethrin while samples collected at the same site on two other sampling days did not have detectable residues.

Water Samples

Water samples collected on three sampling dates from the stream at the point of runoff had 0.014 ppb to 0.094 ppb cypermethrin. Samples collected 165 meters downstream had cypermethrin concentrations ranging from less than 0.001 ppb to 0.024 ppb. Two miles downstream the residues ranged from less than 0.001 ppb to 0.013 ppb. Eight miles downstream the cypermethrin concentration range was less than 0.001 ppb to 0.003 ppb.

Figure 3

Location of Sampling Stations in the Test Cotton Field, Little Mulberry Creek and the Alabama River.
Source: Soil Survey of Autauga County, Alabama, USDA Soil Conservation Service, November, 1977.
Scale: 1:20,000.

C_1, C_2, C_3 – Cotton soil foliar and fall-through sample stations
R_1, R_2 – Runoff Stations
S_1, S_2, S_3, S_4, S_5 – Instream Stations

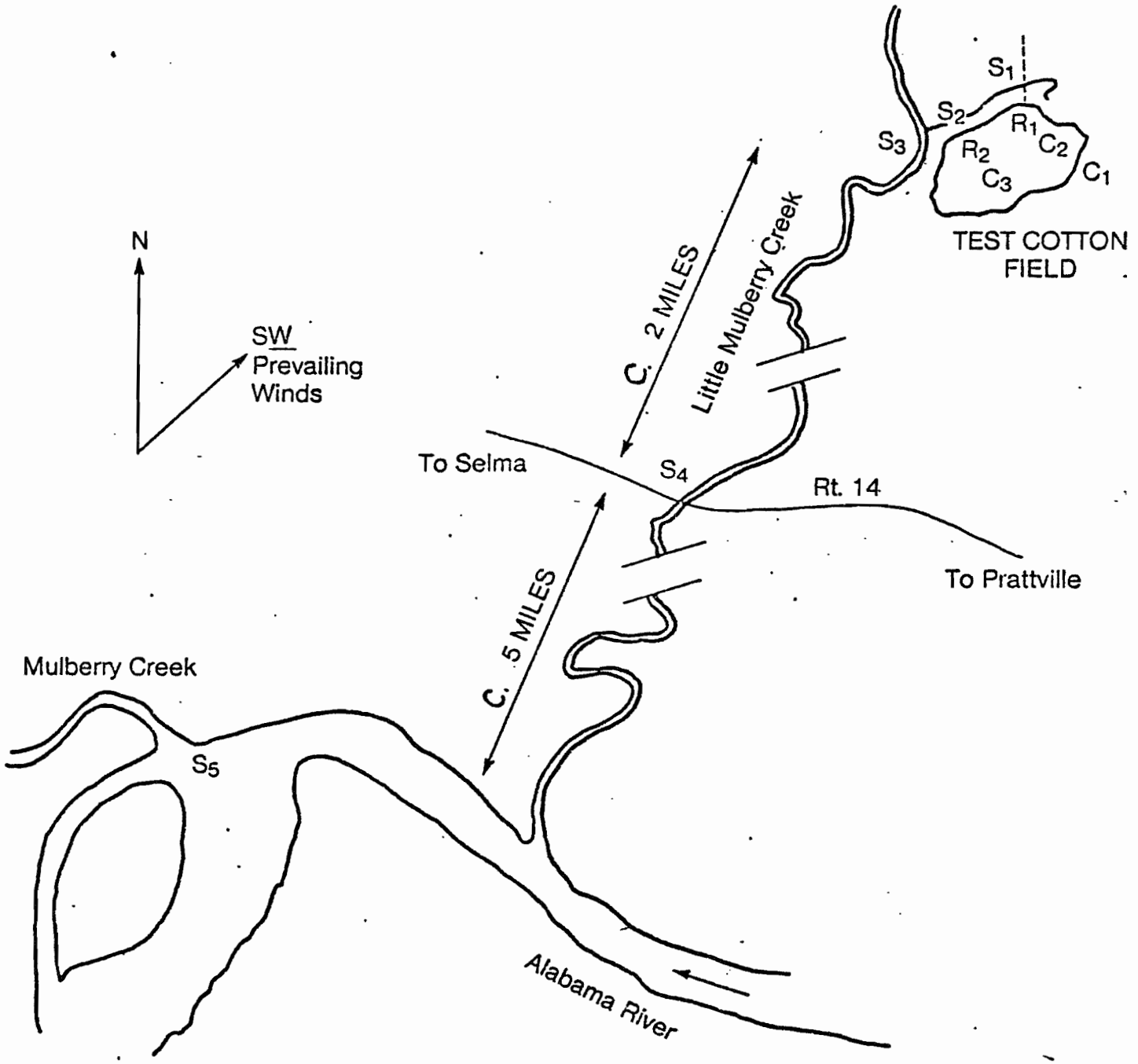

Table 12

Estimates of Soil Properties Specific to the Test Site,
Autauga County, Alabama

Soil Series	Depth to Seasonal High Water Table (feet)	Depth from Surface (inches)	Dominant USDA Texture	Classification Unified/AASHTO		Permeability in/hr	Available Water Capacity inches/inch of soil	Organic Matter Content %	Bulk Density gm/cm³	Infiltration Rate in/hr
Jones-Shubuta Assoc.	>6.0	0-12	Sandy loam & loamy sand	SM	A-2	2.0-6.0	0.08-0.10	0.5-1.0	-	0.6-0.75
		12-52	Sandy loam	SM,SM-SC	A-2	2.0-6.0	0.10-0.12			
		52-73	Loamy sand	SM,SP-SM	A-2	6.0-20.0	0.04-0.08			
Lakeland Soils	>6.0	0-7	Loamy sand	SM	A-2	6.0-20.0	0.05-0.09	0.5-1.0	1.35-1.55*	0.75
		7-82	Sand	SM-SP	A-3	6.0-20.0	0.02-0.06		1.5-1.6*	
Troup Loamy Sand	>6.0	0-64	Loamy sand	SM	A-2	6.0-20.0	0.05-0.10	0.5-1.0	1.35-1.65**	0.75
		64-80	Sandy Loam	SM,SC	A-4	0.60-2.0	0.10-0.13		1.45-1.75** 1.50**	
Wickham Loamy Sand	>6.0	0-6	Fine loamy sand and loamy sand	SM	A-4	0.60-2.0	0.12-0.14	0.5-1.0	1.35-1.65	0.5
		6-42	Clay loam, loam, sandy clay loam	ML,SC,CL	A-4, A-6	0.60-2.0	0.12-0.15		1.30-1.40	
		42-83	Loamy sand	SM	A-2	2.0-6.0	0.08-0.11		Highly variable	

*Depths 0-40", 40-80", respectively
**Depths 0-48",48-64",64-80", respectively

Rainfall Data

There were 31 days of recorded rainfall from the initial spray data (July 16) to October 30, 1980. Of these it only rained sufficiently on five occassions to produce runoff at the test site. The first three runoffs were sampled on July 21, (0.80"), July 27 (1.55") and September 2 (1.16"). No runoff from the test cotton field was ever noted to flow near Station R; Stations S, and R, were therefore never used.

CONCLUSIONS

The results of this runoff study which is not a guidelines data requirement clearly show that cypermethrin when applied under actual use conditions to a cotton field can be transported via runoff to adjacent aquatic sites. Although the maximum concentration detected in the aquatic environment (sediment) did not exceed 2 ppb the residue determined represented cypermethrin per se and did not include its degradation products.

In study 3.5 of this review, 14C-benzyl cypermethrin was shown to have a half life in 3 different soil types of from 1 to 3 weeks with the major degradation products 3-phenxoybenzaldehyde and 3-phenoxy benzoic acid. In an analagous manner to permethrin, ^{14}C-cyclopropane labeled cypermethrin would also rapidly degrade to (IRS-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylic acid in soil. In study 3.15 "Cypermethrin Dissipation in Soils" J.P. Ussary 1980 (S. Malak 5/4/81, review of 1018-EUP-19) it was reported that under field conditions cypermethrin degraded rapidly in four agricultural soils with little or no downward movement of the residue and a half-life of the initial concentration of cypermethrin in soil of 4 to 12 days.

Therefore, considering the spraying and sampling schedule for this experiment wtih spraying commencing on July 6 and continuing at 5 day intervals and with soil sampling for residues continuing until September 26th it is possible that the parent cypermethrin detected in soil, water and sediment at or near the test site represents only a small fraction of the total residue impacting on both the soil and aquatic environment.

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3.23 "Monitoring The Fate of Cypermethrin After Aerial Applications on Cotton" Cella, G.E. Union Carbide Corporation, Environmental Services Tarrytown, N.Y. 10591, Project No. 11507-9 January 1981.

This reference provides a detailed description of the site and conditions recorded and observed during ICI's 1980 Alabama Runoff Study for Cypermethrin Residues cited above in 3.22.

Specifically this report details the site description including the location of ten sampling stations in the test cotton field, the Little Mulberry and the two unnamed streams (Figure 3). The hydrology in and around the test site was discussed in detail and in addition a detailed characterization of the test plot soil was provided (Table 12). On site environmental data during each cypermethrin application including daily soil evaporation and precipitation data (also hourly precipitation data) in inches recorded at the test cotton field site are also presented in the report.

The report states that a total of 31 rain days occurred during the study but only three collectable runoff periods were noted. The test cotton plot could be divided into two major soil types: Troup loamy sand and Wickham loamy sand. When runoff occurred, most of the water landing on the Troup would run off towards the west eventually reaching a tributary stream to the Little Mulberry Creek. The land consisting of the Wickham soils contained less of a slope, but most of the runoff would accumulate near station R_2, leaving the test cotton field at a point nearest to one of the unnamed tributary springs and the Little Mulberry.

The following animal metabolism studies which do not have any environmental chemistry implications are reviewed by title:

41J Hall, B.E., Vickers, J.A. and Hopkins, R. "(^{14}C)-Cypermethrin: A Study to Determine the Bioaccumulation of Radioactivity In The Rat Following Repeated Oral Administration" Hazleton Laboratories Europe Ltd Report No. 2487-7 [October 1980].

42J Jones, B.K. "Cypermethrin: Bioaccumulation Study In The Rat" ICI Central Toxicology Laboratory Report No. CTL/P/599 [June 1981].

43J Bratt, J., Mills, I.H. and Slade, M. "PERMETHRIN: Tissue Retention in The Rat" ICI Central Toxicology Laboratory Report No. CTL/P/352 [July 1977].

44J Swaine, H. and Sapiets, A. "CYPERMETHRIN: Residue Transfer Study with Dairy Cows Fed On A Diet Containing The Insecticide" ICI Plant Protection Division Report No. RJ0186B [May 1981].

45J Swaine H. and Sapiets, A. "CYPERMETHRIN: Residue Levels Of The Major Metabolites Of The Insecticide In The Milk And Tissues Of Dairy Cows Fed On A Diet Containing Cypermethrin At 50 mg/kg^{-1}" ICI Plant Protection Division Report No. RJ0198B [June 1981].

3.24 "CYPERMETHRIN: Accumulation And Depletion of Radioactive Residues in The Tissues of Mallard Duck And Bobwhite Quail Following Daily Dosing" [ICI Plant Protection Division Report No. RJ0147B (September 1980)]

EXPERIMENTAL

Twelve Mallard ducks and twelve Bobwhite quail were dosed orally for up to 28 days with ^{14}C-cis, trans cypermethrin at a rate of 0.18 mg kg^{-1}. Two birds of each species were sacrificed after 7, 14, 21 and 28 days dosing. The remaining birds were withdrawn from dosing and were sacrificed in pairs 7 and 14 days after the administration of the final dose. The radioactive residues in the breast muscle, leg muscle, heart, liver, kidney, brain and fat of the birds were measured.

Results

The highest residue in Mallard duck (0.100 mg kg^{-1}) was found in the liver of one bird (sacrificed after 7 days dosing). The radioactive residues found in all tissues of the birds sacrificed after 7 and 14 day depuration periods were at or below the limit of detection (0.005 to 0.008 mg kg^{-1}).

The highest residue in Bobwhite quail (0.156 mg kg^{-1}) was found in the fat of one bird (sacrificed after 7 days dosing). The radioactive residues found in all tissues of the birds sacrificed after 7 and 14 day depuration periods were at or below the limit of detection.

Conclusions

When Mallard duck and Bobwhite quail were dosed orally for up to 28 days with ^{14}C-cypermethrin at a rate of 0.18 mg kg^{-1}. The radioactive residues found in the tissues during dosing and in the two weeks following the final dose were very low. No accumulation of radioactivity took place.

3.25 "Permethrin: Accumulation and Depletion of Radioactive Residues in the Tissues of Mallard Duck and Japanese Quail Following Daily Dosing with ^{14}C-Permethrin." J.P. Leahey, D.W. Bewick, R. Saunders Report No. AR 2726 B (March, 1977)

Experimental

Mallard ducks and Japanese quail were treated with daily doses of either cyclopropane-labeled or methylene-labeled permethrin for up to 28 days, and for up to 14 days after last dose. Doses administered in corn oil by stomach tube. After sacrifice, gross examination of organs for abnormalities was made and organs combusted for radioassay. Due to freezer failure, samples from the first two weeks were lost, and the experiment was repeated for that interval. Although eggs and carcass samples were retained, there is no report on these tissues. The treatment rate was 0.2 mg/kg/day for both birds. Excreta was not examined for residues of permethrin.

Results:

No apparent difference in tissue retention between the two radio-labeled compounds. Highest levels of ^{14}C were found in fat at about 0.2 ppm average concentration. Liver, kidney, brain and gizzard were at lower levels, and the leg or breast muscle tissue had the lowest levels of ^{14}C. Significant depletion of tissue ^{14}C occurred within 2 weeks after withdrawal of exposure. The report does not present a material balance of recovered radioactivity versus applied radioactivity.

Conclusions:

Permethrin is shown to occur in several tissues of Mallards and Quail, at fairly low levels. Metabolism of permethrin by the birds is not demonstrated, since tissues examined only for ^{14}C and not for identification of residues. Material balance is lacking, and residual radioactivity in bird carcass, excreta, and eggs is not reported. The accumulation does not appear to be significant.

3.26 "The Accumulation And Elimination of WL 43467 By The Rainbow Trout (Salmo gairdneri)" Baldwin, M.K. and Lad, D.D. [Shell Research Ltd Report No. TLGR. 0041-78 (March 1978)].

EXPERIMENTAL

Rainbow trout (N = 100/tank) weighing between 2 to 3 grams/fish were added to a 400 liter capacity stainless steel tank containing 300 liters of dechlorinated water held at 14±1°C. The water (total hardness of 270 mg l^{-1}) was aerated for 24 hours before the fish were put into it to ensure that chlorine was removed. Before a tank was filled it was cleaned and disinfected using 0.1% v/v cetyltrimethylammonium bromide.

The water was changed each day during the 22 day exposure period, but after the end of the exposure period the frequency of water change depended upon the cleanliness of the tank. In general, a change was made at 2 or 3 day intervals. The average concentration of [^{14}C]-WL 43467, labeled in the ring of the benzyl group measured in the water of a fresh tank was 0.165 ug l^{-1} and after 24 hours of exposure was 0.064 ug l^{-1}. After 22 days exposure the remaining 50 fish were transferred to water containing no [^{14}C] - WL 43467 for an additional 51 days.

Water samples were taken for analysis 10 minutes after mixing and 24 hours after mixing on each day of the 22 day exposure period. Pairs of fish were also taken periodically during the exposure and depuration phases of the experiment, homogenized and analyzed for total radioactivity by LSC or for residues of WL 43467 by GLC with electron capture detection.

RESULTS

The apparent concentrations of [^{14}C] - WL 43467 found in water which had been occupied by fish for 24 hours were much lower than those found in fresh water averaging 39% of the initial concentration due in part to removal of radioactivity from the water by fish.

The concentration of radioactivity in fish rose until approximately 11 days after the start of the exposure. Between 11 and 22 days there was no observable increase in the concentration of radioactivity in the fish. The average concentration in the fish between 11 and 22 days of exposure was equivalent to 0.083 ug g^{-1} of [^{14}C] WL 43467.

After 22 days exposure when the remaining 50 fish were transferred to water containing no [^{14}C]-WL 43467. The total ^{14}C residues had fallen to half the plateau level in about 11 days.

When fish were sampled during the 11 to 22 day exposure period and analyzed by GLC for residues of WL 43467 only 67% of the extracted total ^{14}C activity could be identified as the parent compound. No attempt was made to identify the other radioactive components because of the small quantities present.

CONCLUSIONS

The changes in water concentration of [^{14}C] - WL 43467 observed in this "static" exposure environment make it difficult to calculate an accumulation factor for radioactivity in fish, which the Authors estimate from a constant concentration of [^{14}C] - WL 43467 in water to be approximately 1000X.

After 51 days depuration total ^{14}C residues in whole fish dropped to approximately 50% of that observed at the plateau level of 11 to 22 days after initiation of exposure.

The only compound identified in the fish was the parent compound with approximately 33% of the remaining radioactivity unidentified.

This study does not satisfy the guidelines requirement for a flow through exposure study in 165.4 (Laboratory studies of pesticide accumulation in fish).

3.27 "The Accumulation, Distribution and Elimination of Ripcord by Rainbow Trout Using a Continuous -Flow Procedure" Bennett, D. [Shell Research Ltd. Report No. SBGR 81.026 (May 1981)]

EXPERIMENTAL

Two aquaria were prepared both containing 400 l of water. One used for accumulation of RIPCORD (Cypermethrin, WL 43467) unlabeled (50/50 cis/trans isomer distribution) 98.1% analytically pure, received both dechlorinated mains water (hardness typically 230-260 ppm as C_aCO_3 and pH 8.0-8.2) and a saturated aqueous solution of RIPCORD. The proportions were adjusted to give a concentration of RIPCORD of 0.2 ug. l^{-1} and a total flow of about 1 l. min^{-1} (equivalent

to approx. 3.6 complete exposure medium changes per day). The second aquarium, for the elimination of RIPCORD, received only dechlorinated mains water at 1 l. min^{-1}. The temperature in both aquaria was maintained at 15±1°C.

Small Rainbow Trout

The aquarium containing 0.2 ug. l^{-1} RIPCORD was stocked with 100 small (2-13 g) trout and the accumulation period started. Two fish were removed for analysis at +2, t6 and + 24 hours and then until it was apparent from the daily analysis of fish and water that a plateau concentration had been reached.

After the accumulation period was completed the remaining 60 fish were transferred to the aquarium receiving only dechlorinated mains water and the elimination period started. Fish were removed for analysis every other day until RIPCORD residues declined to values near the lower limit of GLC/ecd detection.

Large Rainbow Trout

The aquarium containing 0.2 ug.l^{-1} RIPCORD was stocked with 10 large (130-260g) rainbow trout immediately following the removal of small fish. Five fish were removed for dissection and analysis after 17 and 24 days exposure.

Analytical

Water Samples of the water column in the accumulation aquarium were taken daily. For the elimination aquarium samples were taken and analyzed on four occasions. All water samples were analyzed by gas liquid chromatography with electron capture detection.

Rainbow Trout

Whole small fish, including head, gut and tail were either analyzed immediately by GLC/ecd or were stored at - 20°C until required for analysis. Large fish were dissected and the following tissues were weighed and stored separately (-20°C) before required for analysis: Brain, liver, stomach and intestine, muscle (one side of fish) body fat, (if present), skin (one side of fish), gonads (if present) and remaining carcass.

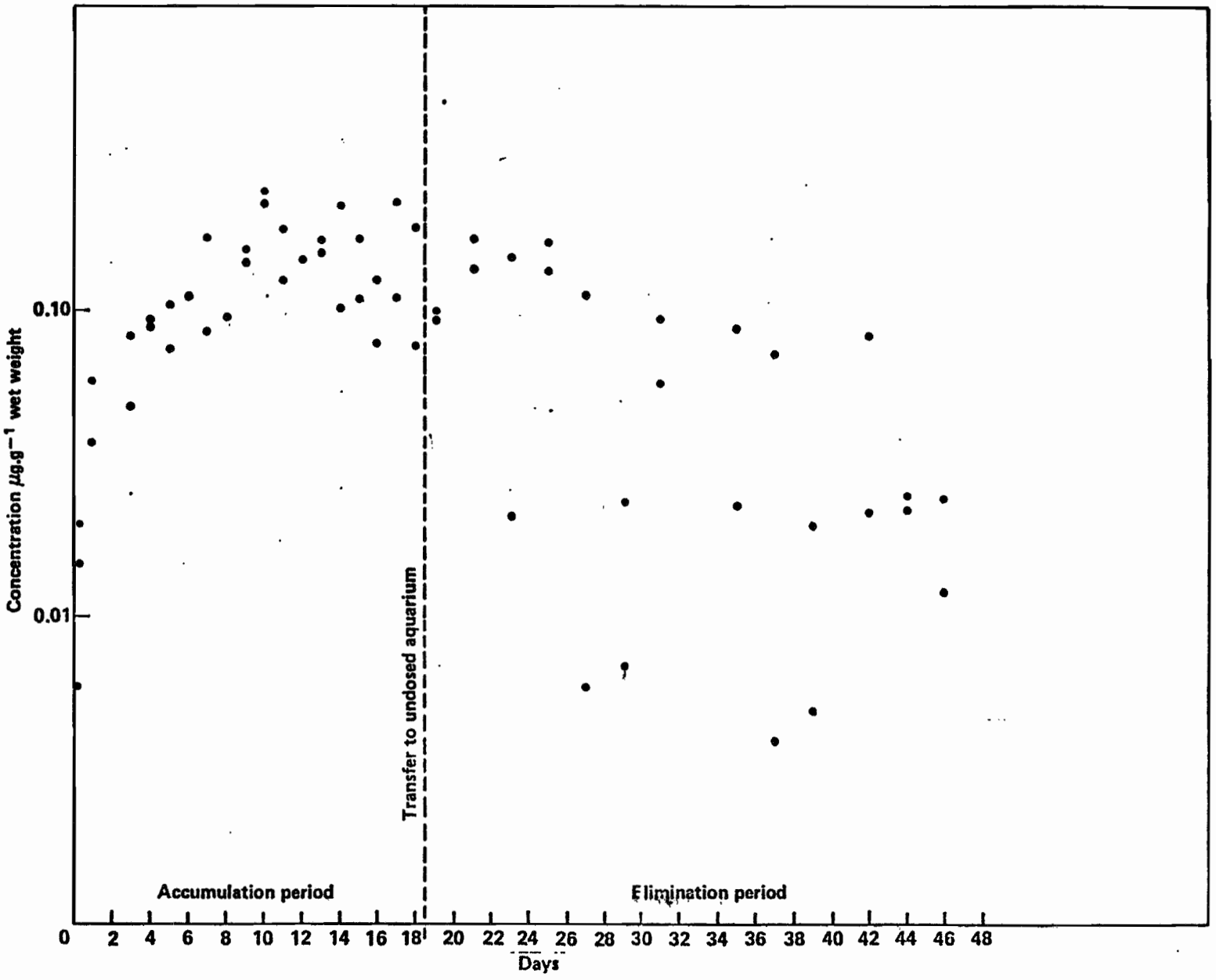

Fig 4 RIPCORD concentrations (wet weight) in small rainbow trout

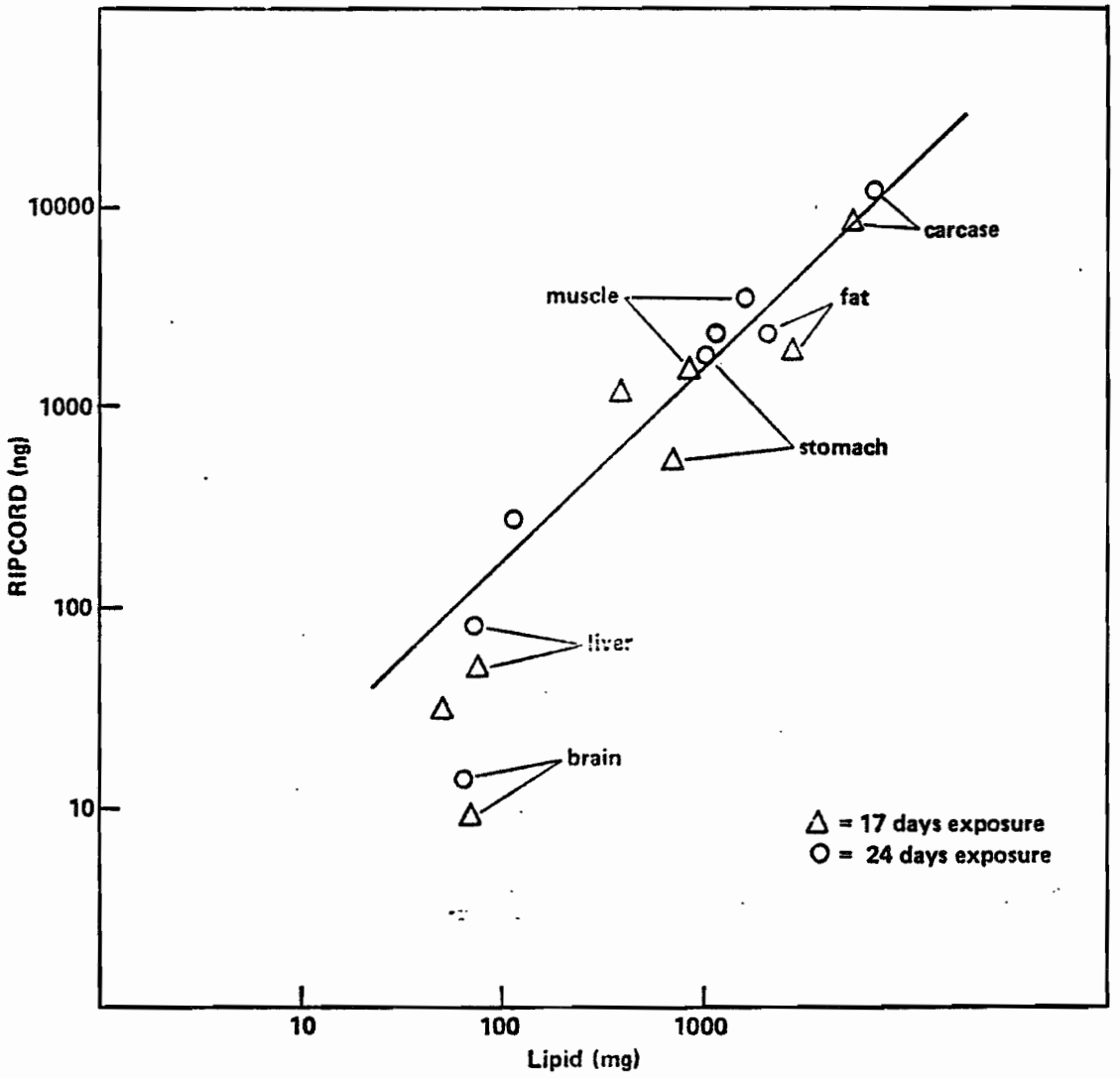

Fig 5 Correlation of total RIPCORD mass and total lipid mass in trout tissues

Statistical analysis

The statistical analysis of this experiment was based on a one compartment model in which 1) the concentration in water is assumed to be constant and 2) an assumption that errors observed are related to the size of the observations and are normally distributed. Based on these assumptions the Author calculated the following: the asymptotic steady state concentration, the accumulation factor time of exposure to achieve 95% of the plateau concentration time of exposure for a predicted value to be within the 95% confidence limit (one-sided) of the plateau concentration and 'half-life' of residues during the elimination period.

RESULTS

Accumulation and Elimination of RIPCORD in Small Rainbow Trout

Statistical analysis, using a one-compartment model of the RIPCORD concentrations in fish, has shown that the accumulation factor (water into fish, on a wet weight basis) is 1200. The approach to the calculated equilibrium concentration in fish (0.23 $ug.g^{-1}$, wet weight) is slow after an initial rapid build-up period of approximately 10 days (Fig. 4) and the time to reach 95% of the equilibrium concentration is 34 days. However, the variation in fish concentration data results in wide confidence limits for the time to equilibrium and thus the time for a predicted concentration to lie within the confidence limits (95%) is only 7 days exposure. This period and also the calculated time for residues to decline to half the equilibrium concentration (8 days) are similar to those found in the static water test reviewed in 3.26 above. Examination of fish residue concentrations on a lipid weight basis gave a similar time (9 days), for values to be within the 95% confidence limits of the plateau concentration, compared with that obtained from wet weight data (8 days). Time to achieve the plateau concentration (25 days) on a lipid weight basis was, however, somewhat shorter than on wet weight (34 days).

Distribution of Residues of Ripcord in Large Rainbow Trout

Analysis of aquarium water samples taken during the exposure of large trout to RIPCORD shows that a similar mean concentration (0.18 $ug.l^{-1}$) was maintained to that for small trout accumulation (0.19 $ug.l^{-1}$).

However, the calculated mean concentration in large trout (0.07 $ug.g^{-1}$, wet weight) after 17 days exposure is lower than that for small trout (ca 0.15 $ug.g^{-1}$). After 24 days exposure the mean concentration in large trout was 0.12 $ug.g^{-1}$ and therefore an equilibrium value may not have been achieved in these considerably larger fish. On a wet weight basis, RIPCORD residues in the individual tissues also show an increase from 17 to 24 days exposure, but an increase is less apparent on a lipid weight basis.

Mean residue concentrations (wet weight) in abdominal fat were at least 10 times higher than those in skin, muscle and in stomach and intestine. The lowest wet weight residues were found in brain, gonads and liver (0.020.04 $ug.g^{-1}$, mean). On a lipid weight basis, however, residues in fat, skin, muscle, stomach, liver and gonads were all similar (1-2 $ug.g^{-1}$, mean), but the residue in brain was again lower. RIPCORD content of the tissues is well correlated with lipid content as shown in Fig. 5; only brain deviates notably from a linear relationship.

No principal depository for RIPCORD was found in the tissues examined. The highest proportions of total content of RIPCORD in the fish were in muscle tissue and in skin; mean contents (after 24 days exposure) 19 and 16% respectively. Twelve and 10 percent of the total content were found in fat and in stomach and intestine respectively.

Conclusions

Residues of parent Cypermethrin at a concentration of 0.19 ug/l in water reached an equilibrium concentration in small trout in 34 days during continuous flow-through exposure with a calculated bioaccumulation factor of 1200X and a half-life for residue depuration of 8 days. After 24 days exposure, mean residues in abdominal fat of large trout were at least seven times higher than in any other tissue. On a lipid weight basis, residues in liver, fat, stomach and intestine, muscle, skin and gonads were similar. The highest proportions of the total RIPCORD content in large trout (mean values) were found in muscle (19%), skin (16%), fat (12%) and stomach plus intestine (10%).

Because equilibrium concentrations of cypermethrin in large trout were not achieved as with the small trout, bioaccumulation factors could not be calculated. The parent compound, cypermethrin, was the only compound analyzed for in fish tissue.

This study satisfies the guidelines data requirements under 165-4 (Laboratory studies of pesticide accumulation in fish).

3.28 "Cypermethrin: The Accumulation of Cypermethrin and its Degradation Products by Channel Catfish in a Model Soil/Water System" Hammer, M.J. and I.R. Hill [ICI Plant Protection Division, Report No. RJ 0153B (December 1980)].

Reviewers note: A "catfish" or soil/water ecosystem accumulation study is not now required by the current Environmental Fate Guidelines. The results of this study are briefly summarized and not reviewed in detail.

Channel catfish (Ictalurus punctatus) were exposed to ^{14}C-Benzyl cypermethrin and its soil degradation products in a soil/water ecosystem for 23 days after which the fish were transferred to flowing, uncontaminated water for a 14 day depuration phase. Soil, water and fish (muscle, viscera and whole fish) were analysed for ^{14}C-residues at regular intervals.

During the initial 21 day aerobic incubation with soil ^{14}Cresidues decreased from 500ug cypermethrin equivalents/kg dry wt soil to 300ug/kg. Cypermethrin accounted for at least 90% of the applied radioactivity after application to the soil; by day 21 only 15% of the applied radioactivity remained as extractable cypermethrin. Following flooding of the soil there was little change in the total radioactivity in the soil. The ^{14}C-residues in the water increased to a plateau of 1.9ug cypermethrin equivalents/ litre; 4% of the applied radioactivity. In the whole fish an apparent plateau concentration of 30ug cypermethrin eqivalents/kg wet wt fish was reached during the exposure phase, equivalent to approximately 0.023% of the radioactivity remaining in the ecosystem. At the end of exposure, muscle tissues contained 20ug cypermethrin equivalents/kg. The mean maximum bioconcentration factors (concentration of ^{14}C-residues in fish/concentration of ^{14}C-residues in water) in whole fish and muscle were approximately x14 and x9 respectively.

The concentration of ^{14}C-residues in the fish fell rapidly during depuration. Approximately 70% and 80% of the residues in the muscle and whole fish, respectively, were eliminated during the 14 day period.

In conclusion, the data presented in this report show that bioconcentration of residues of the ^{14}C-benzyl moiety of cypermethrin from a sediment/water ecosystem by channel catfish is relatively minor. Rapid loss of these same residues on depuration also shows that they are unlikely to possess the potential to accumulate through a food chain involving fish, as is also the case with its analogue permethrin. However, data from this study show only residues containing the benzyl moiety. A similar study (see 3.29 of this review) has been conducted using ^{14}Ccyclopropane-/^{14}C-phenyl permethrin, where the distribution of "cyclopropane" hydrolysis products have been included. In that study, the mean maximum bioconcentration factor in muscle was x12, and during a 14 day depuration period 65% of the radioactivity was eliminated from the fish.

3.29 "Kinetics of Aged ^{14}C-PP557 In A Model Aquatic Ecosystem" Ellis, S.J. and Sleight, III., B.H. [EG & G Bionomics Report (January 1977)].

Reviewers note: This study was reviewed in detail in the 2/7/78 review by R.W. Cook and R.F. Carsel on Registration Submission 10182-RI (Registration of Permethrin on Cotton).

The reviewers concluded at the time based on the data submitted in the study that because of the position of the ^{14}C label in permethrin (labeled <u>both</u> in the cyclopropyl and phenyl ring) that is was <u>not</u> possible to determine whether the material remaining in the soil during the 30 days incubation was the parent compound or some of its degradates. Likewise, it was not possible to determine the chemical nature of the ^{14}C material which accumulated in catfish muscle at 12X and catfish viscera at 93X above levels in water approaching 0.74 ppb during 30 days exposure.

3.30 "Cypermethrin: Rotational Crop Study" Woods, T.M., Bewick, D.W. and J.P. Leahey [ICI Plant Protection Division, Report No. 0161B November 1980].

EXPERIMENTAL

Greenhouse pots (27) of 23 cm diameter were filled with a sandy loam soil from an unknown source and having the following characteristics (pH 6.8, 5.08% OM, CEC 21meq/ 100g soil, coarse sand 25.4% fine sand 26.5%; silt 20.1% and clay 28.0%). The top 7.5 cm of the soil in the greenhouse pots was treated with ^{14}C-cypermethrin at 1.0 kg ai/ha rate which is about one-half of the maximum recommended rate of 1.875 lb/acre/season.

^{14}C-cypermethrin radiolabeled in the alcohol part of the molecule (^{14}C-benzyl labeled cypermethrin) was used in this experiment. In addition a study was carried out with the ^{14}C-cypermethrin radiolabeled in the acid part of the molecule (^{14}C-cyclopropane labeled cypermethrin). In this case only sugar beet seeds were sown in the treated soil.

The cypermethrin was applied to the soil in a formulated state by adding formulation premix containing all the formulation adjuvants. The formulated radiolabeled cypermethrin was emulsified in 100 ml of water and added to the soil, which was thoroughly stirred with a spatula and then returned to the pot containing the remainder of the untreated soil. The treated soil pots including 12 control pots were maintained in the greenhouse during aging and during the plant growth stages of the experiment.

Four rotational crops were used in this experiment: sugar beets, wheat, lettuce and cotton. Fifteen seeds of cotton, sugar beet, wheat and lettuce were sown to each pot at intervals of 30, 60, and 120 days after the application of ^{14}-cypermethrin. Each crop was thinned several times during the study and the thinnings were analyzed for total ^{14}C residues. At maturity wheat grain, chaff and straw, sugar beet foliage and root, cotton lint, seed boll husks and lettuce were analyzed for total ^{14}C activity.

Soil cores from the top 7.5 cm of each pot were taken for analysis at the respective sowing intervals of 30, 60 and 120 days after treatment. When the crops were harvested soil cores were taken to the bottom of each pot and the activity in the topsoil and the subsoil measured by combustion and LSC.

The radioactive residues in the various crop samples were measured by combustion and LSC. Duplicate subsamples of each crop were analyzed and these had a wet weight in the region of 0.08-0.8g.

Results

^{14}C radioactivity is lost from the top 7.5 cm of soil with time. For example, residues of ^{14}C-Benzyl Cypermethrin at time of treatment (1.77 ppm) decreased to 0.81 ppm at 120 days and 0.57 ppm at 252 days. For ^{14}C-Cyclopropane Cypermethrin residues at time of treatment 1.81 ppm decreased to 0.86 ppm at 120 days and 0.39 ppm at 252 days.

After 274 days of the experiment only 7.6% of the radioactivity resulting from ^{14}C Benzyl labeled Cypermethrin leached to the bottom of the soil pots and for ^{14}-C Cyclopropane labeled Cypermethrin 13.4% of the radioactivity leached to the bottom of the soil pots.

The radioactive residues present in the crops sown 29-30, 60 and 120 days after treatment are given in the following tables. The residues in these tables are the averages of the duplicate measurements made.

The presence of significant radioactive residues in both mature wheat and cotton plants grown along side treated plants as controls invalidated the residues detected in treated wheat and cotton plants. The Author's postulated that significant ^{14}-C residues detected in control plants resulted from fixation of $^{14}CO_2$ which was evolved from the soil treated with ^{14}C-cypermethrin.

The maximum radioactive residues derived from ^{14}C-Benzyl Cypermethrin and detected in mature crops (0.05ug/g) was in the seeds of cotton plants sown 60 days after soil treatment. Slightly higher residues (up to 0.063 ug/g) were detected in immature lettuce plants. In general total ^{14}C residues in the crops tested derived from either ^{14}-C Benzyl or ^{14}-C Cyclopropane labeled cypermethrin showed a downward trend when the crop sowing interval was increased from 30 to 120 days.

Sugarbeets showed a significant difference in rate of accumulation based upon position of the ^{14}C, with the cyclopropane label uptake much higher than from the benzyl label ^{14}C. The difference in total ^{14}C residues resulting from each label in sugar beet thinnings, foliage and root tended to decrease or narrow as the interval between application and re-planting increased from 30 to 120 days.

No attempt was made to characterize the nature of the ^{14}C residues taken up any of the crops tested in this study.

Wheat

days after treatment	days after planting	total days	Plant Part	PPM ^{14}-C Benzyl Cyper-Methrin
29	17	46	thinnings	0.043
29	32	61	thinnings	0.044
29	115	144	grain	0.063*
29	115	144	chaff	0.07*
29	115	144	straw	0.06*
60	18	78	thinnings	0.013
60	37	97	thinnings	0.015
60	131	191	grain	0.055*
60	131	191	chaff	0.062*
60	131	191	straw	0.043**
120	14	134	thinnings	<0.01
120	28	148	thinnings	0.014
120	122	242	grain	0.036*
120	122	242	chaff	0.034*
120	122	242	straw	0.024*

Cotton

29	137	166	thinnings	0.023
29	153	182	thinnings	0.039
29	300	329	lint	0.023
29	300	329	seed	0.031
29	300	329	boll husk	0.02
29	300	329	foliage	0.01
60	18	78	thinnings	0.014
60	37	97	thinnings	0.04
60	246	306	lint	<0.01
60	246	306	seed	0.05
60	246	306	boll husk	0.03
60	246	306	foliage	<0.01
120	14	134	thinnings	<0.01
120	28	148	thinnings	0.012
120	200	320	lint	0.016*
120	200	320	seed	0.026*
120	200	320	boll husk	0.024*
120	200	320	foliage	<0.01*

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* Control values as high as samples

** Control values higher than sample

Lettuce

days after treatment	days after planting	total days	Plant Part	PPM ^{14}-C Benzyl Cyper-Methrin
24	24	53	thinnings	0.063
29	32	61	thinnings	0.044
29	98	127	Mature	<0.01
60	18	78	thinnings	0.048
60	37	97	thinnings	0.026
60	92	152	Mature	<0.01
120	25	145	thinnings	0.016
120	40	160	thinnings	0.011
120	81	201	Mature	<0.01

Sugar Beet

days after treatment	days after planting	total days	Plant Part	PPM Benzyl ^{14}-C	PPM Cyclo ^{14}C
29	46	75	thinnings	No Sample	No Sample
29	69	98	foliage	0.012	0.063
29	69	98	root	0.023	0.145
29	137	166	foliage	0.013	0.029
29	137	166	root	0.014	0.021
60	31	91	thinnings	0.02	0.048
60	37	97	foliage	0.02	0.026
60	37	97	root	0.06	0.074
60	192	252	foliage	<0.01	<0.01
60	192	252	root	<0.01	<0.01
120	14	134	thinnings	<0.01	0.017
120	40	160	foliage	0.01	0.015
120	40	160	root	0.016	0.022
120	153	273	foliage	<0.01	0.01
120	153	273	root	<0.01	<0.01

CONCLUSIONS

The Author's conclude that there is only a very minor transfer of residues containing the benzyl moiety of cypermethrin from soil into crops. The reviewer generally agrees with this conclusion, however, due to experimental difficulties arising from ^{14}C contamination of cotton and wheat control plants grown to maturity this conclusion cannot be arrived at with any degree of certainty. In addition the ^{14}C application rates used in this experiment are only ca one-half of the maximum allowable rates under actual field use conditions. In contrast, the permethrin rotational crop study cited by the applicant in Reference 53J of this submission employed ^{14}C labeled Permethrin at 2 kg/ha which is approximately 1x the maximum allowable field application rate.

The Author further concludes that ester cleavage is a major degradation pathway for cypermethrin in soil and therefore the potential for uptake of degradation products containing the cyclopropane moiety of cypermethrin is not fully assessed by this study (sugar beet only was planted in ^{14}C-cyclopropane-labeled cypermethrin treated soil). However, the author further postulates that the cyclopropane moiety of Cypermethrin will behave exactly the same as its closely related analog permethrin (viz a viz uptake by rotational crops) since ester cleavage of permethrin in soil releases exactly the same cyclopropane moiety that is present in cypermethrin. In Reference 53J of this submission it was shown, with the exception of mature wheat planted after an interval of 120 days, that residues containing the cyclopropane moiety of permethrin transferred to a greater extent into lettuce, cotton and sugar beets than residues containing the phenyl moiety. Therefore, residues of concern in that study although not characterized or identified were derived from the cyclopropane moiety. In Reference 54J of this submission it was further shown that when sugar beets were planted into soil which had been treated 30 days previously with ^{14}C-cyclopropane-labeled-permethrin and the plant harvested at maturity (136 days of plant growth and 166 days after soil treatment) that about one-half of the initial ^{14}C material present in the plant tissues are present as degradates of permethrin, notably the mono-acids (cis and trans dichlorovinyldimethylcyclopropanecarboxylic acids) and the dicarboxylic acid (dichlorovinylmethylcyclopropane-1,2-dicarboxylic acid).

In a later study, "Permethrin Crop Rotation Study" Swaine, H., Edwards, M.J. and J.P. Usary Report No. TMU 0378/B May 19, 1978 submitted by ICI on 5/28/78 as an amendment to EPA Reg. 10182-NNNRI and reviewed by R.W. Cook EFB it was shown that in this non-radioactive study of field grown rotational crops, residues of dichlorovinyldimethyl-cyclopropanecarboxylic acid (mono acid) and dichlorovinyl-methylcyclopropane-1,2-dicarboxylic acid (di-acid) were found in a variety of rotational crops. The rotational crops were grown in two locations, one location having a silt loam soil and the other soil was unspecified. No residues were found in any crop sown 60 days or more after treatment of the soil. Maximum residues of the mono acid of 0.04 ppm were found in cotton, soybeans, grain sorghum, cabbage, wheat and whole sugar beet plants and the di-acid at 0.03 ppm in grain sorghum and cabbage. The EFB reviewer of this study concluded that the field rotational crop data will support a rotational crop interval of 60 days, at which time it is not expected that residues of permethrin or its degradates will occur in rotational crops.

Because of experimental difficulties of ^{14}C contamination of control plants, application rates of ca 1/2 the recommended field application rates and the fact that the experiment (with the exception of sugar beets) determined only the crop uptake of ^{14}-C Benzyl residues of cypermethrin instead of ^{14}C-cyclopropane residues (although presumably identical to those already reported for Permethrin in previous submissions) which would probably constitute the residues of toxicological concern in rotated crops we conclude that the study does not satisfy guideline data requirements under 165-1 (confined accumulation studies on rotational crops).

3.31 "Permethrin: Rotational Crop Study" Leahey, J.P., P.K. Carpenter [ICI Plant Protection Division, Report No. TMJ 1501B April 1977].

Experimental

The soil used in this rotational crop residue accumulation study is a sandy loam soil of unspecified soil characteristics and unknown source. Two radiolabeled positions in the permethrin structure were studied, the cyclopropane position and the phenyl ring position. The permethrin was applied to the soil in formulated state, by adding formulation premix containing all the formulation adjuvants. The permethrin was applied to the soil at 2 kg/ha rate, equivalent to 1.78 pounds active ingredient per acre.

The formulated radiolabeled permethrin was emulsified in 100 ml of water and added to the soil, which was thoroughly stirred with spatula, and then returned to the pot containing the remainder (untreated) of the soil. Only the top three inches of the soil in each pot was treated. The treated soil pots were maintained in the greenhouse during aging and during the plant growth stages of the experiment.

Four rotational crops were used in this experiment: sugar beets, wheat, lettuce and cotton. The rotational crops were seeded into the pots 30 days after permethrin application, while additional pots were aged for 60 or 120 days prior to the seeding of the rotational crops. Each crop was thinned several times during the study and the thinnings were analyzed for ^{14}C residues. The ^{14}C residues are reported on a fresh weight basis.

Results

Wheat

days after treatment	days after planting	total days	Plant Part	ppm phenyl ^{14}C	ppm cyclo ^{14}C
30	11	41	thinnings	0.28	1.47
30	18	48	thinnings	0.71	2.13
30	115	145	straw	0.49	0.33
30	115	145	chaff	0.20	0.73
30	115	145	grain	0.50	0.86
60	21	81	thinnings	0.04	0.48
60	37	97	thinnings	0.04	0.39
60	134	194	straw	0.06	0.57
60	134	194	chaff	0.08	0.51
60	134	194	grain	0.08	0.22
120	12	132	thinnings	0.02	0.26
120	34	154	thinnings	0.02	0.25
120	102	222	straw	0.08	0.02
120	102	222	chaff	0.08	0.02
120	102	222	grain	0.09	0.02

days after treatment	days after planting	total days	Plant Part	ppm phenyl ^{14}C	ppm cyclo ^{14}C
			Sugar Beet		
30	11	41	thinnings	0.32	3.40
30	25	55	thinnings	0.27	2.15
30	136	166	foliage	0.07	0.35
30	136	166	root	0.05	0.21
60	21	81	thinnings	0.08	0.49
60	37	97	thinnings	0.03	0.21
60	115	175	foliage	0.01	0.14
60	115	175	root	0.03	0.14
120	12	132	thinning	0.07	0.39
120	34	154	thinnings	0.02	0.15
120	102	222	foliage	0.01	0.10
120	102	222	root	0.01	0.04
			Lettuce		
30	11	41	thinnings	1.12	1.18
30	25	55	thinnings	0.32	1.04
30	67	97	foliage	0.02	0.08
60	21	81	thinnings	0.28	1.80
60	37	97	thinnings	0.34	0.64
60	85	145	foliage	0.03	0.08
120	12	132	thinnings	0.07	0.20
120	34	154	thinnings	0.02	0.05
120	67	187	foliage	0.03	0.03
			Cotton		
30	11	41	thinnings	0.07	0.62
30	25	55	thinnings	0.20	0.76
30	143	173	lint	0.01	0.03
30	143	173	seed	0.04	0.06
30	143	173	boll husk	0.03	0.07
30	143	173	foliage	0.04	0.18
60	21	81	thinnings	0.09	0.27
60	37	97	thinnings	0.12	0.18
60	150	210	lint	0.03	0.02
60	150	210	seed	0.05	0.03
60	150	210	boll husk	0.05	0.03
60	155	210	foliage	0.09	0.11
120	12	132	thinnings	0.02	0.22
120	34	154	thinnings	0.02	0.15
120	102	222	foliage	0.04	0.13

Results

The chemical nature of the residues in the four rotational crops has not been examined. However, from the significant differences between uptake of the phenyl and the cis cyclopropane labels, it is fairly certain that the material being accumulated is not parent compound. With the one exception of mature wheat planted after an interval of 120 days from chemical application, the uptake of the phenyl labeled ^{14}C was less than the uptake from the cyclopropane labeled permethrin. Therefore, the residue of concern is the highest residue found, which is the residues from the cyclopropane ^{14}C.

Immature lettuce contained high levels of ^{14}C equivalent to permethrin, which was apparently diluted by plant growth. The ppm equivalent of the ^{14}C from the cyclopropane label was 0.08, 0.08, and 0.03 ppm when replanted at intervals of 30 days, 60 days, or 120 days respectively, in the mature plant at harvest. The chemical identity of the ^{14}C-residue is not known.

Sugarbeets also showed the significant difference of accumulation based upon position of the ^{14}C, with the cyclopropane label uptake much higher than from the phenyl label ^{14}C. The ppm equivalent to parent permethrin from the cyclopropane label dropped as the interval between application and replanting increased. Foliage and roots at maturity showed 0.35 ppm and 0.21 ppm when replanted at 30 days, 0.14 ppm and 0.14 ppm when replanted at 60 days, and 0.10 and 0.04 ppm when replanted at 120 days, respectively.

Cotton replanted after 120 rotation interval was not mature enough to have bolls, so the only analysis was of cotton foliage at 102 days of maturity at total of 222 days after application of the ^{14}C-permethrin. The cotton foliage at this interval showed 0.04 ppm of phenyl and 0.13 ppm of equivalent ^{14}C from the cyclopropane label. At 30 and 60 days after application, the cotton foliage at 143 and 150 days of maturity respectively showed 0.04 ppm (phenyl) and 0.18 (cyclopropane), and 0.09 ppm (phenyl) and 0.11 ppm (cyclopropane), respectively. The lint, seed, and boll husks at both 30 and 60 days replant intervals showed less than 0.10 ppm of ^{14}C equivalent to permethrin from either of the two radiolabels, but these plant parts were not formed when the 120 day replant cotton was harvested.

Wheat showed the reverse of the other crops, in uptake of positional ^{14}C, in that by maturity, the phenyl ^{14}C was higher than the cyclopropane ^{14}C, but only when the soil had aged for 120 days before replanting. At shorter intervals of 30 and 60 days after application the cyclopropane ^{14}C was higher than the phenyl ^{14}C.

Wheat planted after 60 day rotation interval and harvested 134 days after planting showed cyclopropane ^{14}C-equivalent to permethrin of 0.57 ppm, 0.51 ppm, and 0.22 ppm in straw, chaff, and grain respectively; while wheat planted after 120 rotation interval showed phenyl ^{14}C-equivalent to permethrin of 0.08 ppm, 0.08 ppm and 0.09 ppm in straw, chaff, and grain respectively, with the cyclopropane ^{14}C at lower levels.

Conclusions

The rotational crop data do not identify a time interval at which rotational crops do not contain ^{14}C equivalent to permethrin, even at intervals up to 120 days.

Based on additional field rotational crop data cited below in 3.32 it was concluded that a rotational crop interval of 60 days between the last application of permethrin and the replanting of the treated area would be required.

3.32 "Permethrin: Identification of Residues in Sugar Beet grown in Soil Treated with ^{14}C-Permethrin" Leahey, J.P. and P.K. Carpenter [ICI Plant Protection Division Report No. TMJ 1508B, May 20, 1977].

EXPERIMENTAL

In this study, rotational crop was grown to the outline in Report TMJ 1501 B (submitted as Reference 53J in this submission for registration). The rotational crop sugar beet was planted into soil which had been treated 30 days previously with ^{14}C-cyclopropane-labeled-permethrin, and the plant was harvested at maturity (136 days of plant growth and 166 days after soil treatment). The sandy loam soil was treated with radiolabeled formulated permethrin at rate equivalent to 2 kg/ha (1.8 lbs/acre). The rotational crop sugar beet was analyzed by combustion and lsc assay, reporting ^{14}C-equivalent-to-permethrin of 0.35 ppm in foliage and 0.21 ppm in root.

In this study, the chemical nature of the ^{14}C-residues in sugar beet plants is examined. Subsamples of roots and foliage were separately extracted with 1:1 acetone:water and aliquots counted. Non-extractable ^{14}C in the plant tissue combusted and counted. The acetone was evaporated, leaving the aqueous solution which was then partitioned with diethyl ether (and counted). The aqueous phase remaining after the diethyl ether extraction was refluxed for 1 hour in 0.5 M hydrochloric acid. After reflux, the solution was again extracted with diethyl ether. The ether extract was analyzed by thin-layer chromatography. For confirmation of structural identities, portions of the ether extract were cleaned up on preparative layer chromatographic plates, and radioactive spots scraped and eluted with acetone. The ^{14}C material was then methylated with diazomethane and analyzed by GC/mass spectra.

Results:

	Roots	Foliage
Total 14C by combustion	0.35	0.20
Extracted into acetone/water	0.30	0.19
Ether extract before acid reflux	0.01	<0.01
Water after ether extract before acid	0.25	0.18
Water after acid and 2nd ether extract	0.07	0.03
2nd ether extract after acid reflux	0.22	0.14
Combined mono-acids (DCVA)	0.11	0.04
Dicarboxylic acid	0.05	0.06

CONCLUSIONS

The acid reflux converted the major portion of the initially water soluble 14C into ether soluble ^{14}C material. When identified by gc/ms, about one-half of the initial ^{14}C material present in the plant tissues are present as degradates of permethrin, notably the mono-acids (*cis* and *trans* dichlorovinyl-dimethyl-cyclopropanecarboxylic acids) and the dicarboxylic acid (dichlorovinylmethyl-cyclopropane-1,2-dicarboxylic acid). Although permethrin *per se* was not analyzed in this study, the amount of permethrin which could be present can be calculated: parent permethrin would either be non-extractable in acetone/water or if extracted, would appear in the first diethylether partition prior to acid reflux. In the samples analyzed, the sugar beet root could

contain 0.06 ppm of permethrin per se, while the foliage could contain 0.02 ppm. The degradates of permethrin, cis and trans forms of the mono-acid and the dicarboxylic acid, occur at levels higher than the parent compound in sugar beet grown as a rotational crop. The implications of this study are that the analytical procedure used in the analysis of permethrin residues in field grown (non-radiolabeled permethrin) rotational crop is not adequate to determine total residues of permethrin and its degradates in plant tissues. It should be noted that standard fortification/recovery data would not bring this inadequacy to light, and that 14C data is necessary when the parent compound and its degradates have a diversity of lipophilicity characteristics.

3.33 "Uptake of FMC 33297 in Pinto Bean Plants" E.G. Brandau, A.A. Nethery, M.G. Goertler, A.M. Schlaf Report No. M-3784 (December 19, 1975) FMC Agricultural Chemical Division

Experimental

This reference examines the systemicity of permethrin in pinto beans. Carbonyl-labeled permethrin was used to treat plants by foliar application, by soil application, and by hydroponic application. The plants were about two weeks old when the application of permethrin by various means was made. Treated samples of plants were obtained 1, 3, and 7 days after permethrin application. Plant parts examined by autoradiography, and extracts examined by thin-layer chromatography. Experimental design is faulty, in that the pinto bean plants are too young and not grown to maturity, and the sampling interval of only seven days is far too short an interval to determine permethrin systemicity for the whole life of the plant. The design is not to be construed as a rotational crop-type study.

Results:

Less than 2% of the ^{14}C moved from the site of foliar application in 7 days. Recovered ^{14}C (82% of applied) was parent compound, with no degradates found and little loss of ^{14}C through volatilization or other loss mechanisms. Very little of the ^{14}C was taken up by plants from the soil application. From hydroponic solution, 43% of applied ^{14}C was found in roots after one day, and increased to 63% after 7 days. ^{14}C in shoots increased over 7 days, and 2.7% of applied ^{14}C was found in the shoots at day 7.

Conclusions:

The duration of exposure of the pinto bean plants to permethrin residues is far too short to determine systemicity of permethrin over the entire life of the plant. Hydroponic exposure is the only treatment which resulted in significant uptake of permethrin by pinto bean plants. The study was too short to determine if degradates of permethrin can be accumulated by the pinto bean plants.

3.34 Uptake of FMC 33297 by Cotton Plants. D. M. Munger, FMC Agricultural Chemical Division. Analytical Report No. M-3791 (December 22, 1975).

Experimental

This reference examines the systemicity of permethrin in cotton plants. Carbonyl-labeled permethrin was used to treat plants by foliar application, by soil application, and by hydroponic application. The plants were about two weeks old when the application of permethrin by various means was made. Treated samples of plants were obtained 1, 3, and 7, days after permethrin application. Plant parts examined by autoradiography, and extracts examined by thin-layer chromatography. Experimental design is faulty, in that the cotton plants are too young and not grown to maturity, and the sampling interval of 7 days is far too short an interval to determine permethrin systemicity for the whole life of the plant. The design is not to be construed as a rotational crop study.

Results:

About 1% of the ^{14}C moved from the site of foliar application in 7 days. Recovered ^{14}C (89% of applied) was parent compound, with no degradates found and very little loss through volatilization or other loss mechanism. Very little of the ^{14}C was taken up by plants from the soil application. From hydroponic solution, 39% of applied ^{14}C was found in roots after one day, and increased to 48% after 7 days. The ^{14}C in shoots increased after 7 days, and 1.7% of applied ^{14}C was found in shoots after 7 days.

Conclusion:

The duration of exposure of the cotton plants to permethrin residues is far too short to determine systemicity of permethrin over the entire life span of the plant. Hydroponic exposure is the only treatment which resulted in significant uptake of permethrin by plants. The study was too short to determine if degradates of permethrin can be accumulated by the cotton plants.

Because of experimental difficulties of ^{14}C contamination of control plants, application rates of ca 1/2 the recommended field application rates and the fact that the experiment (with the exception of sugar beets) determined only the crop uptake of ^{14}C-benzyl residues of cypermethrin instead of ^{14}C-cyclopropane residues (although presumably identical to those already reported for Permethrin in previous submissions) which would probably constitute the residues of toxicological concern in rotated crops, we conclude that the study does not satisfy environmental fate data requirements for rotational crop studies.

4.0 Executive Summary and Conclusions

4.1 Hydrolysis: Cypermethrin is stable to hydrolysis, with an estimated T 1/2 exceeding 50 days at environmentally expected temperatures and pH values. Under conditions of elevated temperature and pH ranges, (9 and above), cypermethrin hydrolyzes to DCVA, and 3-phenoxybenzoic acid.

4.2 Photodegradation: Cypermethrin is extremely stable to photolysis in water with an estimated T 1/2 exceeding 100 days at environmentally expected temperatures and pH values. Photoproducts produced included DCVA, 3-phenoxybenzaldehyde and 3-phenoxybenzoic acid.

Cypermethrin photodegrades rapidly on soil surfaces (T 1/2 8 to 16 days) to many photoproducts the major ones identified as 3-phenoxybenzoic acid and compound XIV.

4.3 Soil Degradation: Cypermethrin degrades in soil under laboratory conditions. The rate is more rapid on sandy clay and sandy loam soils than on clay soils and more rapid on soils lower in organic matter content and CEC all under aerobic conditions. The T 1/2 in aerobic soils ranged from 2 to 8 weeks. In sterile aerobic soils Cypermethrin degraded with a T 1/2 of 20-25 weeks indicating that microbes play a significant role in soil degradation.

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Cypermethrin degraded more slowly under anaerobic or waterlogged conditions with the major metabolite 3-phenoxybenzoic acid produced. Under aerobic conditions the major metabolites produced were DCVA and 3-phenoxybenzoic acid.

4.4 Aerobic and Anaerobic Aquatic Metabolism

Cypermethrin degraded rapidly in natural pond and river water including their associated sediments with a T 1/2 of <2 weeks and the major degradates produced were DCVA, 3-phenoxybenzaldehyde and 3-phenoxybenzoic acid. 3-phenoxybenzaldehyde plus other unindentified and unextracted metabolites were present in sediment for over 1 year following application.

4.5 Microbial Degradation

Microbes play a significant role in the soil degradation of cypermethrin, in addition, cypermethrin at exaggerated application rates 4-10x had no effect on microbial soil counts or microbial processes in soil nor on earthworm or soil microarthropod populations. Cypermethrin is also not likely to produce adverse effects on the sewage treatment process.

4.6 Mobility: Cypermethrin, as parent, does not leach significantly in soil. It has a low solubility in water (0.2 ppm) and, consequently, high adsorption characteristics. Cypermethrin has a Kd of approximately 2000 after 24 hours on a loamy sand soil with an O.M. of 2.1% which indicates an extremely high degree of adsorption. The degradates, on the other hand, are less adsorbed by soil (with K_d values of <2.0 for DCVA and 10 for 3-phenoxybenzyl alcohol). These degradates including 3-phenoxybenzoic acid may be available for leaching in soils either low in organic matter content or having neutral to alkaline pH values.

Under field conditions runoff of cypermethrin has been shown to occur to some degree and was probably due to physical transport of the soil particles via erosion. Runoff resulted in cypermethrin residues in water of up to 0.1 ppb and in aquatic sediments of up to 2 ppb. Cypermethrin can be expected to adsorb strongly to soil or organic matter in hydrosoil or sediment situations, however, subsequent desorption from soil particles and further degradation to more water soluble metabolites could have an effect upon the toxicity to aquatic organisms.

4.7 Terrestrial Field Dissipation:

Cypermethrin per se degrades rapidly in the field with a T 1/2 of 4 to 12 days for the four soils tested. The formation and decline of the major metabolites identified in the soil metabolism studies (3-phenoxybenzoic acid and DCVA) was not determined under field conditions.

4.8 Accumulation, Fish: The laboratory studies of accumulation of cypermethrin residues per se in rainbow trout and catfish indicate that these residues will accumulate in the edible and non-edible portions of these species, but depuration of these residues does occur. Bioconcentration factors of approximately 1200x were calculated in the rainbow trout flow through study. A maximum bioconcentration factor of 14X in whole fish for ^{14}C residues arising from cypermethrin was observed in the static catfish study.

4.9 Accumulation, Rotational Crops:

Rotational crops (sugar beets, wheat, cotton, lettuce) will accumulate levels of cypermethrin residues calculated as total ^{14}C activity in the range 0.01 to 0.06 ppm within 60 days following application. IN A LABORATORY STUDY. No attempt was made to identify the ^{14}C residues taken up by non-target crops, although it is highly unlikely that this residue is due to the parent compound. We conclude that the rotational crop study submitted does not satisfy environmental fate data requirements for the reasons cited under 5.2 below.

5.0 Data Gaps

The following data gaps were noted in the Environmental Chemistry data submitted under Section J accession No. 070559, PP Nos. 2F2623 and 2H5334, on 12/28/81.

5.1 Although the field dissipation study submitted in support of 10182-EUP-19 was considered adequate for the purpose of that submission it does not satisfy registration requirements under 3(c)(5) of FIFRA. The applicant has determined the rate of dissipation of cypermethrin per se in four soils tested to be generally in the range (t1/2 = 4 to 12 days), however, no attempt was made in the field to identify the

formation and decline of the major metabolites identified in the soil metabolism studies (3-phenoxybenzoic acid and DCVA). We recommend that analytical methodology be developed to determine the presence of these degradates in the field environment. We further recommend that soil sampling continue until patterns of formation and decline of degradation products in the field are established or until 18 months have elapsed since cypermethrin application whichever comes first. In addition one of the soils employed for this field dissipation study should have an organic matter content of at least 5%.

5.2 The laboratory crop rotation residue data submitted do not satisfy registration requirements under 3(c)(5) of FIFRA. Due to experimental and procedural deficiencies in the submitted study, namely ^{14}C contamination of control plants, application rates of ca 1/2x the recommended field application rate and labeling of the cypermethrin molecule in only one position which will not identify residues of probable toxicological concern in rotated crops (as identified for its analogue Permethrin in previous submissions) we conclude that the study does not satisfy environmental fate data requirements for rotational crop studies. We recommend that a ^{14}C laboratory crop rotation study be submitted in which the parent molecule is labeled in either the ^{14}C benzyl or ^{14}C - cyclopropane moieties to determine the <u>total</u> ^{14}C residue uptake by non-target crops from a sandy loam soil treated with the test substance applied at the maximum rate permitted under actual field use conditions. In addition soybeans should be added to the list of nontarget rotated crops to be tested and attempts should be made to identify where feasible the nature of the ^{14}C residues taken up by non-target crops.

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Recommendations

We recommend a conditional registration be given for cypermethrin with the following conditions being imposed.

1. Until a satisfactory rotational crop study is submitted under the current guidelines, a crop rotation restriction is needed on the label, such as, "Do not rotate to other crops".

2. The registrant must submit data on the formation and decline of degradates of cypermethrin under field conditions.

DJS

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Environmental Fate Branch, HED

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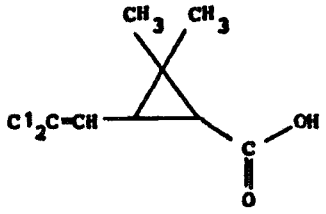
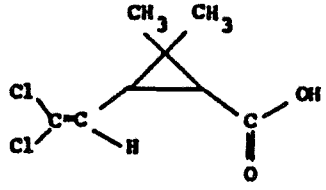
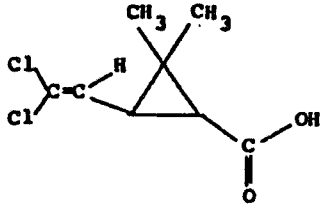
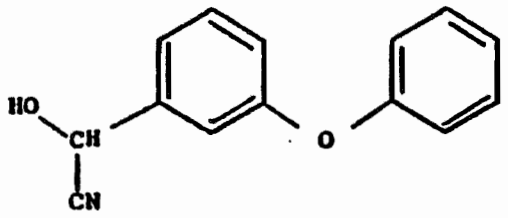
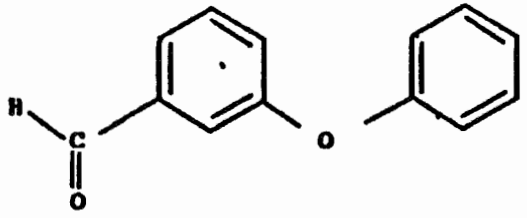
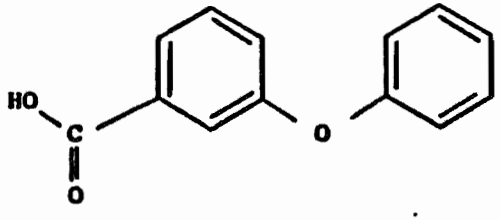
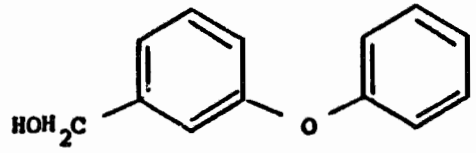
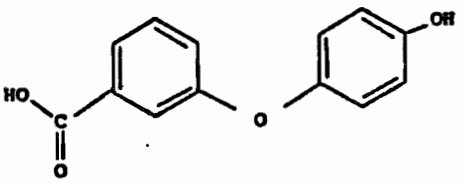
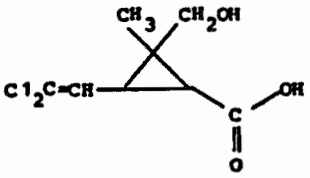
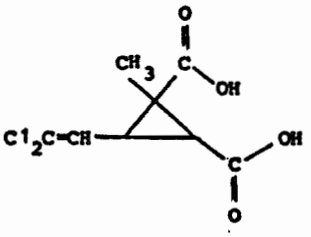
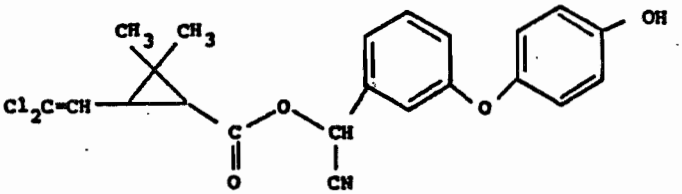
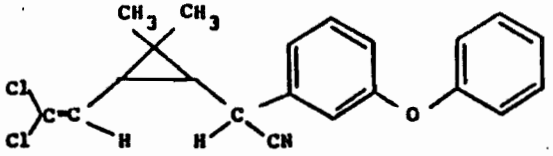
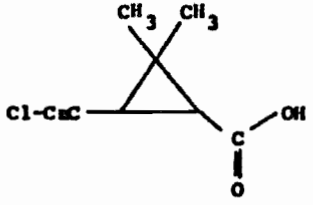
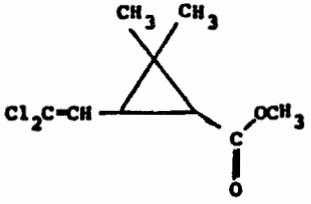
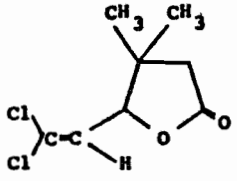
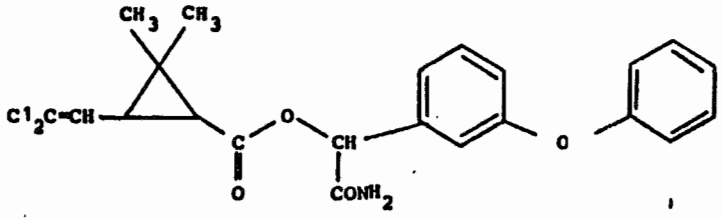
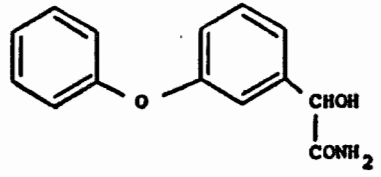
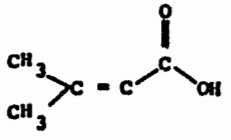
4.91 Summary Of Cypermethrin Degradation Products On Plants, In Animals And In The Environment

Compound No.	Structure and Systematic Chemical Name	Whether Identified And If So Whether Metabolites Are Major Or Minor					
		In Soil	On Soil Surface	In Activated Sludge System	In Water	In/On Plants	In Mammals
I	 (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA) or (1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid	Major	Minor	Major	Major	Major in rotational crops	Major
Ia	 (1RS)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid or (1RS)-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid						
Ib	 (1RS)-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA) or (1RS)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid						

Compound No.	Structure and Systematic Chemical Name	Whether Identified And If So Whether Metabolites Are Major Or Minor					
		In Soil	On Soil Surface	In Activated Sludge System	In Water	In/On Plants	In Mammals
II	 α-cyano-3-phenoxybenzyl alcohol or α-cyano-3-(phenoxyphenyl)methanol	No	No	No	Minor	No	No (would be converted rapidly to IV)
III	 3-phenoxybenzaldehyde	Minor	Minor	Major	Major	No	No (would be converted rapidly to IV)
IV	 3-phenoxybenzoic acid	Major	Major	Major	Major	Minor	Major
V	 3-phenoxybenzyl alcohol	No	Minor	No	Minor	No	Minor from per-

Compound No.	Structure and Systematic Chemical Name	Whether Identified And If So Whether Metabolites Are Major Or Minor					
		In Soil	On Soil Surface	In Activated Sludge System	In Water	In/On Plants	In Mammal
VI	 4'-hydroxy-3-phenoxybenzoic acid or 3-(4-hydroxyphenoxy)benzoic acid	Minor	No	No	No	No	Major
VII	 3-(2,2-dichlorovinyl)-2-hydroxymethyl-1-methylcyclopropane-2-carboxylic acid or 3-(2,2-dichloroethenyl)-1-hydroxymethyl-1-methylcyclopropane-2-carboxylic acid	No	No	No	No	No	Minor
VIII	 3-(2,2-dichlorovinyl)-1-methylcyclopropane-1,2-dicarboxylic acid or 3-(2,2-dichloroethenyl)-1-methylcyclopropane-1,2-dicarboxylic acid	Minor	No	No	No	Major in rotational crops	Minor
IX	 (RS)-α-cyano-4'-hydroxy-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate or (RS)-α-cyano-3-([4'-hydroxyphenoxy]phenyl)methyl (1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	Minor	No	No	No	No	No

Compound No.	Structure and Systematic Chemical Name	Whether Identified And If So Whether Metabolites Are Major Or Minor					
		In Soil	On Soil Surface	In Activated Sludge System	In Water	In/On Plants	In Mammals
X	 3-(2,2-dichlorovinyl)-2,2-dimethyl-α-(3-phenoxyphenyl)cyclopropaneacetonitrile	No	No	No	No	No	No
XI	 3-(2-chloroethynyl)-2,2-dimethylcyclopropanecarboxylic acid	No	No	No	No	No	No
XII	 Methyl-(1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate or Methyl (1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	Not usually, but reported in flooded soil	No	No	No	No	No
XIII	 5-(2,2-dichlorovinyl)dihydro-4,4-dimethyl-2(3H)-furanone or 5-(2,2-dichloroethenyl)-4,4-dimethyloxacyclopentan-2-one	No	No	No	No	No	

Compound No.	Structure and Systematic Chemical Name	Whether Identified And If So Whether Metabolites Are Major Or Minor					
		In Soil	On Soil Surface	In Activated Sludge System	In Water	In/On Plants	In Mammals
XIV	 (RS)-α-amido-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate or (RS)α-amido-3-(phenoxyphenyl)methyl (1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	No	Major	No	No	Minor (but not found in rotational crops	No (would be converted rapidly to I and IV
XV	 3-phenoxymandelamide	No	Minor	No	No	No	No
XVI	 3,3-dimethylacrylic acid	No	No	No	No	No	No

Although several of the compounds listed above are listed as not having been identified, they are included in this table for consistency of numbering between this table and each of the reports in which a standardized numbering system was used.