Date Out EFB: MAY 4 1981

FILE COPY

TO: Product Manager 17 Gee
TS-769

FROM: Dr. Willa Garner
Chief, Review Section No. 1
Environmental fate Branch

Attached please fine the environmental fate review of:

Reg./File No.: 1018-EUP-19

Chemical: Cypermethrin

Type Product: Insecticide

Product Name: Cymbush

Company Name: ICI

Submission purpose: Request for extension of EUP

ZBB Code: Section 5

ACTION CODE: 355

Date in: 1/26/81

EFB # 748

Date Completed: MAY 4 1981

TAIS (level II)	Days
60	12

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1.0 INTRODUCTION

1.1 Purpose

ICI Americas, Inc. is requesting an EUP extension and expansion, allowing the 1981 and 1982 continued testing of cypermethrin (cymbush) for insect control in cotton [File No. 10182-EUP-19, submitted on 12/29/80].

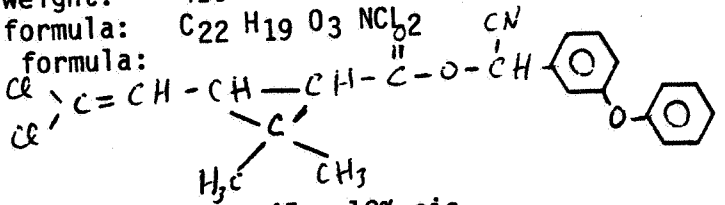
1.2 Background

An EUP No. 10182-EUP-19 was recently issued allowing the 1980 testing of cypermethrin for insect control in cotton. According to our review of 5/8/80, EFB did not concur with issuance of such a permit because of environmental chemistry data gaps. Data needed for issuance of the EUP were outlined in EFB review of 5/8/80 as follows: (1) Hydrolysis, (2) Aerobic soil metabolism, and (3) Rotational crop study.

1.3 Previous Review

10182-EUP-19 5/8/80

1.4 Chemical

Common name:	Cypermethrin
Trade names:	Cymbush pyrethroid Insecticide
Code numbers:	PP 383, NRDC 149, WL43467
Chemical name:	(±)-cyano-(3-phenoxyphenyl) methyl (±) - Cis, trans-3-(2,2-dichloroethenyl)-2,2-dimethylcylopropane carboxylate-22.86% (2 lbs ai/gal).
Type:	Insecticide
Molecular weight:	416
Molecular formula:	$C_{22}H_{19}O_3NCl_2$
Structural formula:	

Isomer ratio: 45 ± 10% cis,
55 ± 10% trans

Physical and Chemical Properties of Technical Grade Material:

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

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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
Famability	not fl.	not fl.	not fl

2.0 PROPOSED PROGRAM

The company is proposing testing cypermethrin for control of the following insects in cotton:

Cotton boll weevil
Cotton bollworm
Tobacco budworm
Pink bollworm
Lygus bugs
Whitefly
Cotton aphid
Cabbage Looper
Thrips
Cotton Leafperforator
Beet armyworm
Flea beetle
Flea hopper

The company is proposing a two year test program to begin 12/8/81 and terminate on 12/8/83. For this the company is requesting 6,000 gallons of cymbush containing 12,000 pounds of the active ingredients, for shipment and use over 6,000 acres of cotton grown in the following states: Alabama, Arkansas, Arizona, California, Georgia, Louisana, Missouri, Mississippi, North Carolina, Oklahoma, South Carolina, Tennessee, and Texas.

The company is proposing foliar multiple application, not to exceed 15 times, at 5-7 days intervals. Proposed dosage is 0.01-0.125 lb ai/A/application to be applied in a minimum of 1.5 gallons of water/A by aerial equipment or 9 gallons of water/A by ground equipment.

Precautionary Statements

(a) Do not exceed 0.125 lb ai/A/ application except for phytotoxicity testing at 0.5 lb ai/A (4x) per application.
(b) The higher rates may be required under conditions of heavy worm infestation or when weevils or late instars of worms are present.
(c) This product is toxic to fish. Do not contaminate water by cleaning of equipment or disposal of waste. Keep out of lakes, streams, ponds, tidal marshes or estuaries.
(d) Do not use or store near heat or open flame.
(e) Do not reuse container. Triple rinse residue from empty container and add rinse to mixture in spray tank. Dispose of container in sanitary land fill in accordance with state and local regulations.

3.0 DISCUSSION OF DATA

Data submitted were filed under EPA No. 10182-EUP-19 accession No. 244018, dated 12/29/80. The following is a list of the studies submitted:

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].

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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]

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.

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

11J Arnold, D. J., Cleverly, 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. TJM1190A [January 1976].

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 14, 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 29, 1980].

3.1 Cypermethrin: Degradation in river water and sediments. Rapley, J. H., Arnold, D. J., Vincent, J. and Moore, D. [ICI Plant Protection Division Report No. RJ0119B, March 1980].

Procedure

The distribution and fate of radiolabelled cypermethrin was studied in aquatic model systems in the United Kingdom. Soil sediments, water samples, and agricultural soils were collected and employed in a laboratory study. Water samples were reconstituted to produce water quality of: PH 7.2-7.6; hardness 40-48 mg/dm^3 as Ca CO_3; and alkalinity 30-35 mg/dm^3 as Ca CO_3.

The physical and chemical characteristics of sediments and water are shown in Table 1.

The sediments were loosely packed into 5 cm x 30 cm glass cylinders to 5 cm depth and the corresponding river water was added to each sediment to a depth of 10 cm. In one set of experiments, the water columns were aerated with CO_2-free air. In another set, a static experiment, the CO_2-free air was passed over the samples of water. All incubation units were kept in the dark at 16°C. Samples were then spiked with either cis, trans-^{14}C-benzyl labelled cypermethrin or cis, tran-^{14}C-cyclopropane labelled cypermethrin at rates equivalent to 0.14 kg/na.

Measurements

Qualitative and/or quantitative analysis were accomplished by the use of:

1. Liquid-Scintillation Counting (LSC): was employed for quantitative measurements of radioativity using a toluene scintillator cocktail solution for organo-soluble samples, or insta-gel for water miscible samples.

2. Thin-Layer Chromatography (TLC): For quantitative analysis using authentic compounds in two solvent systems consisting of: [TDA] Toluene-diethyl ether - acetic acid (75-25-1); and [PAA] petroleum spirit - acetone - acetic acid (70-30-1). Radioactive spots were eluted and combusted for quantative measurements using LSC.

Analyses

[A] River Water: Samples were taken at zerotime and at weeks 2, 5 and 12 hours after pesticide application. Samples were applied directly to TLC and co-chromatography with authentic compounds in solvent systems TDA and PAA mentioned under measurements above.

All river water containing >5% of the applied radioactivity, was extracted with diethyl ether. The ether extracts were combined. The aqueous phase was then adjusted to pH 1.5-2.5 using H Cl and re-extracted with diethyl ether. Radioactivity in the ether and the aqueous phases was quantified by LSC. The ether extracts were concentrated using rotary evaporation under vacuum at a temperature of 30 °C. The concentrated extracts, adjusted to a final volume of 2 ml using diethyl ether, were chromatographed in solvent systems TDA and PAA.

[B] Sediments: At weeks 0 and 2, sediment extracts from aerated treatments containing >5% of the applied radioactivity were concentrated by rotary evaporation. Since this resulted in some losses of radioactivity which could not be recovered, in all other analyses, the extracts were partitioned between distilled water and n-hexane. The hexane phase was combined. The pH of the aqueous phase was adjusted to pH 1-2 using H Cl, then re-extracted with n-hexane followed by diethyl ether. The radioactivity in the organic aqueous phases was quantified by scintillation counting. The organic phases were concentrated by rotary evaporation and chromatographed in solvents TDA and PAA.

TABLE 1. Physical and Chemical Characteristics of Sediments and Waters

CHARACTERISTIC	SAMPLING SITE			
	KENNET	LODDON	WHITE WATER	WARFIELD
Particle size (a) distribution (% of total sediment content)				
Plant debris (large sticks and leaf matter removed prior to use)	0.4	0.0	0.1	37.0
Stones > 5mm	6.0	38.7	31.7	0.0
" 3-5mm	0.8	6.1	0.3	0.0
" 2-3mm	1.4	1.4	6.6	0.0
Soil < 2mm	91.4	53.8	61.3	63.0
Mechanical analysis of soil (b)				
0.2-2.0mm coarse sand	53.6	24.3	78.1	6.6
0.02-0.2mm fine sand	33.7	39.7	14.4	22.1
0,002-0.02mm silt	7.6	15.4	5.0	26.7
< 0.002mm clay	5.1	20.6	2.5	44.6
Soil classification (c)	loamy coarse sand	sandy loam	coarse sand	silty clay loam
Organic matter content (%) (d)	3.0	5.0	1.2	21.6
Water temperature at time of sampling (^{o}C)	17	15	15	20
pH of water (e)	8.2	8.1	8.2	8.1

(a) Particle size distribution: plant debris and stones removed by sieving.

(b) Mechanical analysis of soil: coarse sand fraction is removed by wet sieving; fine sand by sedimentation/washing; silt and clay by sequential sedimentation and analysis of supernatent (using Stokes Law of particle sedimentation).

(c) Soil classification ADAS (based on New Jersey scale)

(d) Organic matter analysis for Kennet, Loddon and White water: using potassium dichromate/concentrated H_2SO_4 to oxidise the organic matter, followed by titration of excess dichromate with ferrous sulphate (Walkley - Black Method).

Organic matter analysis for Warfield: by loss on ignition; soil heated to approximately 550^{o}C in a muffle furnace for > 2 hours.

(e) pH determination by glass electrode.

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[C] Acetone Washings: Acetone washings of incubation units which contained >5% of the applied radioactivity were concentrated by rotary evaporation. The concentrated solutions were chromatographed in solvents TDA and PAA.

The parent pesticide and radioactive degradation products in the surface water, sediment extracts, and acetone washings were quantified by scraping the appropriate areas of silica from TLC plates developed in solvent systems TDA followed by combustion and scintillation counting the evolved $^{14}CO_2$.

Results

Table 2 shows the distribution of ^{14}C-radioactivity in sediment extracts, river water extraction traps, acetone washings, evolved $^{14}CO_2$, and "bound" non-extractable radioactivity in both the aerated and the non-aerated (static) systems.

Total radioactivity recovered were:

0 time	96-105%
2 weeks after pesticide application	89-100%
5 weeks after pesticide application	88-102%
12 weeks after pesticide application	72-92%

It was evident from experimental results that cypermethrin rapidly degraded in both aerated and static incubation units. Up to 50% of the applied radioactivity was evolved in the form of CO_2 after 15 weeks. Also approximately 50% of the compound was degraded in less than 5 days and 90% by 4 weeks.

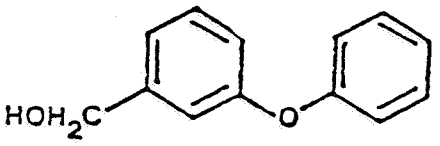
According to ICI Americas, the primary route of degradation was hydrolysis at the ester-link leading to the formation of 3-phenoxybenzyl alcohol (I) and Cis, trans-3-(2,2-dichlorovinyl)-2,2- dimethyl cyclopropane carboxylic acid (II). Amounts of the radioactivity in the river water rapidly decreased in the ^{14}C-benzyl labelled treatments. The major product was 3-phenoxybenoic acid (III) which accounted for up to 12% of the recovered radioactivity. In contrast, after 12 weeks, up to 57% of the total recovered radioactivity remained in the river water of units treated with ^{14}C-cylopropane label. The majority of cyclopropane carboxylic acids.

In the sediments, up to 30% of the total recovered radioactivity was present as 3-phenoxybenzaldehyde (IV) and the cyclopropane carboxylic acids. An unidentified product derived only from the ^{14}C-cyclopropane label also accumulated in the sediment, accounting up to 30% of the recovered radioactivity. Up to 30% of the recovered radioactivity was "bound" in ^{14}C-benzyl treatments after 12 weeks compared with approximately 5% in the ^{14}C-cyclopropane treatments.

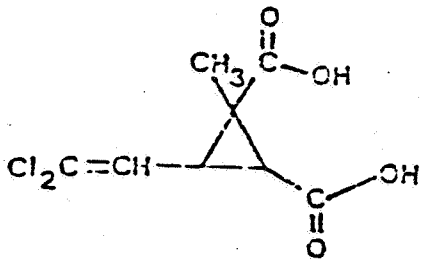
TABLE 2. Distribution of Radioactivity from Incubation of ^{14}C-cypermethrin Aquatic Units

	Distribution of radioactivity as percentage of total ^{14}C-recovered															
	AERATED								STATIC							
	benzyl/A/KEN				cyclo/A/KEN				benzyl/S/KEN				cyclo/S/KEN			
	INCUBATION TIME (WEEKS)															
	0	2	5	12	0	2	5	12	0	2	5	12	0	2	5	12
Sediment extracts (1st + 2nd)	21.4	57.7	49.4	30.4	25.3	57.2	54.1	48.9	20.8	44.1	35.2	28.9	7.8	30.2	35.0	34.6
River Water	74.5	17.2	8.4	1.6	68.4	38.6	39.8	41.8	76.0	24.1	29.6	8.1	86.4	55.5	57.3	56.9
Extraction 'traps'	<0.01	0.4	2.3	1.9	<0.01	0.1	0.1	0.2	<0.01	2.9	<0.01	4.0	<0.01	0.1	0.2	<0.01
Glassware (acetone washings)	3.3	12.2	0.5	0.7	5.8	2.0	2.0	1.5	2.4	11.8	4.0	1.1	5.6	11.8	4.3	3.5
$^{14}CO_2$	<0.01	4.7	18.2	34.6	<0.01	0.4	0.9	2.5	<0.01	8.7	20.6	35.8	<0.01	0.3	0.8	0.9
'Bound' (non-extractable radioactivity	0.8	7.8	21.2	30.8	0.5	1.7	3.1	5.1	0.8	8.4	10.6	22.1	0.2	2.1	2.4	4.1

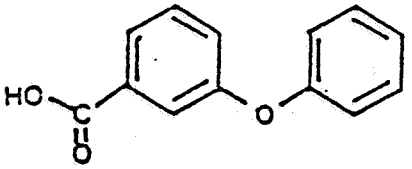
Structural Formulas of Degradation Products



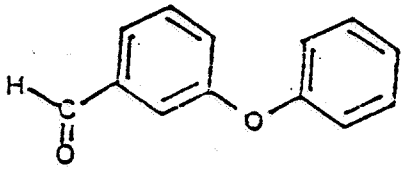
(I) 3-phenoxybenzyl alcohol



(II) 3-(2,2-dichlorovinyl)-1-methylcyclopropane-1,2-dicarboxylic acid



(III) 3-phenoxybenzoic acid



(IV) 3-phenoxybenzaldehyde

3.2 Degradation In River Sediments, River Water And In Flood Soils. Hill, I. R., Harvey, B.R., and Weissler, M.S. 1979.

Procedure

The distribution and fate of radiolabelled cypermethrin was studies in aquatic model systems in the United Kingdom. Natural soil, sediment, and water samples were collected for this laboratory study. Water samples were reconstituted to produce water quality of: pH 7.2-7.6; hardness 40-48 mg/dm^3 as $CaCO_3$, and alkalinity 30-35 mg/dm^3 as $CaCO_3$. The physical and chemical characteristics of sediments, soil and water are shown in Table 3.

The soil and sediments were packed into glass cylinders to a depth of 7 cm. To each sediment, 200cm^3 of the corresponding water was added. The aquatic models used in the study were: aerated water, aerated water and fish (guppies), static, and continuous flow where water was aerated by circulation using a pump. Samples were then spiked with either cis or trans-cyclopropane labelled permethrin at rates equivalent to 0.2 kg/ha. All the treated units were incubated at 15^{o}C in darkness. A stream of CO_2-free air was passed through each unit and the effluent air bubbled through ethanolamine "trapping" solutions to collect volatile degradation products.

Analyses

[A] Analysis of ^{14}C-permethrin applied to surface waters: samples were chromatographed on TL plates using silica gel, and co-chromatography with authentic compounds in a solvent system consisting of n-hexane-ether (10-1).

[B] Measurement of volatile products: samples of ethanolamine were taken at the times of sediment analysis for LSC.

[C] Analysis of surface water: Samples of surface water were taken at 0, 8, 23, and 57 days after exposure. The samples were applied directly to TLC plates using silica gel. Plates were developed in (I) nhexane-diethyl ether, (10:1) or (II), cyclohexane saturated with formic acid-diethyl ether (3:2), or (III), chloroform-ethyl acetatemethanol (6:3:1)). Radioactive spots were eluted for LSC.

[D] Analysis of sediments: The complete sediment was removed and extracted by refluxing in n-hexane-acetone (HA, 6:4) followed by methanol-water (MW, 1:1), each for 18 hours. Radioactivity in the extracts was quantified by LSC and the remaining radioactivity was quantified by combustion of subsamples. The extracts were concentrated by rotary evaporation under vacuum and chromatographed with authentic reference compounds using silice gel and solvent systems H:E, CF:E, and C:EAc:M. The relative amounts of permethrin and degradation products were determined by radiochromatograph scanning.

TABLE 3. Physical and chemical sediment, soil and water characteristics

Characteristic	'Loddon'	'Peartree 7'	'New Mill'	'Warfield'
	Soil code (a)			
	3/17/A	3/27/A	3/20/A	3/23/A
Particle size distribution (%)				
>10.0mm	-	-	26.3	-
5.0 -10.0mm	0.2	-	30.1	-
3.0 - 5.0mm	10.6	-	10.1	1.9
2.0 - 3.0mm	4.8	-	1.6	0.9
0.2 - 2.0mm	46.2	38.5	29.6	18.7
0.02 - 0.2mm	12.2	21.0	1.2	17.4
0.002- 0.02mm	5.7	17.0	0.3	19.2
<0.002mm	20.3	24.2	1.1	43.8
organic matter(%)	4.1	7.0	0.8	7.7
cation exchange capacity	12.5	19.0	8.5	22.5
pH; sediment/soil	7.0	7.0	7.1	6.0
water	7.2	7.3	7.2	6.5

(a) soil codes from Soil Data Book 3 (Mr J Stevens, Jealott's Hill Research Station)

[E] Analysis of fish: On day 23, radioactivity in the fish was quantified by combustion.

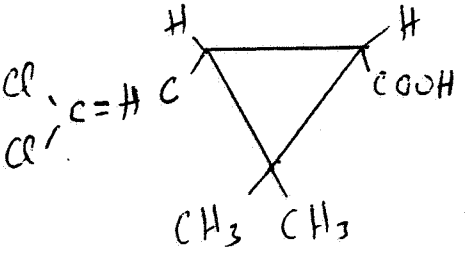
[F] Recovery of radioactivity from apparatus: All parts of the apparatus were cut and soaked in acetone. Radioactivity was determined in the acetone extracts using LSC.

Results

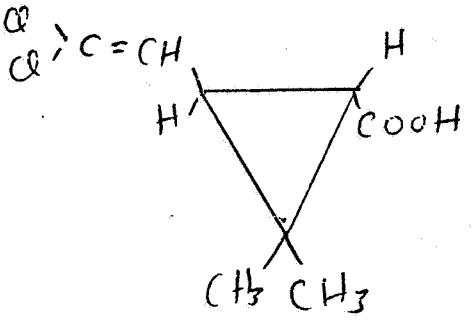
Table 4 shows the distribution of ^{14}C-radioactivity in sediment. It was evident from the data presecuted that the parent pesticide rapidly disappeared from the surface water, both by degradation and association with the sediments. In the majority of the treatments, no permethrin was detected in the water after 8 days incubation.

The major products in water was cis and trans 3 (2,2 dichlorovinyl) 2,2 dimethyl cyclopropane carboxylic acids (I & II). Between 35-82% of the applied radioactivity became associated with the sediments during the course of incubation, about 75% of which was extractable. After 57 days incubation, less than 25% of the extractable radioactivity was present as permethrin, again the major identified degradation products were compounds I & II.

Less than 5% of the radioactivity was evolved as volatile degradation products in the majority of treatments. The presence of fish had no or little effect on the rates of degradation products. Less than 5% of the applied radioactivity was evolved as volatile degradation products except in 2 speciments in which aerated water evolved 12% and 8% during the 57 days incubation. Finally, no major differences were found in the fate of permethrin between any of the sediments treated with the same formulation.



(I) cis



(II) trans

3 (2,2-dichlorovinyl) 2,2-dimethyl cyclopropane carboxylic acid.

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TABLE 4 Radioactivity in sediments

Sediment or soil	Treatment code (see Table 2)	Analysis time (days)	% of applied radioactivity					Efficiency of sediment extraction (^{14}C extracted from sediment as % of total present)[a]
			sediment extraction			Unextracted ('bound')	total in sediment	
			hexane: acetone	methanol: water	total extracted			
'Ladbon'	AM/F_1	0[b]	33.1	1.1	34.2	0.5	34.7	99
		21	39.8	14.6	54.4	8.9	63.3	86
		57	31.2	12.4	43.6	7.9	51.5	85
	AM/F_2	21	56.4	13.0	69.4	13.0	82.4	84
		57	43.6	9.5	53.1	8.9	62.0	86
	AMF/F_1	21	32.0	19.0	51.0	10.5	61.5	76
	AMF/F_2	21	41.8	18.4	60.2	15.1	75.3	80
	AS/F_1	21	39.1	13.7	52.8	12.5	65.3	81
		57	22.7	12.3	35.0	14.2	49.2	71
	AS/F_2	21	44.2	19.5	63.7	11.3	75.0	85
	ST/F_1	21	22.7	13.4	36.1	15.1	51.2	70
		57	19.6	15.5	35.1	11.7	46.8	75
	ST/F_2	21	37.8	25.8	63.6	11.9	75.5	84
	CF/F_1	21	8.9	6.5	15.4	20.4	35.8	43
'Position 7'	AM/F_1	21	38.3	11.4	49.7	13.7	63.4	78
	AM/F_2	21	50.1	11.1	61.2	9.6	70.8	87
	AMF/F_1	21	22.1	11.6	33.9	11.7	45.6	74
	AMF/F_2	21	30.2	16.9	47.1	15.8	62.9	75
'New Mill'	AM/F_1	21	71.7	5.8	77.5	1.3	78.8	98
		57	39.9	2.2	42.1	6.1	48.2	87
'Hatfield'	AM/F_1	21	54.2	15.4	69.6	7.2	76.8	91
		57	33.4	8.9	42.3	22.3	64.6	65

(a) Total radioactivity was calculated by adding the amounts measured in the extracts to that remaining unextracted.

(b) 'Zero' time analysis at 5 hr after pentiolds application.

3.3 Hydrolysis of Cypermethrin. Leahey, J.P., K. Richardson, T.M. Woods and D.W. Bewick, 1980.

The hydrolysis of cypermethrin in sterile distilled water was studied in the dark using ^{14}C-acid and ^{14}C-alcohol- labelled cypermethrin. Hydrolysis were carried out ot three pH's (pH 4,7 and 9) two concentrations (1 and 0.1 ppm) and at two temperatures (25°C and 45°C).

Test results shaved that at pH 4 and 7 cypermethrin was hydrolysed slowly. However, at pH 9 fairly rapid hydrolysis occurred. Cis - and trans-3-(2,2-dichlorovinyl)-2,2- dimethylcyclopropane carboxylic acid [I & II] and 3-phenoxybenzaldehyde (III) were the major product, of hydrolysis. Trace amounts of a-cyano 3-phenoxybenzyl alcohol (IV), and 3-phenoxybenzoic acid (V) were also formed.

In addition, two unidentified compounds were formed, but these were only significant after 29 days incubation at pH 9 (see page 15 for structural formulas).

3.4 Hydrolysis of FMC 33297 Insecticide. All sup, T.L. 1976.

Although this is ancillary study in which one of the pyrethroids insecticide, and not cypermethrin, was employed, it is fully covered in our review.

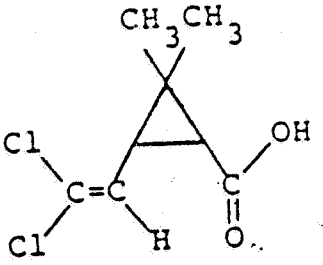
This study was conducted according to EPA guidelines. ^{14}C-alcohol-labelled and 14C-acid labelled FMC 33297 (See structural formula below) were used. TLC and LSC were used for quantitative and qualitative analysis of aparent and hydrolysate products.

Test results showed that at pH 9, FMC 33297 is not subject to hydrolytic degradation under acidic to slightly acidic (pH 3-6) conditions. Under basic conditions (pH 9) degradation was slow at 25°C, but increased rapidly as the temperature was increased. After 42 days, the pH 9 samples maintained at 25°C had degraded only 11%. The pH 9 samples maintained at 35°C had degraded 43% after 42 days. The half-life of the pH 9 samples maintained at 45°C was 3 days. At pH 9, the cis isomer was significantly more stable to hydrolysis than the trans-isomer.

The hydrolytic degradation route of FMC 33297 was: (See Page 16):

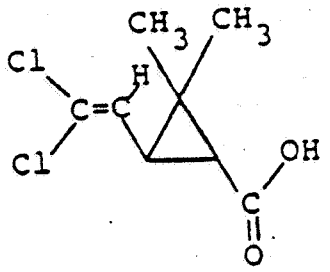
Structural Formulas of Hydrolysis Products

(I)



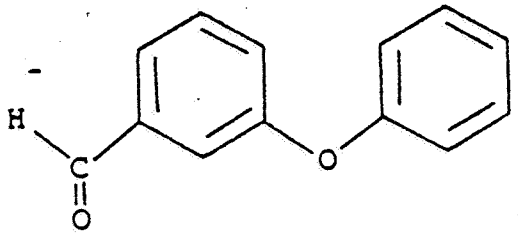
(cis-3-(2,2-dichloro-vinyl)-2,2-dimethyl-cyclopropanecarboxylic acid)

(II)



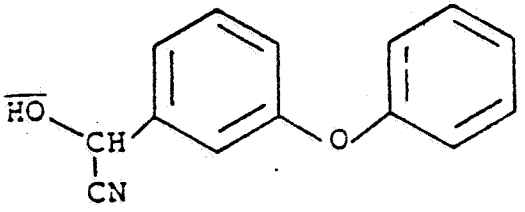
(trans-3-(2,2-dichloro-vinyl)-2,2-dimethyl-cyclopropanecarboxylic acid)

(III)



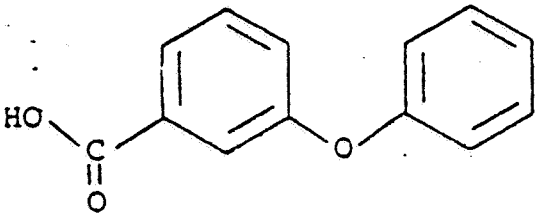
(3-phenoxybenzaldehyde)

(IV)



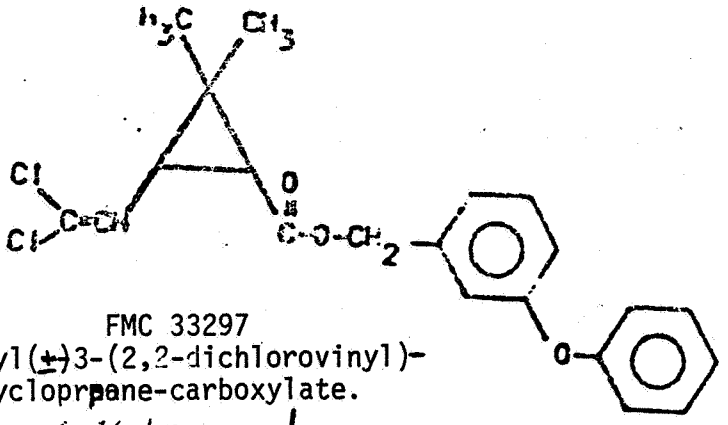
(α-cyano-3-phenoxy-benzyl alcohol)

(V)

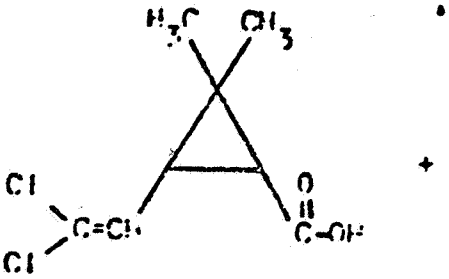


(3-phenoxybenzoic acid)

The hydrolytic degradation route of FMC 33297

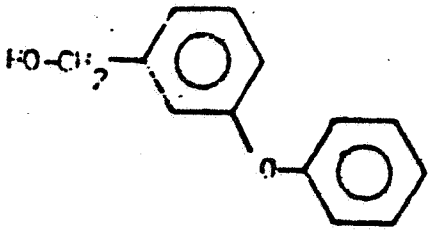


FMC 33297
3-phenoxybenzyl(±)3-(2,2-dichlorovinyl)-
2,2-dimethylcyclopropane-carboxylate.
40% cis - 60% trans.



cis and trans 3-(2,2-dichlorovinyl)-2,2-
dimethylcyclopropanecarboxylic acid.

cis DCVA* and
trans DCVA*



+ an unidentified
polar product

3 -phenoxybenzyl alcohol

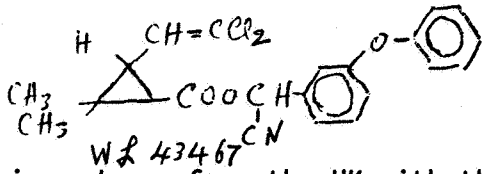
+

an unidentified polar product

17

3.5 The Degradation of the Insecticide WL 43467 Cypermethrin In Soil Under Laboratory Conditions. Standen, M.E. 1976.

The degradation of the insecticide Cypermethrin, referred to as WL 43467 (see structural formula below) and its separate isomers, Cis and trans forms was studied in the laboratory under aerobic and an aerobic conditions in soils.



WL 43467

Two soils from Spain and one from the UK with the following characteristics, were used in the study.

Physical Properties of Soils Used

Soil Texture	pH	Clay	Mineral fraction (% dry weight) Sand	Silt	%OM
Sandy Clay	8.0	33.3	53.5	13.2	1.44
Clay	7.7	65.7	1.9	32.4	1.83
Sandy Laom	6.8	23.5	76.5	6.0	1.37

Treatments were made with compounds labeled in the ^{14}C-benzyl or ^{14}C-Cyclopropyl ring positions. The moisture contents of the soils were readjusted periodically to thier original values. Samples were stored under either aerobic, or anerobic (flooding) conditions.

Sampling for analysis was conducted at 0, 32, 60, 120, and 160 days for the aerobic conditions; and at 32, 60, 120, and 160 days after incubation for the anaerobic conditions. They were extracted with acetonitrile: water (7:3 v/v), followed by filtration and the combined filtrate was radiocounted.

Radioactivity in the extracts and solutions was determined by LSC. The amount of radioactivity remaining in the soil samples after extraction was measured by combustion followed by absorption of $^{14}CO_2$ into basic scintillator solution. HPLC and TLC were employed for quantification and characterization of degradation products.

Tests results are shown in Table 5, and Figures 1. It was obvious from the data submitted that the major degradative route in all soils was hydrolysis at the ester linkage leading to the formation of 3-phenoxybenzoic acid (SD 36750) and 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic accid (WL44776).

Table 5

The analysis of degradation products formed from [^{14}C]-WL 43467 in Leiston sandy loam soil stored under aerobic and anaerobic conditions

[^{14}C-Benzyl]-WL 43467 (cis:trans isomer ratio 3:7) was used and soils were examined after the intervals shown (days).

Component	Aerobic					Anaerobic			
	0	32	60	120	160	32	60	120	160
WL 43467	98.1	25.3	11.1	5.6	5.0	31.7	21.5	11.3	7.5
SD 36750	0.6	0.8	0.5	0.2	0.2	52.1	62.5	67.6	72.5
Unidentified products	1.2	1.9	1.1	1.9	1.5	5.1	2.1	4.2	5.8
Unextracted radioactivity	<0.1	19.5	22.9	22.0	20.8	8.5	12.7	11.0	14.1
Total	99.9	47.5	35.6	29.7	27.5	97.5	98.7	94.1	99.9

NOTE: Soils stored under aerobic conditions were kept at 15.6% moisture (54% field capacity).

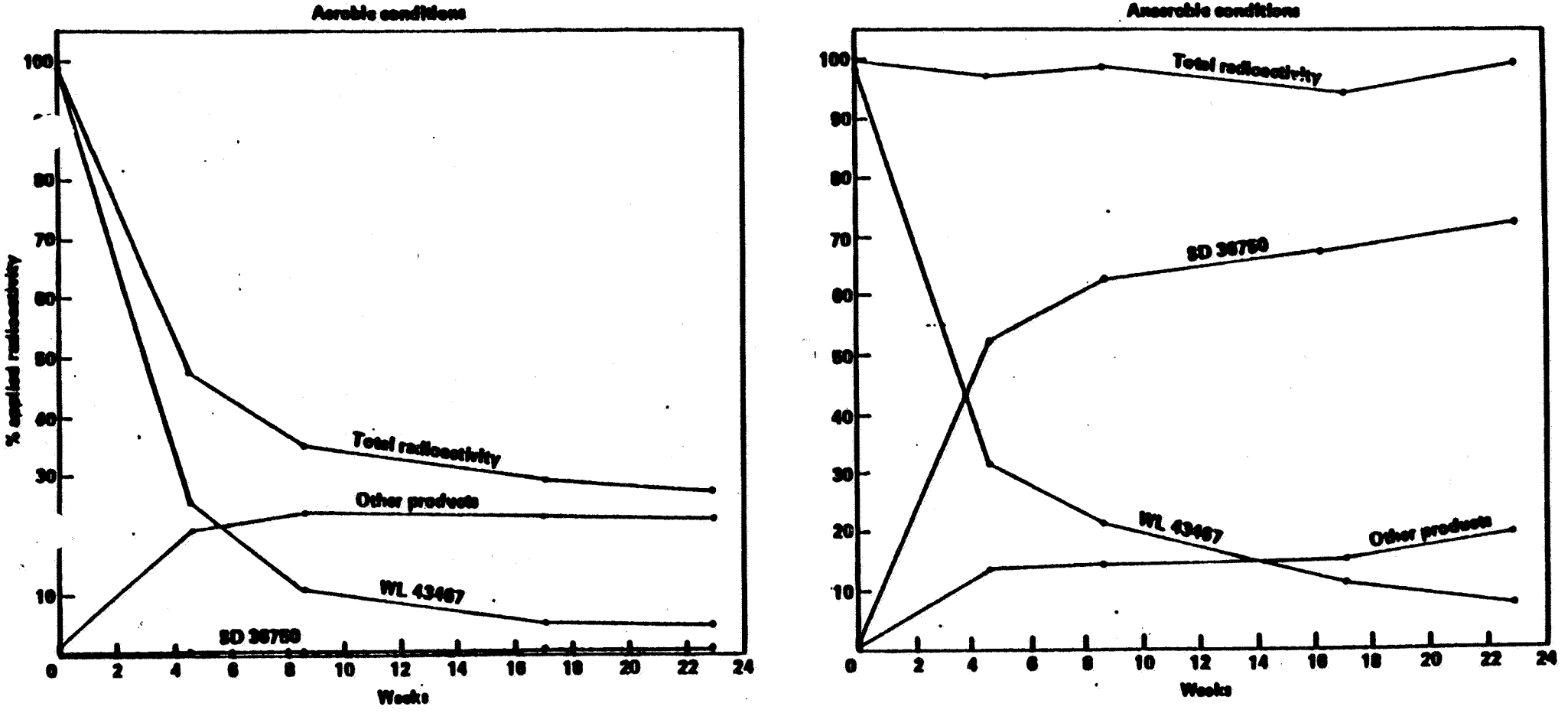


Fig 1 The degradation of [^{14}C–Benzyl] WL 43467 in Leiston sandy loam under aerobic and anaerobic conditions

A minor degradative route was the formuation of a hydroxy derivative of the parent insecticide, followed by hydrolysis at the ester linkage (compound I).*

The rate of degradation was most rapid on sandy clay and sandy loam soils. The initial half lives of WL 43481 and WL 42641 on both soils being 4 weeks and 2 weeks respectively. On clay soil, the degradation rate was much slower and larger amount (up to 60%) of SD 36750 accumulated.

When sandy clay soil was treated with either benzyl-or cylcopropyl-labelled materials, $^{14}CO_2$ was evolved at a steady rate amounting to 42-52% of the applied radioactivity after a 26 week period.

Under aerobic conditions the rate of hydrolysis of [^{14}C-benzyl]-WL43467 was slower than under aerobic conditions and the metabolite SE 36750 accounted for up to 72% of the applied radioactivity after 23 weeks.

Figure 2 shows a proposed degradation pathway for WL 43487 in soil. The followings degradation products appearing in Figure 2:

WL43467: [S,R] x-cyano-3-phenoxybenzyl-(IR, IS, Cis, trans)-2,2-dimethyl-3-(2',2'-dichlorovinyl) cyclopropane carboxylate.

WL43481: [S,R] x-cyano-3-phenoxybenzly-(IR, IS, cis)-2,2-dimethyl-3-(2',2'-dichlorovinyl) cyclopropane carboxylate.

WL42641: [S,R] x-cyano-3-phenoxybenzyl (IR, IS, trans)-2,2-dimethyl-3-(2',2'-dichlorovinyl cyclopropane carboxylate.

SD36750: 3-phenoxylbenzoic acid

*Compound I: x-cyano-3-(4'-hydroxyphenoxybenzyl)-3-(2,'2' dichlorovinyl) cyclopropane carboxylate.

3.6 Further studies of the Degradation of the Insecticide WL43467 (Cypermethrin) In Soil Under Laboratory Conditions. Standen, M.E. 1978.

The degradation of cypermethrin (WL43467) in soil under laboratory conditions has been further examined. Soils, Techniques, and analyses employed in this study are similar to those mentioned under 3.5 above. In this study, however, incubation was for a period of 52 weeks under aerobic conditions in the laboratory.

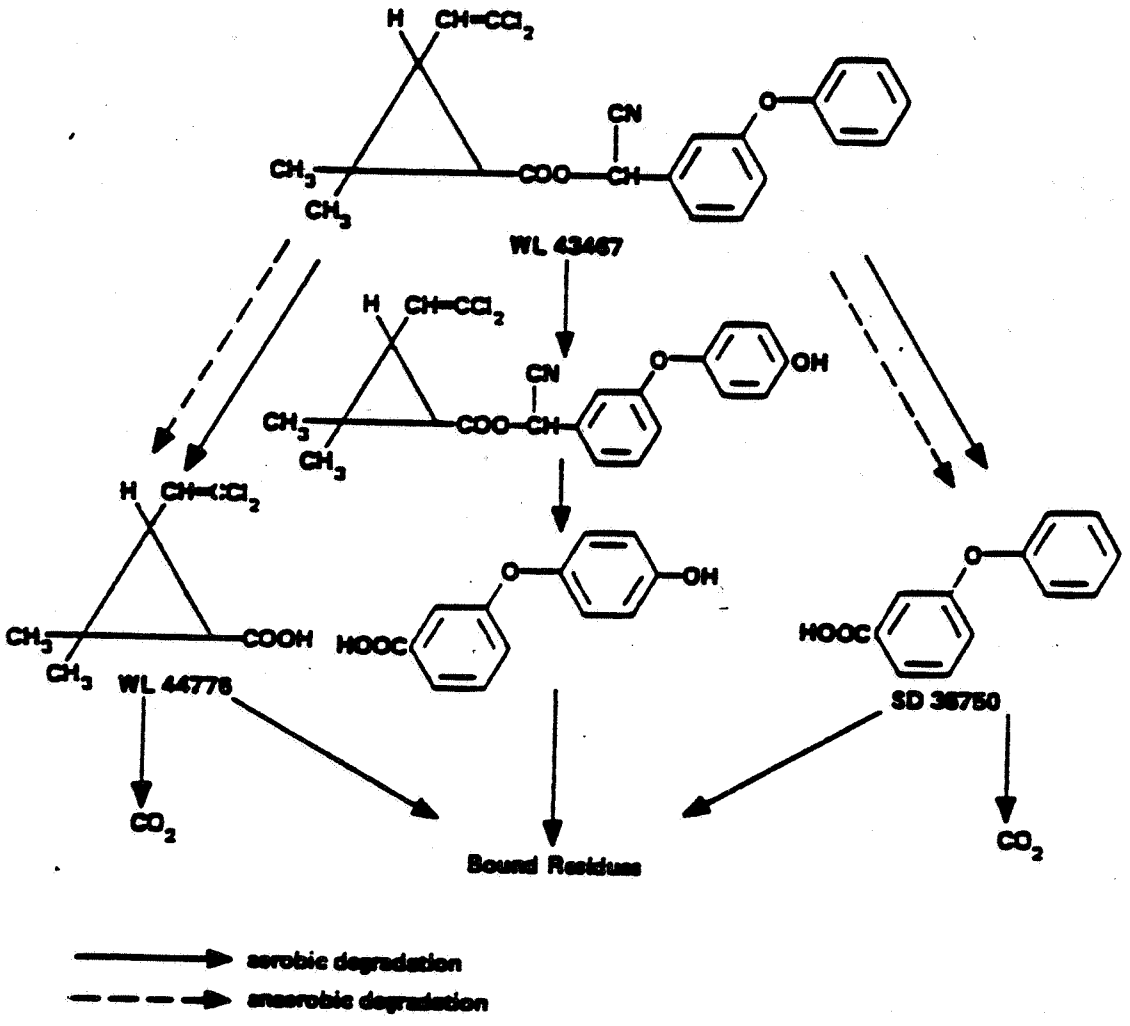


Fig 2 A proposed degradation pathway for WL 43467 in soil

Tests results are shown in Tables 6 and 7. It was evident from data submitted that the major degradative route in all soils was hydrolysis at the ester linkage leading to the formation of 3-phenoxybenzoic acid (WL44607) and 2,2-dimethyl-3-(2', 2'-dichlorovinyl) cylcopropane carboxylic acid (WL 44776). A minor degradative route was the formation of a derivative of the parent insecticide: α-cyano-3-(4'-hydroxyphenoxy-benzyl)-2,2-dimethyl-3-(2',2'- dichlorovinyl) cyclopropane carboxylate [WL 48394 for cis, and WL 48393 for trans]. This was followed by hydrolysis at the ester linkage [See structural formulas in Figure 2].

After 52 weeks, unchanged ^{14}C-benzyl-labeled (cis) amd ^{14}C-cylopropryl-labelled (trans) forms of cypermethrin, accounted for 1.4% and 10.7% of the radioactivity applied to the soils. Trace amounts of the amide: α-amido-3-phenoxybenzyl-2,2-dimethyl-3- (2',2'-dichlorovinyl) cyclopropane carboxylate (WL 47133) were found in one sample, after 52 weeks.

A new degradation product, compound A, which was shown to be a cyclopropane dicarboxylic acid, was found at a concentration 5.8% of the applied radioactivity in sandy clay soil treated with ^{14}C-cyclopropyl (trans form of cypermethrin). It was presumably formed from 2,2-dimethyl-3-(2',2'-dichlorovinyl) cyclopropane carboxylic acid which was present in larger amounts in the soil [WR 44776].

In a separate experiment, it was shown that compond A was formed in concentrations of 3-12.8% of the applied radioactivity in soils treated with either cis or trans isomers of the cyclopropane carboxylic acid (WL 44776), and stored in the laboratory for 8 weeks.

3.7 Degradation of the Pyrethroid Cypermethrin (NRDC 149, (+)-α-cyano-3 phenoxybenzyl (±)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethyl-cyclopropanecarboxlate) and the Respecitive cis-(NRDC 160) and trans-(NRDC 159) Isomers In Soils. Roberts, T.R. and Standen, M.E. Pestic. Sci. 8:305-319. 1977

The degradation of the pyrethroid insecticide, cypermethrin, and the geometric isomers NRDC 160 (cis-) and NRDC 159 (trans-) in three soils was studied under Laboratory conditions.

Samples of the insecticide labeled separately with ^{14}C in the cyclopropyl and benzyl rings were used. The rate of degradation was most rapid on sandy clay and sandy loam soils. About 50% of the NRDC 160 and NRDC 159 applied to both soils being decomposed in 4 weeks and 2 weeks respectively.

Table 6

The analysis of the degradation products formed from [^{14}C]-WL 43480 and [^{14}C]-WL 42640 in Reculver soil 8 weeks after treatment

(Results expressed as a percentage of applied radioactivity)

Component	Compound added and dosage level (mg/kg)			
	WL 42640 (13.5)	WL 42640 (2.0)	WL 42640 (10.0)	WL 43480 (9.6)
WL 48714	3.4	ND	ND	ND
Unidentified material	2.0	5.1	2.4	ND
Compound A*	4.4	12.8	6.9	3.0
WL 42640	62.3	33.9	64.7	1.3
WL 43480	3.7	3.6	5.1	77.3
WL 48234 + WL 48235	0.5	1.0	1.0	2.0
Hydrophilic material	2.2	4.5	3.2	0.7
Unextracted radioactivity (ie. "bound residues")	12.3	39.5	16.4	17.1
Total	90.8	100.4	99.7	101.9

ND not detected

* 2-methyl-2-carboxy-3-(2',2'-dichlorovinyl)cyclopropane carboxylic acid

Table 7

Evolution of $^{14}CO_2$ from Reculver soil treated with [^{14}C]-WL 42640 at a dosage level of 2.7 mg/kg

Weeks	Amount of $^{14}CO_2$ evolved (Expressed as a % of applied radioactivity)
2	1.2
4	1.6
8	2.0

The major degradative route in all soils was hydrolysis of the ester linkage leading to the formation of 3-phenoxybenzoic acid and 3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane-carboxylic acid. Soils treated with the cis-isomer (NRDC 160) was found to contain both cis-and trans-isomer forms of the cyclopropane carboxylic acid. Further degradation of these carboxylic acids was evident sine $^{14}CO_2$ was released from cyclopropyl-and benzyl labeled. cypermethrin in amounts equivalent to 24 and 38% of the applied radioactivity over a 22 week period. A minor degradative route was ring-hydroxylation of the insecticide to give an x-cyano-3-(4-hydroxyphenoxy) benzyl ester followed by hydrolysis of the ester bond.

Under anaerobic conditions, the rate of hydrolysis of cypermethrin on sandy loam soil was slower than under aerobie conditions and 3-phenoxy-benzoic acid accumulated in the anaerobic soil.

3.8 Cypermethrin: Laboratory Degradation on Two Standard Soils. Swane, H. and Hayward, G.J. 1979.

The degradation of cypermethrin was studied under laboratory conditions for a period of 16 weeks under 22 °C. Two soil samples, one, speyer 2/2 with moisture retention capacity of 50%, and the second, speyer 2/3 with moisture retention capacity of 30%; were fortified with cypermethrin at 1ppm.

Test results showed that cypermethrin degraded on both soils used in the study (Fig 3 and 4). The time taken for half 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 12% and 13% of the initial residue remained on the Speyer 2/3 soil after 16 weeks, the corresponding amounts remaining on the Speyer 2/2 soil being 42% to 43%.

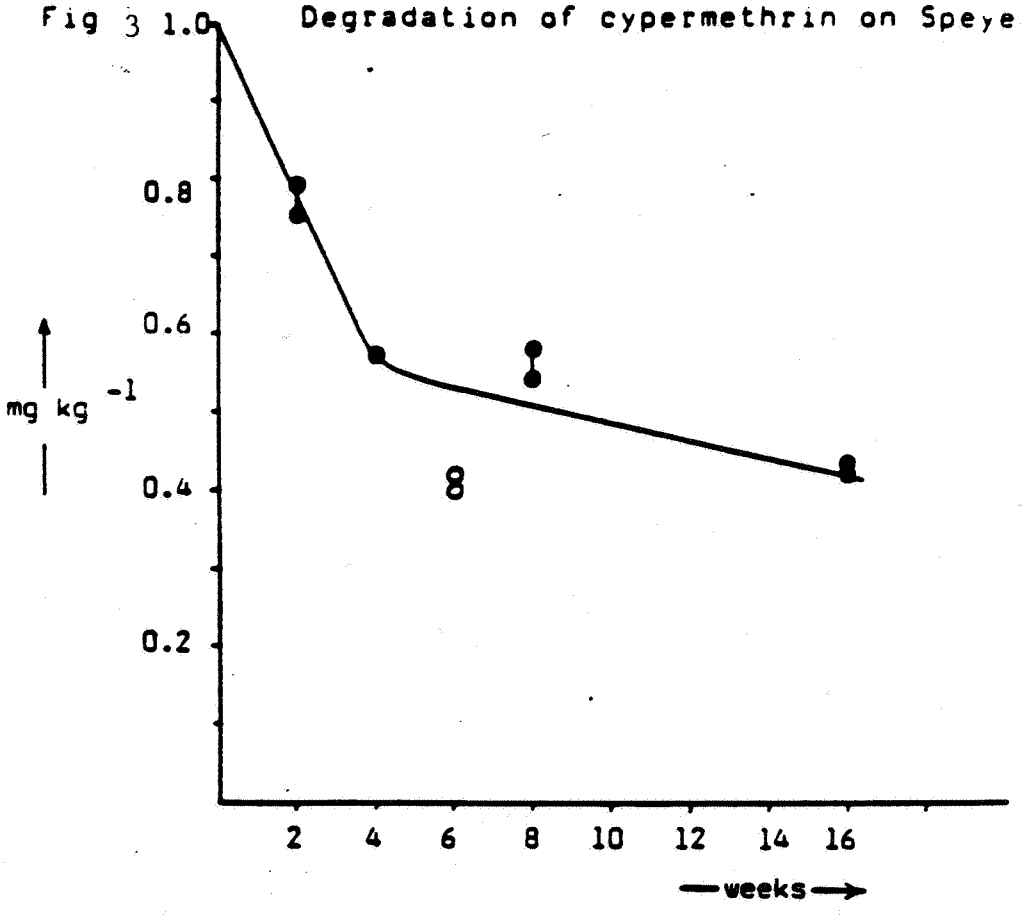
3.9 Permethrin: Laboratory Studies of the Degradation of the Pesticide in Soil. Arnold, D.J., B.A. Cleverley, and I.R. Hill 1976.

In this study, the degradation of permethrin was examined in four soils under laboratory conditions. The physical and chemical characteristics of soils used in the study are shown in Table 8.

Unlabeled and radiolabeled samples of the cis and trans-isomers of permethrin, [in the $^{14}C\text{-}H_2$ and $^{14}C\text{-}cl_2$ positions], were used in this study. The pesticide was applied at rates equivalent to 0.2 Kg/ha. Soils were then incubated aerobically in CO_2-free air, or anaerobically under water logged conditions [in peartree 7 soil].

Soil sample were removed at zero time and after 2 and 14 weeks incubation. Soils were extracted in hexane/acetone (4:1), followed by methanol.

Fig 3 Degradation of cypermethrin on Speyer 2/2 soil



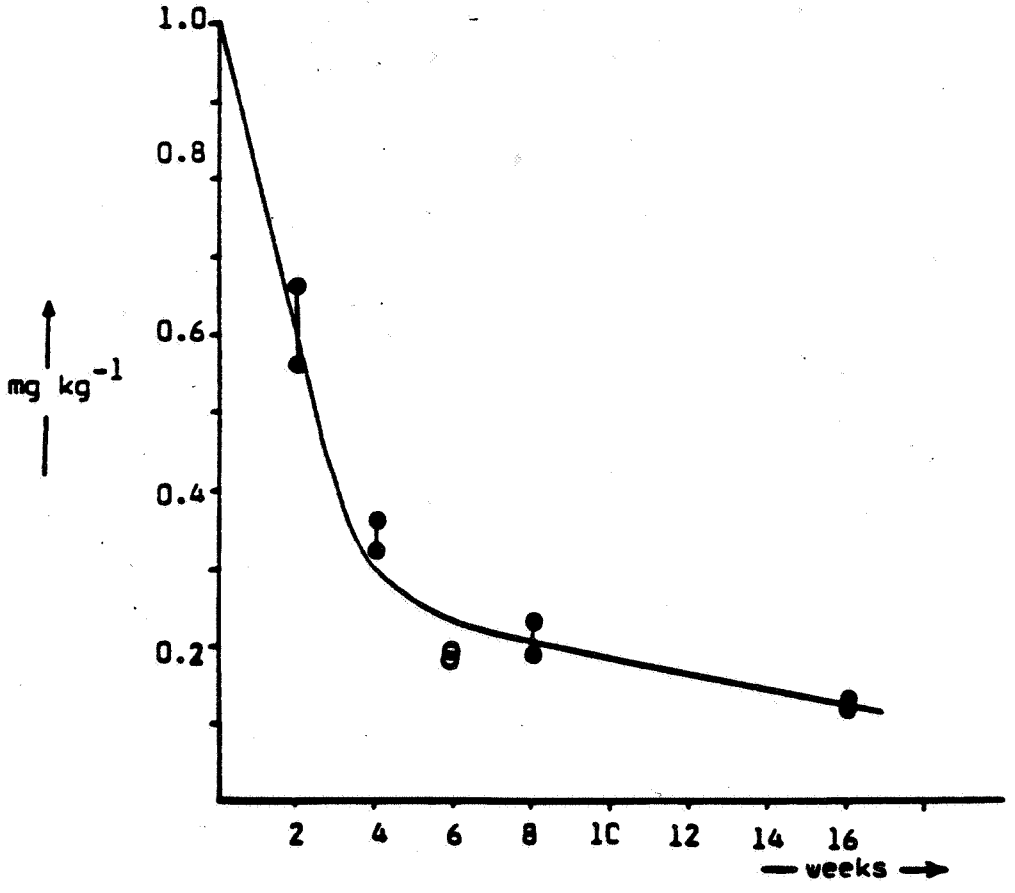


Fig 4 Degradation of cypermethrin on Speyer 2/3 soil.

N.B. The analysis results at 6 weeks are given less weight as the

TABLE 8

PHYSICAL & CHEMICAL SOIL CHARACTERISTICS (a)
USED IN DEGRADATION STUDIES WITH PP557

IL	Mechanical Analysis %			Organic Matter %	CEC (m eqiv/ 100 g)	MHC %	% Moisture content at field capacity at 1/3 bar	pH	Soil Classification
	Sand	Silt	Clay						
artree 6'	67	12	21	4.7	21.0	73	21.7	6.2	Sandy clay loam
artree 7'	66	11	23	6.6	23.0	72	23.1	7.2	Sandy clay loam
artree 8'	62	12	26	5.2	18.0	81	22.5	7.8	Sandy clay loam
nsham'	81	11	8	1.6	7.3	45	20.9	6.5	Loamy sand

sing the USDA system of soil classification.

methods of analysis shown in Hill and Arnold (1976)

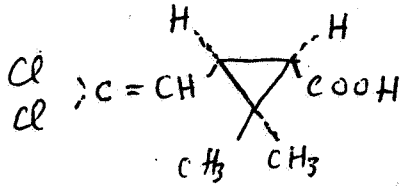
The solvents were concentrated and radioactivity from the the extracts were quantified by LSC, and that remaining in soil after extration, were determined by combustion and scintillation counting. Compound characterization in the extracts were made using TLC on silica gel, and co-chromatography with authentic compounds in cyclohexane saturated with formic acid-Diethyl ether (10:1).

Test results are shown in Tbles 9 and 10. It was evident from the data submitted that both ^{14}C-H and ^{14}C-Cl_2 permethrin were rapidly degraded when incubated aerobically in all the soils. About 40-90% of the applied pesticide was evolved as $^{14}CO_2$ over a 14 week period. The rate of $^{14}CO_2$ evolved from "peartree 7" soil, incubated with ^{14}C-H_2 and ^{14}C-Cl_2 permethrin under anaerobic conditions, was considerably reduced when compared with the corresponding aerobic treatment. However, the rate of $^{14}CO_2$ formation was still increasing at the termination of the experiment.

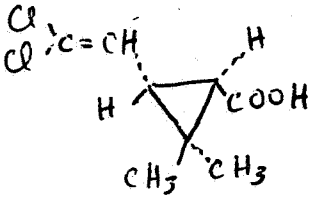
From analysis of selected soils treated with permethrin, less than 5% of the applied radioactivity was extrated as the parent pesticide after 14 weeks incubation.

Products of permethrin degradation identified in soil were cis and trans 3 (2,2-dichlorvinyl)2,2-dimethylcyclopropane carboxylic acid (I & II); 3-phenoxybenzyl alcohol (III); and 3-phenoxybenzoie acid (IV). According to the researchers, all of these were further degraded.

Structural Formulas of Degradation Products



(I) cis-3(2,2-dichlorvinyl)2,2-dimethyl cyclopropane carboxylic acid.



(II) trans-3(2,2-dichlorovinyl)2,2-dimethyl cyclopropane carboxylic acid

9

ABLE 9. Distribution of radioactivity from the aerobic incubation of C^{14}-permethrin in 'Peartree 7' soil

	Permethrin and degradation products (a) (b)	Distribution of radioactivity (as a % of total recovered C^{14} from 'trapping solutions, extraction of a single pot of soil and combustion of extracted soil)											
		C^{14}-H_2						C^{14}-Cl_2					
		cis			trans			cis			trans		
		weeks incubation						weeks incubation					
		0	2	14	0	2	14	0	2	14	0	2	14
n xtracts f oil	I cis-permethrin	90.5	20.4	2.1	3.0	1.3	0.1	95	36.0	4.1	5.2	4.1	0.2
	II trans-permethrin	4.5	1.8	0.2	88.0	4.4	1.5	2.7	0.3	0.5	84.5	24.6	1.2
	'p', 'polar' products	2.1	31.6	8.1	2.8	15.0	4.9	1.1	35.2	13.5	2.4	8.9	3.3
	Remainder of radio-activity in soil extracts	0.8	1.4	0.5	4.8	1.3	0.2	0.5	3.5	1.3	7.1	1.2	0.6
	$C^{14}O_2$	<0.1	20.5	58.3	<0.1	43.9	66.1	<0.1	12.7	57.5	<0.1	38.8	80.6
	'Bound' (non-extract-able) radioactivity	2.0	24.3	30.7	1.5	34.0	27.1	0.5	12.3	23.0	0.7	22.5	14.3

a) Where soils were extracted with both n-hexane/acetone and methanol or methanol/water, the total radioactivity extracted is given.

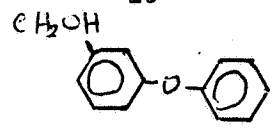
b) 'polar' products ('p') are those on TLC with an Rcp or Rtp of 0.25 and below (where cp = cis permethrin = 1.0 tp = trans permethrin = 1.0)

BLE10. Distribution of radioactivity from the aerobic incubation of C^{14}-permethrin in 'Frensham' soil

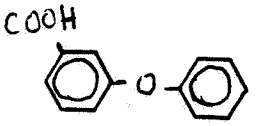
	Permethrin and degradation products (a) (b)	Distribution of radioactivity (as a % of total recovered C^{14} from 'trapping' solutions, extraction of a single pot of soil and combustion of extracted soil)											
		$C^{14}H_2$						$C^{14}Cl_2$					
		cis			trans			cis			trans		
		weeks incubation						weeks			incubation		
		0	2	14	0	2	14	0	2	14	0	2	14
n xtracts f oil	I cis-permethrin	93.6	36.7	2.9	3.0	1.2	0.1	93.1	38.7	4.8	7.6	1.5	0.4
	II trans-permethrin	3.4	2.0	0.4	90.0	6.7	0.8	3.7	1.2	0.4	78.1	9.8	1.0
	'p' .polar products	1.5	25.2	8.8	4.0	11.0	3.9	1.6	23.7	13.1	3.4	43.9	7.6
	Remainder of radio-activity in soil extracts	0.7	1.2	1.2	2.2	1.4	0.4	1.1	2.3	1.4	9.8	2.6	0.8
	$C^{14}O_2$	<0.1	12.0	55.0	<0.1	47.9	73.5	<0.1	11.6	52.2	<0.1	14.9	60.0
	'Bound' (non-extract-able radioactivity)	0.7	22.9	31.7	0.8	31.8	21.3	0.5	22.5	28.1	1.1	27.2	30.1

a) Where soils were extracted with both n-hexane/acetone and methanol or methanol/water, the total radioactivity extracted is given.

b) 'polar' products ('p') are those on TLC with an Rcp or Rtp of 0.25 and below (where cp = cis permethrin = 1.0 tp = trans permethrin = 1.0)



(III) 3-Phenoxybenzyl alcohol



(IV) 3-Phenoxybenzoic acid

3.10 The Degradation of the Pesticide Permethrin in Soil Under Labhoratory Conditions. Arnold, D.J; Cleverly, B.B. and Hill, I.R. 1977.

This study is similar to that reportd under 3.9 above. The same soils, techniques, Laboratory conditions, and analyses. The only exception was the use of different radiolabeled permethrin which was: cis and trans-permethrin, with ^{14}C-labelled in the dichlorovinyl group, the cyclopropane ring, the methylene group and the terminal phenyl ring. Furthermore, incubation was for a period of 20 weeks.

Test results showed that permethrin wa rapidly degraded in all non-sterile soils incubated aerobically and anaerobically (under flooded conditions). More than 50% of the pesticide was degraded in 6 weeks or less. Negligible permethrin degradation occurred under sterile conditions.

Approximately 20%-80% of the applied radioactivity was evolved as $^{14}CO_2$ from all ^{14}C labels of permethrin in non-sterile aerobic soils. Flooded conditions reduced the rate of $^{14}CO_2$ evolution. Incubation temperatures of 35° and 15° initially had little effect on the rate of permethrin degradation compared with that at 25°, but after the first few weeks of incubation the rates of degradation were slightly reduced.

Products of permethrin degradation which were identified were cis and trans 3(2,2-dichlorovinyl)2,2-dimethylcyclopropane carboxylic acids; 3-phenoxybenzyl alcohol; and 3-phenoxybenzoic acid. Other radioactive products were also present in the soils. According to the researchers, all the extractable degradation products were further degraded.

"Bound" radioactivity increased with time during the first weeks of incubation in all soils and accounted for up to 50% of the recovered radioactivity. In some aerobic soils, however, the level of "bound" radioactivity had decreased after 10 weeks incubation.

3.11 Degradation of Permethrin In Soil Under Laboratory Conditions. Arnold, D.J., Cleverly, B.A., and Hill, I.R. 1976.

This study is similar to that reported under 3.9 and 3.10 above. The soils, techniques, Laboratory conditions,and analyses were essentially the same. Radiolabel permethrins used in 3.10 above, were used in this study. Aerobic and anaerobic conditions were maintained for a period of 10 weeks. Test results showed that permethrin was rapidly degraded in all soils under both aerobic and anaerobic (flooded) conditions. More than 50% of the pesticide was degraded in less than 5 1/2 weeks.

About 10-70% of the applied radioactivity was evolved as $^{14}CO_2$ from all treatments in aerobically incubated soils. Flooded conditions drastically reduced the rate of $^{14}CO_2$ evolution.

Products of permethrin degradation which were identified in soils were cis and trans 3(2,2-dichlorovinyl) 2,2-dimethyl cyclopropane carboxylic acids; 3-phenoxy benzyl alcohol and 3-phenoxy benzoic acid. Other unidentified radioactive products were also extracted from the soil. According to the researchers, these products were all further degraded.

3.12 Determination of the Physical and Chemical Properties of Soils. Gowman, M.A., and D. Riley.

This is an ancillary research in which techniques and procedure for determining the physical and chemical properties of soils were outlined. According to the authors, such soil properties are among the most important factors affecting the behavior of pesticides in the environment. Methods discussed included:

1. Particle size distribution.
2. Pipette method.
3. Hydrometer method.
4. Soil water retention properties.
5. Cation exchange capacity.
6. pH
7. Organic matter content.
8. Walkley-black wet oxidation.
9. Loss of ignition.
10. "Available" phosphorous and potassium.
11. Extractable phosphorous.
12. Extractable potassium

3.13 Leaching of Cypermethrin on Thick-Layer Soil Chromatograms. Prashad, and S.E. Newby, 1977.

In this study, four soil samples were employed. The physical and chemical characteristics of these soils are shown in table II.

A 5 cm thick layer of soil was placed on a 5 cm wide, 30 cm long aluminium plate, at one end of which cloth wick was attached. The wick then immersed in 80 ml of a 0.01 M C_a Cl_2 solution, spiked with 40: 60 cis/trans mixture of cyclopropane labeled cypermethrin at rates equivalent to 1.1 Kg/ha. Since the plate had a cross sectional area of 2.5 cm^2, 80 ml Ca Cl_2 solutions equilavent to 32 cm "rain." These quantities were taken up by lily field soil in about 4 days and by other soils in 2 days. The amount of leachate collected were:

Pear tree soil	17 ml
Lily field	32 ml
Gore Hill	7 ml
Black borough	30 ml

After being leached, the plates were sectioned, ground, and combusted. The $^{14}CO_2$ evolved was trapped in 2-methoxyethylamine for scintillation counting. Detailed results for the leaching of cypermethrin on soil chromatograms are shown in table 12.

Table 12. Mean leaching of ^{14}C-labeled cypermethrin in dpm, recovered per segment in each of four soil types.

Distance from top of Chromatogram (cm)	Pear Tree	Lily Field	Gore Hill	Blackborough
0-2	58,558	15,882	229,389	351,814
2-4	6,713,720	6,805,420	6,408,622	6,253,925
4-6	54,820	87,894	241,182	18,410
6-8	6,804	12,466	7,816	5,848
8-10	4,743	6,534	4,266	35,175
10-15	6,561	12,736	7,231	2,535
15-20	4,990	8,052	4,323	2,319
20-25	3,943	5,723	4,409	1,141
25-30	2,416	6,847	3,180	1,444
Leachate	1,745	1,395	1,016	17
Total dpm	6,858,300	6,962,949	6,911,434	6,672,628
% of applied	97	99	98	95

TABLE 11. PROPERTIES OF SOILS.

NAME	✳	Pear Tree	Lily Field	Gore Hill	Blackborough
TYPE		Coarse sandy loam	Coarse sand	Calcareous clay loam	Peat
Sample reference number		2/104/A	2/63/A	2/108/A	1/42/A
Coarse sand (200-2000μ)%	1	40.4	82.9	7.4	-
Fine sand (20-200μ) %	1	20.5	11.3	35.9	-
Silt (2-20μ) %	1	22.4	2.7	28.7	-
Clay (2μ) %	1	16.7	3.0	28.0	-
Organic matter %	2	6.9	1.1	12.1	71.2
pH	3	7.1	5.0	7.5	4.3
Moisture holding capacity at zero suction %	4	71.0	25.1	115.9	257.0
at 50 cm suction %	4	47.0	11.9	75.5	151.0
at 100 cm suction %	4	39.3	8.1	67.1	135.3
at 1/3 bar suction %	5	18.0	7.2	35.5	116.9
at 1 bar suction %	5	14.7	3.6	30.0	111.1
at 15 bars suction %	5	11.7	1.7	23.9	71.8
Cation Exchange capacity (meq/100g)	6	19.5	2.7	31.0	112.1
Available phosphorous (μg/g)	7	98.0	16.0	20.0	35.0
Available potassium (μg/g)	8	410.0	< 37.0	77.0	130.0
Available magnesium (μg/g)	8	137.0	< 16.0	< 16.0	37.0

✳ Methods used (Ref 3)

1. Determined by pipette method after treatment with hydrogen peroxide and dispersion with sodium metaphosphate (calgo
2. Determined by Walkley-Black dichromate oxidation method.
3. In distilled water with soil:water ratio of 1:2.5.
4. Determined on sand tank.
5. Determined on ceramic pressure plate.
6. Determined at pH 7 using sodium acetate as saturating and ammonium acetate as displacing solution.
7. Extracted with 0.5 M sodium bicarbonate adjusted to pH 8.5 with sodium hydroxide.
8. Extracted with 1M ammonium nitrate.

3.14 Pesticide Mobility In Soil: Determination by Soil thick-layer chromatography. Stevens, J.E., and D. Riley, 1977.

Studied Leaching of some pesticides other than cypermethrin; e.g. diuron and atrazine.

3.15 Cypermethrin Dissipation in Soils. J.P. Ussary, 1980.

This study was conducted at Goldsboro, N. C.; Champaign, Ill; Visalia, CA; and Vicksburg, MS.: according to a protocol submitted by ICI (See attached one page protocol). Single applications of 2 lbs ai/A. Soil samples were then collected at depth of 0 to 3 inches 3-6 inches, and 6-12 inches before the application, immediately after the application, one week, two weeks, one month, three months, six months and nine months after the application.

Soil properties used in the study were as follow:

Location	Goldsboro, NC	Champaign, ILL	Visalia, CA	Vicksburg, MS
Soil type	Loamy fine	Silty clay loam	fine sandy loam	Silty loam
% OM	0.8	5.2	0.8	1.9
pH	5.6	6.0	8.4	5.7
Sand	90.2	38.1	74.8	38.0
Silt	9.4	35.7	17.4	51.2
Clay	0.4	26.3	7.8	10.8

Soil samples were analyzed with a modification of the ICI plant protection Division method PPRAM-45, the determination of residues of cypermethrin in soils. Test resuts are shown in Table 13. It could be seen from the table that cypermethrin degraded rapidly in soil and there was little or no downward movement of the residue. The half-life of the initial concentration of cypermethrin in the soil was 4 to 12 days.

The cypermethrin concentration in the top 3 inches of the Goldsboro soil was 2.79 ppm immediately after the application. After one week the concentration had decreased to 1.95 ppm. The residue continued to degrade until after nine months only 0.04 ppm cypermethrin remained.

In the Champaign, Illinois trial there was 1.14 ppm cypermethrin in the 0 to 3 inch layer on the day of the application. After one week 0.72 ppm remained and after three months the residue was 0.33 ppm. After nine months 0.23 ppm cypermethrin remained which indicated that the residue degradation was slow through the cold winter months.

The residues in the alkaline Visalia soil degraded very rapidly. There was 1.23 ppm measurable residue on the day of the treatment in the top 3 inches of soil and after one month, only 0.02 ppm remained.

At Vicksburg, Mississippi a residue of 2.71 ppm on the day of the treatment decreased to 0.18 ppm after one month. No measurable residue was found in the three month sample and only 0.03 ppm was found in the six month sample.

Soil Dissipation Trial Procedure for PP383, PP021, PP009 and PP333

Scope

This procedure is designed to determine the rates of dissipation of chemical residues in soil under natural field conditions and to assess the tendency of these chemicals to leach.

Location

There will be one trial each at Goldsboro, N. C., Champaign, Illinois, Visalia, California and a site to be selected in Mississippi Delta.

Soil Types

Goldsboro, North Carolina-Norfolk sandy loam, Champaign, Illinois-Drummer silty clay loam, Visalia, California-Foster fine sandy loam, Mississippi Delta-typical cotton soil.

Trial Design

Single plots that are approximately 20' by 40' will be used. The plots must be located so they will not be disturbed by other work in the area. (The trials will require as long as 18 months to complete.) The plots should be tilled and free of vegetation. They are to be kept free of vegetation throughout the trial by applying paraquat, glyphosate or by hand weeding. (If other herbicides are necessary, please consult the Manager of Residue Chemistry before making the application.)

Controls

Control plots are not required. Pre application soil samples will be taken and used as control samples.

Application Rates

Spray the plots evenly with the chemical at the rate of 2 lb of active ingredient per acre. Do not incorporate.

Sample Collection

Collect at least 3 pounds of soil from each plot 0 to 3 inches, 3 to 6 inches and 6 to 12 inches before the application, immediately after the application and 1 week, 2 weeks, 1 month, 3 months, 6 months, 9 months, 12 months and 18 months after the application. Take care not to cross-contaminate the samples from different depths.

The samples must be frozen soon after collection and stored at -10°F until they are to be analyzed.

JPU/bc/5-9

Table 13. Dissipation of Cypermethrin in Soil

Trial Number and Location	Soil Type	Sampling Depth (in.)	Cypermethrin, ppm /a,b						
			Control	0 days	1 wk	2 wk	1 mo	3 mo	6 mo	9 mo
RU_1-79-03 Goldsboro, NC	loamy fine soil	0 to 3	ND	2.79	1.95	0.62	0.73	0.08	-	0.04
		3 to 6	ND	0.18	0.05	0.02	0.01	ND	-	TR
		6 to 12	ND	0.23	0.07	TR	TR	TR	-	TR
RU_4-79-001 Champaign, IL	silty clay loam	0 to 3	ND	1.14	0.72	-	0.33	0.33	-	0.23
		3 to 6	ND	0.72	0.47	-	0.17	0.19	-	0.08
		6 to 12	ND	0.06	0.19	-	TR	TR	-	TR
RU_2-79-01 Visalia, CA	fine sandy loam	0 to 3	TR	1.23	0.29	0.22	0.02	TR	TR	
		3 to 6	TR	0.01	TR	TR	TR	TR	TR	
		6 to 12	TR	0.02	TR	TR	TR	TR	TR	
DU_5-79-01 Vicksburg, MS	silty loam	0 to 3	ND	2.71	0.35	0.12	0.18	TR	0.03	
		3 to 6	ND	0.15	0.05	0.01	0.02	TR	TR	
		6 to 12	ND	0.09	0.01	TR	0.03	TR	ND	

a/ All values corrected for recovery
b/ ND = none detected, TR = trace (limit of determination = 0.01 ppm)

Residues were found in the 3 to 6 inch and 6 to 12 inch sampling layers even on the days of the treatments. It was assumed that these residues were a result of cross-contamination during the sampling process.

3.16 A Gas-Liquid Chromatographic Method for the Determination of Cypermethrin (PP 383) in Soil. R.D. Fitzpatrick, 1980.

The author presented a method suitable for the quantitative determination of cypermethrin as total isomer content in soils. The limit of detection was set at 0.01 ug/ml, (ancillary study).

4.0 SUMMARY

4.1 Degradation in river water and sediments

Cypermethrin was rapidly degraded under both aerated and static conditions. 50% of the compound was degraded in less than 5 days and 90% in 3-4 weeks.

Cypermethrin was initially degraded by hydrolysis at the ester link. This resulted in the formation of cis, trans cyclopropane carboxylic acid, and 3-phenoxybenzyl alcohol, and led to the formation of 3-phenoxybenzaldehyde and 3-phenoxybenzoic acid.

The major products in the river water were the cis and trans cyclopropane acids and 3-phenoxybenzoic acid (up to 52% and 12% of the total recovered radioactivity respectively).

The major ^{14}C-benzyl labeled product formed in the sediment was 3-phenoxybenzaldehyde (up to 29% of the total recovered radioactivity after 2 weeks incubation).

Radioactivity as $^{14}CO_2$ was evolved rapidly from the ^{14}C-benzyl label (30-50% of the applied in 15 weks); 3% or less was evolved from the ^{14}C-cyclopropane label in the same time period. Up to 30% of the total recovered radioactivity was "bound" after 12 weeks incubation of the ^{14}C-benzyl label compared with 5% from the ^{14}C-cyclopropane label.

4.2 Degradation in river sediments, river water and in flood soils

Permethrin was rapidly lost from all surface waters by degradation and absorption to sediments. In the majority of the treatments, no parent pesticide was detectable after 8 days of incubation.

The major radioactive product in the water was trans-3(2,2-dichlorovinyl)2,2-dimethyl cyclopropane carboxylic acid; but small amounts of the cis-formulation were also formed. Between 36 and 82% of the applied radioactivity became associated with the sediment, after 23 days incubation.

Permethrin was degraded in sediment and soil. In the majority of treatment, more than 75% of radioactivity in the sediment was removed by extraction; of this amount less than 25% was present as permethrin after 57 days incubation. The major radioactive degradation products in the extracts were cis and trans-3(2,2-dichlorovinyl)2,2-dimethyl cyclopropane carboxylic acid. Less than 5% of the applied radioactivity was evolved as volatile degradation products. There were no differences in the fate of permethrin between any of the sediments treated with the same fromulation. Finally, the presence of fish had no or little effect on the degradation or the distribution of permethrin and its degradation products.

4.3 Hydrolysis of Cypermethrin

The ^{14}C-acid labelled cypermethrin was fairly rapidly hydrolysed in sterile distilled water at pH 9 and 45 °C. Cis-and trans-3-(2-2-dichlorovinyl) -2,2-dimethylcyclopropanecarboxylic acid were formed from this hydrolysis, and no significant additional reactions occured during 21 days of incubation.

The ^{14}C-alcohol labelled cypermethrin was hydrolysed very slowly under acid conditions, slightly less slowly under neutral conditions and fairly rapidly under alkaline conditions. The rate of hydrolysis was increased with increased temperature. The major hydrolysis product derived from the alcohol part of the molecule was 3-phenoxybenzaldehyde, with only race amounts of trans-3-(2,2-dichlorovinyl)-2,2-dimethy-cyclopropanecarboxylic acid (<1.1%) and 3-phenoxybenzoic acid (<2%). In addition, two unknown compounds were formed, especially at pH 9.

4.4 Hydrolysis of FMC 33297

FMC 33297, was not subject to hydrolytic degradation under acidic to slightly acidic conditions (pH 3-6) over a temperature range of 25-45 °C. Under basic conditions, (pH 9), FMC 3397, hydrlyzed slowly at 25 °C but increased rapidly as the temperature was increased. After 42 days, the pH samples maintained at 25 °C degraded only 11%. The pH 9 samples maintained at 35 °C degraded 43% after 42 days. The half-life of the pH 9 samples maintained at 45 °C was 3 days.

At pH 9, the cis-isomer was significantly more stable to hydrolysis than the trans-isomer. The major products of hydrolysis were identified as the cis and trans, 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acids and m-phenoxybenzyl alcohol.

4.5 The Degradation of the Insecticide WL43467 (Cypermethrin) In Soil Under Laboratory Conditions

The degradation of the insecticide WL43467 (cypermethrin) and its separate isomers cis and trans in soils has been studied under aerobic and anaerobic conditions. Treatments were made with compounds labeled with ^{14}C either in the benzyl or cyclopropyl ring positions.

The major degradative route in all soils was hydrolysis at the ester linkage leading to the formation of 3-phenoxybenzoic acid and 2,2-dimethyl-3-(2', 2'-dichlorovinyl) cyclopropane carboxylic acid.

The rate of degradation was most rapid on sandy clay and sandy loam soils. The initial half lives of x-cyano-3-phenoxybenzyl-(1R,1S, cis)-2,2-dimethyl-3-(2',2',-dichloroviny) cyclopropane carboxylate was 4 weeks; and that for (α-cyano-3-phenoxybenxyl-(1R,1S, trans)-2,2-dimethyl-3-(2',2',-dichlorovinyl) cyclopropane carboxylate was 2 weeks. On clay soil, the degradation rate was much slower and larger amounts (up to 60%) of 3-phenoxybenzoic acid was accumulated.

When sandy clay soil was treated with either benzyl-or cyclopropyl-labelled materials, $^{14}CO_2$ was evolved at a steady rate amounting to 42-52% of the applied radioactivity after a 26 week period.

Under anaerobic conditions, the rate of hydrolysis of [^{14}C-benzyl]-labelled cypermethrin, was slower than under aerobic conditions and the metabolite 3-phenoxybenzoie acid accounted for up to 72% of the applied radioactivity after 23 weeks.

4.6 Further Degradation of the Insecticide Cypermethrin

Results are similar to those under 3.5. See Text for more detailed information.

4.7 Degradation of Cypermethrin Under Laboratory Conditions

Results are similar to those under 3.5. See Text for more detailed information.

4.8 Cypermethrin: Laboratory Degradation on Two Standard soils

The degradation of cypermethrin on two standard soils, maintained in the Laboratory at 22 °C, was studied over a 16 week period.

The time taken for half of the initial residue to degrade was estimated to be approximately 8 weeks on a speyer 2/2 soil and between 2 to 3 weeks on a speyer 2/3 soil.

4.9 Permethrin: Laboratory Studies of the Degradation of the Pesticide in Soil

Degradation of permethrin proceeded rapidly in all aerobically incubated soils. More than 50% of the parent pesticide was degraded after 10 days and more than 90% after 56 days. $^{14}CO_2$ was evolved from ^{14}C-H_2 and ^{14}C-Cl_2-permethrin-treated soil, showing that both the dichlorovinyl cyclopropane carboxyl and phenoxybenzoate moieties of permethrin were degraded in soils.

Under anaerobic conditions, evolution of $^{14}CO_2$ from both the ^{14}C-H_2 and ^{14}C-Cl_2 cis-permethrin was very slow. Where a radiolabeled isomer was incubated with an unlabled isomer, the rate of $^{14}CO_2$ evolution was very similar to that observed from incubation of the single isomers. Within the first two weeks of incubation of the pesticide in soil, a considerable proposition of both cis and trans permethrin had been degraded to "polar" products which were then further degraded with the formation of $^{14}CO_2$.

Degradation products are shown in the Text.

4.10 The degradation of the Pesticide Permethrin in Soil Under Laboratory Conditions

Results are similar to those under 4.9

4.11 Degradation of Permethrin In Soil Under Laboratory Conditions

Results are similar to those under 4.9

4.12 Determination of Physical and Chemical Properties of Soils

This is an ancillary research in which methods of determining the physical and chemical properties of soils were discussed.

4.13 Leaching of Cypermethrin on Thick-layers Soil Chromatograms

The mobility of a 40:60 cis/trans mixture of ^{14}C cyclopropane labelled cypermethrin, was determined by soil thick layer chromatography, using four soils-a coarse sandy loam (pear tree), a coarse sand (Lily Field), a calcareous clay loam (Gore Hill) and a peat (Blackborough). Atrazine, a moderately mobile herbicide, was leached under the same conditions as a standard. Less than 3.6% of the ^{14}C labelled cyperethrin was leached more than 2 cm by 32 cm "rain", in four soils, whereas, the peak concentration of leached atrazine was at 5cm, 7cm, 20cm, and 3cm in pear tree Gore Hill, Lily Field, and Blacksborough soils respectively. From an application rate of 1.1 Kg/ha, the highest concentration of cypermethrin equivalent in the leachate was 0.006 ug/ml.

4.14 Pesticide Mobility In Soil

Leaching of some pesticides other than cypermethrin was studied; e.g., diuron and atrazine.

4.15 Cypermethrin Dissipation in Soils

Field trials were conducted at four locations in the United States to determine the rate of dissipation of cypermethrin in various soil types. The trials were located at Goldsboro, North Carolina (loamy fine sand), Champaign, Illinois (silty clay loam), Vicksburg, Mississippi (silty loam) and Visalia, California (fine sandy loam). Fallow plots were treated with cypermethrin at a rate of 2 lbs ai/A.

Samples were collected before the treatment, immediately after the treatment and at intervals up to nine months after the treatment at depths of 0 to 3 inches, 3 to 6 inches and 6 to 12 inches. These samples were analyzed for residues of cypermethrin.

Test results showed that residues decreased to less than 10% of the original residue two weeks to three months after the applications at Goldsboro, Visalia and Vicksburg. After nine months 15% of the applied residue remained in the Champaign soil. The residues were mainly in the 0 to 3 inch layer indicating little or no leaching. The initial residue in the 0 to 3 inch layers ranged from 1.14 ppm to 2.79 ppm.

4.16 A Gas-Liquid Chromatographic Method for the Determination of Cypermethrin in Soils.

An ancillary study describing a method suitable for the quantitative determination of cypermethrin as total isomer content in soils. The limit of detection was set at 0.01 ug/ml.

5.0 RECOMMENDATIONS

5.1 The following environmental chemistry data requirements were satisfied in this submission:

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

5.2 We do not recommend issuance of this EUP until "Rotational Crop Studies" are met. Alternatively, ~~an 18 month crop rotation restriction must be imposed.~~ A Statement must be added to the label which denies the rotation of crops.

5.3 At the time of registration, the following studies for a Field-vegetable crop will need be submitted:

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

Sami Malak

Sami Malak, Ph.D.
Review Section #1
Environmental Fate Branch
Hazard Evaluation Division

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