5-11-78

EEB BRANCH REVIEW

DATE: IN _____ OUT _____ IN 11/2/77 3/24/78 OUT 5/11/78 IN _____ OUT _____

FISH & WILDLIFE (ENVIRONMENTAL CHEMISTRY) EFFICACY

FILE OR REG. NO. 201-UNE + 201-UNR

PETITION OR EXP. PERMIT NO. 7F2013

DATE DIV. RECEIVED 10/5/77

DATE OF SUBMISSION

DATE SUBMISSION ACCEPTED 10/18/77 3CID-2B-yes

TYPE PRODUCT(S): (I) D, H, F, N, R, S

PRODUCT MGR. NO. 17 Mitchell

PRODUCT NAME(S) Technical PYDRIN INSECTICIDE and PYDRIN insecticide 2.4 emulsifiable concentrate

COMPANY NAME Shell Chemical Company

SUBMISSION PURPOSE Registration for formulating use and use on cotton

CHEMICAL & FORMULATION Cyano (3-phenoxyphenyl)methyl-4-chloro-alpha-(1-methylethyl) benzeneacetate

PYDRIN, 5D43775

1.0 Introduction

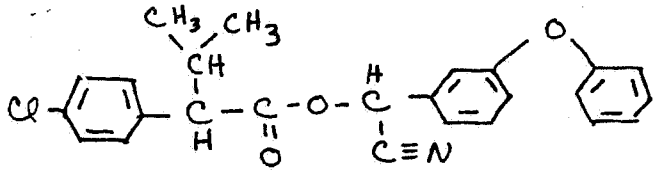
1.1 Active ingredient . cyano(3-phenoxyphenyl) methyl 4- chloro-alpha - (1-methyl-ethyl) benzeneacetate

1.2 Trade name: PYDRIN INSECTICIDE
The following are also used to indicate the active ingredient: SD43775,WL43775 fenvolerate, Sumicidin, and S5602

1.3 This review is for the applications for registration of two products. (1) Technical PYDRIN INSECTICIDE and (2) PYDRIN INSECTICIDE 2.4 Emulsible Concentrate. The formulated product is proposed for use on cotton.

1.4 Physical and Chemical Properties

CHEMICAL STRUCTURE:



EMPIRICAL FORMULA: $C_{25}H_{22}ClNO_3$

Molecular Weight.....419.9
Physical Form at 23°C...clear viscous liquid
Color.....yellow
Odor.....mild chemical odor
Density at 23°C.....1.17 g/ml
Vapor Pressure at 25°C..1.1 x 10^{-5} mmHg

Solubility:

Solvent	g/l at C	
	0 C	20 C
Hexane.....	49	77
Xylene.....	>450	>450
Acetone.....	>450	>450
Chloroform.....	>450	>450
Methanol.....	253	>450
Hexylene Glycol.....	>450	>450
Water.....	---	<20ppb

Hydrolytic Stability:

pH	Percent Recovery After 100 Hours at 75 C
2	100
4	100
6	93
8	29

2.0 Directions for Use

2.1 Technical PYDRIN INSECTICIDE - For formulating use only -(no directions for use)

2.2 PYDRIN INSECTICIDE 2.4 Emulsible Concentration. (contains 2.4 pounds of active ingredient per gallon.

For cotton foliage applications mix required amount of PYDRIN in sufficient water to provide uniform coverage but no less than one gallon per acre by air or four gallons per acre by ground. Do not enter treated field before spray is dry.

Dosage rates 0.05 to 0.20 lbs. ai/acre per application. Repeat as necessary throughout season to maintain control. Do not apply within 21 days of harvest.

Note: Label does not indicate a maximum cumulative dosage per season.

2.3 Disposal: ...dispose of wastes in compliance with local, state and federal regulations. Do not reuse container. Dispose of used container according to local, state and federal regulations.

3.0 Discussion of Data: Data reviewed was found in the following accession numbers: 096385, 096386, 096390 and 097000.

3.0.1 Initial reviews were done by the following individuals:

C. Blalock - Tabs 1, 9, 10, 11, 12, 13
W. Garner - Tabs 2, 3, 14, 15, 16, 19
R. Ney - Tabs 4, 4, 17, 18, 20, 21, 27
K. Sampson - Tabs 6, 7, 8
A. Schlosser-Tabs 22, 23, 24, 25, 26

A. Schlosser - T .s 6, 6, 9, 13, 14, 15

This review includes new data in Accession No. 09700 of 3/24/78

3.1 Hydrolysis

Hydrolytic Stability of WL43775
June 1977, Analytical Dept.
Tab I, page 02841, Accession No. 096386

Experimental Procedure

The aqueous solubility of WL43775 is reported below 20 µg/l. Hydrolytic stability was determined at 1 mg/l in 10% ethanol/water buffered at pH 1.1 and 9.1, and at pH7.2 at 5 mg/l in 10% ethanol 90% tap water. All studies were performed at 38°C

Analytical Method

Aliquots were extracted with $CHCl_3$. Determinations were made with Finnegan Model 3200 GC/MS(SID)

Results :

Half-life (hours) at 38°C

PH 1.1	PH 7.2	PH 9.1
100	570	70
(4.17 days)	(23.75 days)	(2.92 days)

Conclusions:

1. Hydrolysis products are not identified.

2. Material balance data are not given.

3. The study does show that PYDRIN is subject to rapid hydrolysis at PH's of 1.1 and 9.1. It is more stable around 7.2. Therefore it will be probably more stable in soil at PH values of most soils around 5-8. This indicates the need for the study to be done at PH 5. The temperature of 38°C is also out of proportion with soils. We have no recovery data. We also note that

PYDRIN adheres to glass.

(5) It is not clear from the data whether the study was done in the dark.

(6) The study is unacceptable

(7) Review Blalock

3.2 Photodegradation

3.2.1 Photochemical degradation of SD43755 on silicia gel, glass, soil, in water. H.Y.Fan. Report No. TIR-22-101-76, Pg. 02842, Tab 2, Acc. No. 096386.

Experimental Procedure.

1. Silica Gel
^{14}C-SD43755 (labeled at the chlorophenyl group) in an acetone solution (1mg/ml) was spotted on silica gel analytical plates (10 ug/spot). Experiments were conducted for 28-day periods under both sunlight and Vita-Light (Duro-Test Corp.) which has a spectrum very similar to that of sunlight. The plates were placed 5 inches from the light source for Vita-Light exposure and on a building rooftop for sunlight exposure. Mean brightness of the sun at the silica gel surface was 5400 foot lamberts and 1760 foot lamberts for Vita-Light brightness. Temperature in the Vita-Light chamber was relatively constant at 41°C while outdoor experimental temperatures were uncontrolled. Sunlight exposure tests were run during the months of May through October. Four photosensitizers were added (spotted over the spots of SD43755 at a dosage of 20 ug (spot) to determine if the degree of photochemical breakdown might be increased. ^{14}C-Dieldrin was used as a positive control.

2. Analytical Method:
Analyses were carried out by TLC using a solvent system of THF:EtOAc: hexane (4:16:80) and autoradiography.

Conclusions:

SD 43775 was somewhat unstable on silica gel under dark conditions; however, degradation increased with time and light exposure. Direct sunlight exposure was more effective on inducing degradation than Vita-Light. Approximately 14 8-hour-day exposures of sunlight were as effective as 28 24-hour exposures of Vita-Light. After 28 days approximately 49% of SD 43775 remained after Vita-Light exposure and 25% after sunlight exposure. Photosensitizers only slightly increased the amount of SD 43775 degraded.

Photochemical degradation products were TLC characterized but not chemically identified.

Experimental Procedure:

2. Glass
The same acetone solution of ^{14}C-SD 43775 as that used in the silica gel experiment was added to Pyrex petri dishes at a dosage of 10 ug/cm^2. The acetone was vaporized, and the dried dishes covered with Saran wrap were exposed to sunlight and Vita-Light for periods up to 28 days.

Analytical Methods

Analyses were carried out by TLC and autoradiography.

Conclusions:

SD 43775 is somewhat unstable under Vita-Light on glass surfaces in that 48% remained intact after 28 days. Under sunlight only 1% of the parent compound remained after 21 days. The primary metabolite characterized as chromatogram zone 1, forming at the end of 21 days accounted for approximately 14% of the 17% total radioactivity recovered.

Experimental Procedure:

3. Soil
An acetone solution of ^{14}C-SD 43775, labeled at the chlorophenyl group, was applied to Hanford

sandy loam thin layer plates (500 u) at a concentration of 11.9 ug/cm^2. Samples were exposed to both sunlight and Vita-Light, which has a spectrum similar to that of sunlight, for 28-day periods. The plates were placed 5 inches from the 24-hour light source for Vita-Light exposure and on a building rooftop for 8-hour sunlight exposure. Mean brightness of the sun at the silica gel surface was 5400 foot lamberts and 1760 foot lamberts for Vita-Light brightness. Temperatures in the Vita-Light chamber were relatively constant at 41°C while outdoor experimental temperatures were uncontrolled. Sunlight exposure tests were run during the months of May through October.

Analytical Procedure:
Analyses were carried out by TLC using a solvent system of THF:EtOAc:hexane (4:16:80) and autoradiography.

Results:
Table 1. The % of Radioactivity Recovered from ^{14}C-SD 43755-Treated Thin Layer Soil Plate After Exposure to Vita-Light.

Exposure Time(Days)	Acetone Ext.	Soil After Ext.	Total	Acetone Ext.	Soil After Ext.	Total
7	87.7	1.7	89.4	92.9	3.5	96.4
14	94.1	4.7	98.8	80.4	4.0	84.4
21.1	87.0	2.6	89.6	79.7	3.8	83.5
28	84.9	4.3	88.2	78.4	7.3	85.7

Table 2. Photodegradation of ^{14}C-SD43755 on Thin-Layer Soil Plate after Exposure to Vita-Light
% Radioactivity in Chromatogram Zones
Exposure Time Days

Zone	7	14	21	28
1	9.2	13.0	16.7	23.0
6*	85.8	82.4	76.8	69.1

*Zone 6 has the same R_f value as SD 43755
Zone 1 not identified

Table 3. The % of Radioactivity Recovered from ^{14}C-SD 43755 Treated Thin Layer Soil Plate After Sunlight Exposure.

Time of Exposure (Days)	Sample 1 Acetone Ext.	Sample 1 Soil After Ext.	Sample 1 Total	Sample 2 Acetone Ext.	Sample 2 Soil After Ext.	Sample 2 Total
1	85.9	6.4	92.3	84.6	4.5	89.1
7	75.2	6.1	81.3	74.7	6.5	81.2
14	78.0	9.3	87.3	90.0	7.8	97.8
21	85.1	10.2	95.3	75.4	12.3	87.7
28	68.4	8.5	76.9	72.4	6.2	78.6

Table 4. Photodegradation of ^{14}C-SD 43775 on Thin-Layer Soil Plates after Sunlight Exposure
% Radioactivity in Chromatogram Zones

Zone	Exposure Time.Day 1	7	14	21	28
1	4.0	10.9	16.1	18.9	23.0
6	92.1	81.6	70.4	65.7	68.4

Without light SD 43775 degraded very slowly in soil. Under Vita-Light degradation increased slightly with one major product found besides the parent compound. On the 28th day this TLC-characterized product comprised 30% of the total material applied and SD 43775 comprised 60%. Other degradation products were produced in trace amounts.

The degradation pattern of this material on soil thin layer after sunlight exposure was very similar to that observed under artificial light conditions; however, the total amount of metabolites formed was slightly greater and more radioactivity remained in the soil after acetone extraction. 53% of the parent compound and 18% of the primary degradation product remained at the end of the 28-day period.

Experimental Procedure:

4. Water
   Due to the low solubility of SD 43755 a stable suspension of ^{14}C-SD 43755 at 1 ppm in Xylene and

Atlox was made and this added to Triton X-100 and deionized water. A 2% aqueous acetone solution formulated as above was used to mimic the properties of natural waters. The suspensions were allowed to stand for 16 days, without stirring, under sunlight and dark exposure conditions. The flasks were placed on a building rooftop for 8-hour sunlight exposures (5400 foot lamberts) during the months of May through October. ^{14}C-dieldrin formulated in the same way as SD 43775 served as a positive control.

Analyses were carried out by TLC using a solvent system of THF:EtOAc:hexane (4:16:80) and autoradiography.

Results:

Table 5. Recovery of Radioactivity from ^{14}C-SD 43775-Treated Water and 2% Aqueous Acetone (% of Original Activity)

	Water						Acetone		
	Dark			Light			Light		
Exposure Time (Days)	Before Extract	EtOAc Ext.	After Ext.	Before Ext.	EtOAc Ext.	After Ext.	Before Ext.	EtOAc Ext.	After Ext.
1	101.6	89.6	2.6	91.6	84.6	6.3	94.6	93.2	5.6
9	96.1	79.7	2.2	92.1	80.7	10.1	85.3	67.4	10.8
18	92.5	77.2	11.1	86.2	79.6	2.4	77.5	68.1	6.0
28	87.8	81.2	0.4	82.0	81.5	2.0	66.2	66.9	5.4

Table 6. Photodegradation of ^{14}C-SD 43775 in water of 2% Aqueous Acetone at Various Time Intervals
% Radioactivity in Chromatogram Zones

	Water Exposure Time. Days						Aqueous Acetone Exposure Time. Days					
Zone	1	3	5	9	18	28	1	3	5	9	18	28
1	0.8	2.8	2.6	5.3	8.3	10.6	12.4	18.4	18.5	33.0	33.1	35.4
2	0.6	1.8	1.6	4.1	4.6	7.4	5.6	8.5	8.5	11.4	15.4	14.5
3	2.8	6.7	6.9	9.6	11.4	11.6	4.3	4.4	3.7	4.1	4.0	3.8
7*	93.6	84.6	84.0	74.2	62.7	58.8	44.7	55.3	43.7	29.4	23.3	28.3

*Zone 7 has the same R_f value as SD 43775.

Conclusions:

Under dark conditions very little degradation of SD 43775 occured. After exposure to sunlight for 28 days, approximately 52% of the parent compound was degraded. Photodegradation in 2% aqueous acetone

was much faster than in water; approximately 20% of SD 43775 remained with the same exposure time to sunlight.

In water the degradation pattern was slightly different from those of other media, i.e., soil, silica gel, and glass. Besides, the parent material 2 to 3 metabolites were found in significant quantities and were TLC characterized.

Final Conclusions:

1. The T½ of SD 43775 in soil was not reached after 28 days under either sunlight (53% remaining) or Vita Light (60% remaining) exposure. The chemical is stable to photodegradation on soil surface and has 1 major photo product.

2. The primary metabolite (TLC characterized as Zone 1) formed in soil under both sunlight and Vita-Light was present at the end of the 28-day test period in amounts greater than 10%, i.e., 30% in Vita-Light and 18% in sunlight. Before this study is accepted, this material must be chemically identified.

3. The primary metabolite appearing in the aqueous acetone experiment (TLC characterized as Zone 1) was formed in the amount of 23%. Since the 2% aqueous acetone formulation was used to mimic the properties of natural waters this degradation product should be chemically identified.

   All other degradation products found in the water or aqueous acetone experiments were formed in quantities less than 10% of the total parent material applied. This chemical is stable in water to photolysis and has a major photo degradate. The study is not acceptable.

4. Other studies of photodegradation of Pydrin in water containing thioxanthen-9-one, xanthen-9-one, Benzophenoe and anthroquinone are submitted but are only ancillary. These studies give similar results. T½ was 28 days or less in 3 cases and greater in 1. The major photo product like that in soil in water was at Rf 1 but we need data indicating all Rf 1's are the same.

5. Reviewer Garner

3.2.2 Solution Photochemistry of SD 43775. A. Ehmann. Report No. TIR-22-116-77, Tab. 3, Acc. No.096386, Pg. 02865

Experimental Procedure:

Solution Photolysis of SD 43775 (0.2M) in hexane was carried out at 350nm, 300nm, and 254nm to study the effect of wavelengths on photoproduct formation. Samples were irradiated in round window quartz cells for 10 hours in a Rayonet photoreactor (Southern N.E. Ultraviolet Co.) at 35°C using either RPR-3500A, RPR-3000A, or RPR-2537A lamps.

Analytical Method:

The photoproducts were isolated by preparative TLC (silica gel, 0.25mm) in hexane:acetone (7:3) or HPLC. Fractions recovered from TLC and HPLC were analyzed directly by GC-MS.

Results:

% Yield of Photoproducts Formed at Different Wavelengths

	-nm		
Photoproducts	254	300	350
SD 43775	11.9	52.8	0
decarboxilated SD 54597	65.7	26.9	0
reversed oster SD 53036	2.3	1.2	0
mixture of minor photoproducts	20.1	19.1	0

Conclusions:

1. Photolysis of SD 43775 in hexane at 350 nm resulted in no photoproducts. Photolysis at 300nm and 254nm yielded identical products; however, at 300nm 52.8% of the reaction mixture consisted of SD 43775 whereas only 11.9% was still the parent compound, at 254nm.

2. The decarboxylation of SD 43775 is the predominant photoreaction under the experimental conditions used with more than twice as much SD 54597 formed at 254 nm than at 300 nm.

3. This study as submitted is not required for registration and, therefore can be used as a support study only. If the primary photolysis product, the decarboxylated SD 43775, could be identified as the primary degradation product (Chromatogram zone 1) found in soil and water studies (Report TIR-22-101-76, Tab 2) by TLC R_f values or GLC-MS, then these studies combined would support registration of this chemical.

4. The registrant states that "the identification of the remaining photoproducts as well as the quantification of these minor products is in progress." The study is incomplete by Shell's own statement.

5. Reviewer: Garner

3.0 Aerobic-Anaerobic-Sterile

3.1 Degradation of ^{14}C (chlorophenyl) SD 43775 During Exposure to Soil Under Aerobic, Anaerobic, and Sterile Conditions. by J. E. Loefffler. Acc. #096386. Tab 4 pg 02870, Shell No. TIR-22-108-76.

Experimental Procedure

Soil, 150gm Hanford sandy loam. Water was added to bring to field capacity. For sterile soil experiments, the soil was autoclaved at 127°C, flasks were aseptically washed with acetone and stoppers were sterilized.

Aerobic and anaerobic soil were also conditioned with water.

All soils were treated with 2.5ppm.

Top part of flask and stoppers were covered with parafilm and Al foil.

Flasks were shaken thoroughly and stored at greenhouse ambient temperatures. Twice a week they were unstoppered for a 30 minute aeration period. After 30 days those anaerobic study flasks were flushed with N_2 and stored under N_2.

^{14}C study (^{14}C Chlorophenyl)

Analytical Method

LS, Soil from flask was transferred in total and extracted with acetone in a soxhlet extractor for 48 hours and aliquots of the extract were counted by liquid scintillation spectrometry.
TLC. Silica gel strips. Solvents used consisted of hexane, ethylacetate and tetrahydrofuran. Strips were secured with a Berthold 2760 counter.

Results:

(next page)

Sampling Days	^{14}CPPM equivalent to ^{14}C-SD 43775 Aerobic	Anaerobic	Sterile
0	2.51		
15	2.44		
30	2.38		2.54
60	2.24	2.4	2.5
90	2.07	2.06	2.32

Samples of total conbusted

Conclusions

1. Aerobic and anaerobic degradation of total ^{14}C residue was about the same.

2. Very little loss in sterile soil of total ^{14}C residue. No recovery data in any case.

4. The study did not account for bound residues or volatile losses.

5. No data submitted on degradates but registrant states 99% parent at 0 days and 90% parent at 90 days. The 10% at 90 days is 2 or 3 polar compounds.

6. The study was not carried out long enough to determine T½ in soil.

7. The study cannot be used to determine what the study supports.

8. The study also was not carried out long enough to determine degradates and bound residues.

9. The study does not help to determine availability of residues extractable or bound to rotational crops or fish accumulation.

10. The sterile soil does not lead one to determine if microbes degrade SD 43775 because no analysis or raw data submitted.

11. We do not know soil characteristics.

12. The complete analytical methodology has not been submitted for LC and TLC.

13. We would like photographs if available of the TLC.

14. The study by itself does not support an aerobic, anaerobic and sterile studies.

15. Reviewer Ney

Aerobic - Anaerobic - Sterilized - Leaching

3.3.2 Degradation of Fenvalerate (Sumicidin) in soil by Hideo Ohhawa and Kinji Nambu Acc. #096386, Tab 5, pg 02873, code # AM-70-0036.

Experimental Procedures

SiTC	Soil	%Sand	%Silt	%Clay	%DM	pH	CEC
Kodaia	Light Clay(LC)	31	40	29	15.3	5.5	53.7
Azuch:	Sandy ClayLoam(SCL)	65	18	17	2.5	6.3	13.5
Kutano	SandLoam(SL)	80	12	8	1.8	5.8	9.3
Muko	Sand (S)	97	1	1	0.1	7.8	2.3

Aerobic

Aerobic upland conditions. Soil moistened to 50% of H_2O holding capacity and incubated for 1 week at 25°C. ^{14}C -CN or ^{14}C-CO fenvalerate was added at 1.0ppm dry soil weight. Treated soil was mixed, covered with Al foil and kept at 25°C in darkness for up to 8 months. Water was added once a week to keep moisture level up.

Anaerobic

The jar contained anhydrous sodium sulfate, evacuated and refilled 3 times with N_2. After one week 1.0ppm ^{14}C-CN was added and kept under aerobic conditions.

Sterilized Soil

Upland crop conditions, autoclaved at 120°C for 1 hour on each of 2 successive days and treated with 1.0ppm ^{14}C-CN or ^{14}C-CO. Jars kept at 25° in darkness.

The systems were continuously purged with CO_2, free

air, or N_2 through polyurethane plug into a bottle of N_aOH to trap volatiles.

Analytical Methods

1. Polyurethane plugs wash with MeOH, extracts assayed for ^{14}C.

2. N_aOH traps assayed using Insta-Gel.

3. $^{14}CO_2$ $BaCl$ to ppt $Ba^{14}CO_3$, centrifuged, assayed for ^{14}C using Insta-Gel.

4. Soil extracted 3 times with M_eOH, extracts monitored for ^{14}C and analyzed by TLC for degradates. Solvent system A, B, C, D and E were used. Two dimensional TLC used Cx2, D system. Spots are extracted and methylated. This would not help to identify non-radiolabeled compounds.

Results for ^{14}C-CN

The following are estimates from curves. The exact % cannot be estimated from curves submitted.

Soil = Kodaira = Light Clay = LC
Azuchi = Sandy Clay Loam = SLC

	%Recovered in mos.									
	0 LC	-SCL	2LC-	SCL	4LC-	SCL	6LC	SCL	8LC	SCL
Aerobic										
Total ^{14}C	97	99	40	70	31	52	25	40	20	30
MeOH extracts	95	98	24	63	10	40	7	36	6	8
Bound ^{14}C	2	2	12	5	13	6	14	10	14	12

% Recovered in Month

	0		2		4		6	
Anaerobic	LC	- SCL	LC	-SCL	LC-	SCL	LC	-SCL
Total ^{14}C	100	100	82	85	78	78	78	63
MeOH extracts	100	100	75	79	65	69	62	58
Bound14C	0	0	3	2	4	3	12	5
Volatile	0		1		3		6	
Sterile Soil	LC	- SCL	LC	SCL	LC	SCL	LC	SCL
Total ^{14}C	--	---	98	98	98	98	97	97
MeOH extracts	--	---	92	92	92	92	90	95
Bound ^{14}C	--	---	2	2	2	2	4	2

Conclusions

Aerobic

1. Slower degradation in a sandy soil than in clay. Bound residues about the same.

2. $T_{\frac{1}{2}}$ in a light clay for extractables < 2 months and total residues < 2 months.

3. $T_{\frac{1}{2}}$ in sandy clay loam for extractable < 4 months and total residues < 6 months.

4. Much faster dissipation under aerobic than anaerobic.

5. Desphenylfenvalerate was major degradate in 1 month but dissipated in light clay stabilized in sandy clay loam at 8 months. Also included here is 4'-OH fenvalerate and unknown I.

6. Other major degradates found at 1 month dissipated in > 8 months.

Anaerobic

1. Very slow dissipation or degradation in 6 months. A plateau begins to appear at 6 months.

2. $T_{\frac{1}{2}}$ of extractables > 6 months and of total ^{14}C > 6 months in light clay.

3. $T_{\frac{1}{2}}$ of extractabes > 6 months and of total $^{14}C > 6$ months in sandy clay loam.

4. Bound residues were very slow in building up.

5. Major unidentified degradates called "other" were found. Two of these degradates peaked at 3 months in both soils, while the remaining ones declined rapidly in light clay but not in sandy clay loam.

6. Other major degradates were found in 3 months and 6 months that were not found under aerobic conditions.

Sterile

1. Total ^{14}C and MeOH extractable indicated no significant dissipation in 6 months.

2. Micro organisms did not play a role in degradation in this study.

3. One degradate called "other" was present at all time intervals.

Results ^{14}C-CO

% found (month)

	1		2		3	
Aerobic	LC	SCL	LC	SCL	LC	SCL
CL-VA	0.6	1.4	0.6	0.7	0.4	0.2
$CONH_2$ - Fenvalerate	0.2	0.24	0.1	0.2	0.1	0.2
Desphenylfenvalerate)	5.5	1.7				
(4 -OH fenvalerate)	0.6	0	5.2	3.0	3.8	2.8
(Unknown I)	2.8	0.4				
$CONH_2$-Desphenylfenvalerate	0.2	0.1	0.3	0.2	0.3	0.2
Others	2.0	0.9	1.8	0.9	1.7	0.8
Bound	12.2	5.8				
Parent	48.8	73.2				
Volatile	23.9	12.1				

Results

1. The major degradates which have not been identified fall in the 3 called Desphenylfenvalerate, 4'-OH fenvalerate and unknown I.

2. The one called "Others" are also of importance.

3. In any case these residues are <10% of applied.

4. The ether in diphenyls is cleaved to give Desphenylfenvalerate. I believe this to be a minor route and that ^{14}C-CN goes to $^{14}CO_2$ faster leaving the diphenyl ether linkage. The same applies to ^{14}C-CO to give CO_2 faster, leaving the chlorophenyl moiety.

LC = loamy clay
SCL = sandy clay loam
SL = sandy loam
S = sand

Results at 30 days

	^{14}C-CN				^{14}C-CO	
Aerobic	LC	SCL	SL	S	LC	SCL
Volatile ^{14}C	31	172	48	32	10	10
MeOH extracts	58	78.8	41	51	87	85
Parent	47	74,9	33	45	86	85
Bound ^{14}C	11.6	6.4	13	12	3	3.5
Total ^{14}C	100	103	102	95	100	97
Anaerobic						
Volatile ^{14}C	24	12	38	23	0	0
MeOH extracts	61	78	45	67	88	92
Parent	49	73	37	55	86	86
Bound ^{14}C	12	5.8	10	8.9	9.6	8
Total ^{14}C	97	96	92	99	98	99

Conclusion Again:

1. There is enough difference in 30 day in the metabolic pathway or in dissipation in 30 days. CO_2 is a major under aerobic but not under anaerobic. Bound residues are higher under aerobic. $T_{\frac{1}{2}}$ of parent was reached in 3 soils and aerobic, but not in SCL soil. Parent was always major extractable product.

2. There appears to be no influence of CEC, OM, or pH on dissipation or degradation.

Final Conclusion

1. The parent compound was radiolabeled in such a position that a chemist would expect $^{14}CO_2$ and degradation to occur.

2. None of the studies account for the chlorophenyls or the diphenylether portion of the molecule.

3. No recovery data submitted.

4. We do not have adequate information on exact %-ppm to determine the points on the curves.

5. Analytical procedures are not in full detail.

6. The studies may be acceptable if ring label studies are carried out but cannot stand alone.

7. The ^{14}C-CN appears to breakdown rapidly to give $^{14}CO_2$ in 30 days. This would leave a diphenyl ether linkage not accounted for. The ^{14}C-CO appears to break down rapidly to $^{14}CO_2$ in 30 days. This would leave a chlorophenyl linkage not accounted. These 2 linkages appear to be the major degradate but were not examined in this study.

8. The study by itself is unacceptable for aerobic, anaerobic and sterile studies. Leaching is evaluated elsewhere in this evaluation.

9. Reviewer: Ney

3.3.3 Aerobic, Anaerobic, Sterile Soils

Metabolic Fate of Fenvalerate in Rats, Soil, Soil micro organisms and an Aquatic Ecosystem. H. Ohkawa, K. Nambu, H. Kaneko, R. Kikuch; Acc. #096384, Tab 6 pg 02895

1. Fenvalerate Metabolism in Soil Same as Tab 5.

Environmental Procedure

Four types of soils (Kodaira, Azuchi, Katano, and Muko) were wetted with water to 50% soil moisture holding capacity, preincubated at 25±2°C in the dark for one week, treated with ^{14}C-CN- and ^{14}C-CO - Fenvalerate at the Rate of 1.0ppm and held for 8 months. Besides aerobic studies, anaerobic conditions were simulated by sealing the experimental flask under nitrogen. Volatile products were monitored by purging the flask with CO_2 - free air (aerobic conditions) or nitrogen (anaerobic conditions) and collecting $^{14}CO_2$ in a 0.5N NaOH solution and in the polyurethane foam plug.

Analytical Method

At sampling intervals (½,1,2,3,4,6,8mo.), the soil was extracted with methanol and the radioactivity in the CO_2 traps as well as in the extracts and bound residues were determined. Metabolites were analyzed by TLC . Both sterile and nonsterile soils were used.

Experimental Procedure

Leaching tests (same as Tab 5) were conducted with the four types of soils with and without 30 days aging. Soil treated with 1ppm ^{14}C-CN- and ^{14}C-CO- Fenvalerate was added to a 20-cm soil column and percolated with 300ml water.

Analytical Method

Five cm soil sections and effluents were analyzed for ^{14}C.

Conclusions - see review of TAB 5

Almost no degradation of fenvalerate occurred in sterile Kodaira and Azuchi soils after 6 months. Radioactivity decreased slower under anaerobic conditions than under aerobic conditons with a half-life of about 6 months. The half-life for fenvalerate under non-sterile aerobic upland conditions varied from ½-3 months according to the applicant. Ninety-five percent degradation did not occur until 7-12 months.

$^{14}CO_2$ levels varied from 17-48% with the CN- labeled compound and 12-38% with the CO- labeled compound one month after treatment. The majority of the methanol extracts consisted of fenvalerate. Minor degradation products were $CONH_2$ - fenvalerate, desphenyl fenvalerate, 4'-OH- fenvalerate, desphenyl $CONH_2$- fenvalerate, and Cl-VA (with ^{14}C-CO-fenvalerate). Bound residues comprised 3.1 - 13.4% of the total radioactivity in the soil.

There was only slight movement of fenvalerate in the leaching experiment with a maximum occurring in the Muko soil. Aged soils showed a loss of 30-40% of the radioactivity before leaching.

Reviewer: Sampson

3.3.4 One-Year Study of the Fate of ^{14}C-SD 43775 in Soil by H. Y. Fan Acc. #096386 p, 02989, Shell #TIR-22-107-77 Tab 17

Experimental Procedure

^{14}C-chlorophenyl ring labeled SD 43775 was added at a rate of 0.125 lb/A 4 times at 4 week intervals or once at 0.25 lb/A to Hanford sandy loam (coarse textured soil). Soil characteristics by Nelson lab analysis is 57.6% Sand, 26.6% silt, 15.5% clay, o.7% organic content, pH6.1 and CEC 9.3 meq/100 . Container with treated soil was placed inside an outdoor enclosure.

Analytical Methods

1. Soxhlet extract with MeOH, aliquots analyzed by TLC. Solvent systems hexane-ethyl acetate-tetrahydrofuran. Plates of silica gel.

2. Liquid Scintillation for ^{14}C residues

3. GLC-MS

Results

Recovered from 1.25 lb/A as parent

4 weeks	% 0-3	ppm	% 3-6	ppm	% 6-9	ppm	% 7-12	ppm	% 0-12
Total	96.3	.17	0	0	0	0	0	0	9.31
MeOH Ext.	73.4								
Bound	8.6								
12 weeks									
Total	68.6	.39	1.0	.006	0.1	.0006	0.1	.0007	69.8
MeOH Ext.	39.5								
Bound	22.3								
21 weeks									
Total	35.3	.224	15.7	.11	10.5	.07	1.8	.01	61.5
MeOH Ext.	22.5		10.4		8.2				
Bound	10.5		6.1		2.8				
7 months									
Total	27.9	.17	9.1	.06	1.8	.01	--	.003	39.4
MeOH Ext.	12.9		5.9		1.1				
Bound	15.3		3.2		.7				
11 months									
Total	22	.17	4.6	.03	2.7	.01	0.6	.003	29.9

Table continued from previous page

	%	ppm	%	ppm	%	ppm	%	ppm
MeOH Ext.	9.8		0.9		1.5			
Bound	13.4		3.5		1.4			

Conclusion

1. High moisture levels in soil from 12-21 weeks. Maybe if H_2O levels were always high, leaching could occur. Leaching occurred when temperatures were lowest.

2. $T_{\frac{1}{2}}$ total residues > 5 but < 7 months.

3. Bound residues decrease in time

4. No accountability for ^{14}C loss

Results

Recovered from 0.25lb/A as parent

	%	ppm	%	ppm	%	ppm	%	ppm	%
	0-3		3-6		6-9		9-12		0-12
21 weeks									
Total	75.9	.28	0	0	0	0	0	0	75.9
MeOH Ext.									
Bound	7.5								
4 Months									
Total	43.6	.14	2.3	.006	0,2	.0006	0.1	.0004	46.2
MeOH Ext.	24.1								
Bound	21.4								
8 months									
Total	31.2	.1	2.6	.015	0.7	.002	0.3	.001	34.8
MeOH Ext.	13.7		1.4						
Bound	17.9		1.3						
12 Months									
Total	28.1	.1	4.3	.004	0.4	.001	0.1	.0004	29.9
MeOH Ext.	8.7								
Bound	16.4								

Conclusions

1. High moisture level in soil from 4 to 8 months. Maybe if moisture level was always high, leaching would occur. Leaching occured when temperatures were lowest.

2. $T_{\frac{1}{2}}$ of total residues < 4 months

3. Does not account for ^{14}C loss

4. Bound residues appear to decrease in time

5. Studys also shows that the longer the chemical is in the soil the less extractable it is.

Results and Conclusions

1. Data indicated by R_f (Zones x100), the largest residues present are:

Recovery 0.125 lbs/A

	weeks (0-3 inches)				months		
R_f	4	8	12	16	21	7	11
37-46	54	40	19	11	14	7	4
5-8	3	7	7	7	.8	.4	.6

Recovery 0.25 lb/A

	weeks			months		
R_f	2	4	8	4	8	12
37-46	59	53	37	12	7.3	4.8
0-5	8.4	9.9	7.7	7.3	3.5	2.2

Result

Bound Residues found in different soil fractions

	% of applied					
	0.125 lb/A			0.25 lb/A		
	21W	.7m	11 m	4 m	8 m	12m
Bound before NaOH	10.5	15.3	13.4	21.4	17.9	16.4
Humin	3.1	4.8	5.4	3.7	5.3	5.9
Sol. in NaOH	6.4	9.4	10.6	16.5	12.1	11.7
Humic Acid	0.8	0.9	1.0	0.9	1.1	0.8
Fulvic Acid	5.4	2.7	8.3	12.9	10.6	10.5
Remaining in Soil after ext-Bound	9.3	13.4	14.7	17.6	12.0	17.2

Conclusion

1. The greater amount of residues are found in fulvic acid soil fraction, and humin contains the next highest amount. Even after all this the greatest amount remains in soil as Bound.

Results Identification

Identity of residues in soil MeOH extract

1. Parent SD 43775

2. SD 53065 This may be incorrect as structure charts submitted pg 02827 - 02829 give SD 53085 for this chemical name. Any way the diphenyl ether is no longer part of the molecule.

3. SD 47117. The diphenyl ether linkage is still part of the molecule.

Final Conclusion of TAB 17

1. The ^{14}C label chlorophenyl ring did dissipate from soil probably via volatilization as indicated by ^{14}C loss.

2. The $T_{\frac{1}{2}}$ total residues in soil was around 5 months.

3. Parent and Bound residues are the major residues in soil. About 25% of total residues remain in soil at 12 months

4. The diphenyl ether linkage is still unaccounted for.

5. The chlorophenyl ring, ^{14}C-CN and ^{14}C-CO portions of the molecule are accountable. The ^{14}C-CN and ^{14}C-CO go off as $^{14}CO_2$ and the ^{14}C closing appears to volatilize.

6. The complete detailed analytical methods have not been submitted.

7. Raw data and recovery data have not been submitted.

Reviewer Ney

3.3.5 One-year study of the fate of 14C SD 43775 in soil. H. Y. Fan TIR-22-107-77 Addendum #2 Accession No. 097000, Tab 15, Page 00279

A Hanford sandy loam soil was treated with ^{14}C-SD 43775, and 0-3" inch samples were taken after two treatment periods. (1) Four weeks after an 0.25 lb/acre treatment and (2) Sixteen weeks from the date of the first application after four 0.125 lb/acre treatments. Methanol extracts of the soil samples were analyzed by a combination of thin-layer and high-performance-liquid chromatography.

Analytical Methods:

Portions of the methanol extracts were applied separately to EM Silica Gel 60 F-254 preparative plates and chromatographed in hexane/ethyl acetate/tetrahydrofuran Resulting chromatograms were revealed by X-Ray filming and divided into 8 zones. These zones were scraped off, extracted with acetone, and ultimately analyzed by HPLC with the U.V. detector set at 225nm. Two different columns were used Spherisorb ODS and Lichrosorb C_2. Sample materials were tentatively assumed to be chemically identical to standards with similar retention times.

Zone 8 of the original chromatograms was not further analyzed due to lack of standards and insufficient radioactivity.

Nine major metabolites including SD 43775 were found in the various thin-layer chromatographic zones by HPLC

Zones 1 + 2	SD 53065 and SD 47117
Zone 3	SD 10944
Zone 4	SD 55886 in four week soil for 0.25 lb/acre treatment
Zone 5	Two minor metabolites
Zone 6	SD 43775, SD 54597, SD 47116
Zone 7	SD 39009 and SD 43774

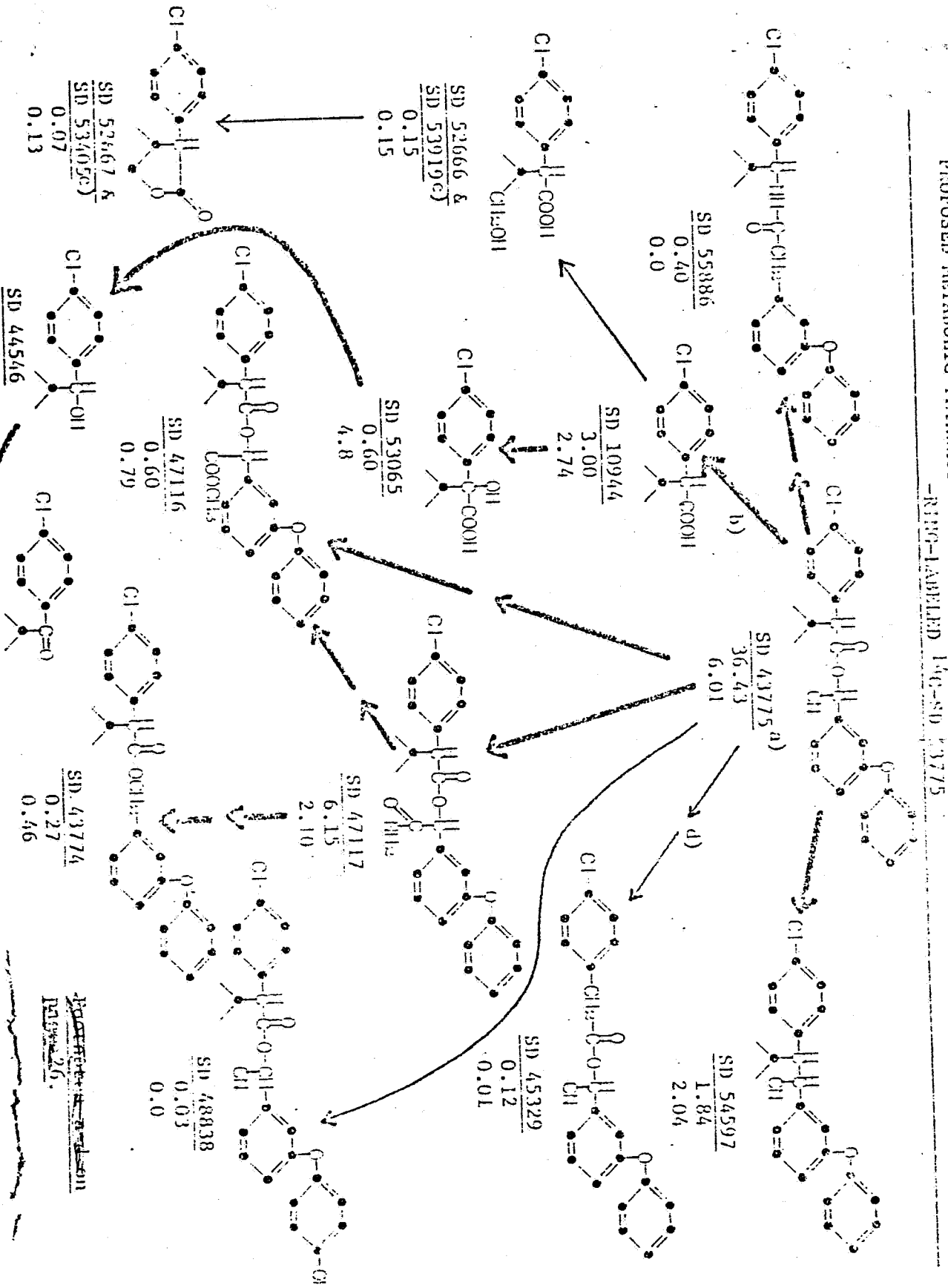
Five additional minor metabolites were found in these zones - SD 52666 and/or SD 53919, SD 52667 and/or SD 53405, SD 44546, SD 45329, and SD 48838

The formation of SD 43775 may be an artifact formed by the reaction of methanol with one of the unstable metabolites of SD 43775 such as the acid obtained by hydrolysis of the amido group of SD 47117.

Zone 6 was reanalyzed by HPLC twelve months after treatment at the 0.25 lb/acre rate (methanol extract of 0-3 inch soil level). This zone contained most of the extractable activity and SD 43775 at 4 weeks. At the twelve month interval only about 5% of originally applied activity was found with about 1 % as SD-43775.

THE ^{14}C IN THE VARIOUS ZONES OF THE CHROMATOGRAMS OF THE PREPARATIVE PLATE OBTAINED FROM METHANOL EXTRACTS OF SOILS AT 0-3-INCH LEVELS

Chromagogram Zones	R_f Values X100	Soils Four Weeks after 0.25 lb/Acre Treatment		Soils 16 Weeks (from First Treatment) After Four 0.125 lb/Acre Treatments	
		Distribution of Radioactivity,%	% of Originally Applied Radioactivity	Distribution of Radioactivity,%	% of Originally-Applied Radioactivity
1	0-3	8.9	6.5	12.2	4.0
2	3-8	6.5	4.8	16.3	5.3
3	8-14	4.7	3.4	11.6	3.8
4	14-19	1.7	1.2	1.8	0.6
5	19-32	3.2	2.3	1.8	0.6
6	32-40	67.8	49.7	32.2	10.4
7	40-48	6.4	4.7	23.4	7.6
8	48-72	0.9	0.7	0.7	0.2



a) The amount of the metabolites found were written under the SD number expressed in percent o originally-applied radioactivity in the four-week and 16-week soils for the 0.25 and 0.125 Atrials.

b) Bold arrows indicate major metabolic route.

c) Diastereoisomers.

d) Double arrows mean that process may take more than one step.

Conclusions

(1) At least 14 chlorophenyl-ring soil metabolites of SD 43775 in Hanford sandy loam soil have been tentatively identified by TLC/HPLC, and a proposed metabolic pathway is given.

(2) The fate of the phenoxyphenyl ~~mi~~ moiety is not demonstrated in this study.

(3) The half-life of extractable SD 43775 in the top three inches of soil is indicated as less than 4 weeks by this study.

3.4 Impact of PYDRIN INSECTICIDE on micro organisms in the soil environment. W. E. Rader and W. Love. Acc. # 096386, Tab. 8, By 02919, TIR-22-108-77.

3.4.1 A nonsterile Hanford sandy loam moistened to 6% with a field capacity of 10.8%, pH of 5.5, and soil volume of 41.3ml/100g was treated with varying concentrations of PYDRIN. A portion of the soil heated with 0.2ppm and 0.8ppm PYDRIN, 10ppm etherel and 100ppm pentachlorophenol was planted with pinto beans. After 3 weeks growth, the roots were washed and nodule formation was observed.

In another experiment, the effect of PYDRIN on cellulose decomposition was studied by placing cotton duck strips into moistened soil treated with 0.2ppm and 0.8ppm. After 40 days incubation, the tensil strength of these strips was measured with a spring balance.

Toxicity tests were conducted with two bacteria (Azotobacter beijerinckii and Rhizobium phaseoli) and one fungus (Trichodema viride) using the standard tube-dilution method. Varying concentrations of PYDRIN were added to growth media seeded with the three different organisms. The cultures were incubated 10 days at 25° C and growth was observed.

Table 1. GROWTH INHIBITION EVALUATION OF PYDRIN AGAINST TEST ORGANISMS

Compound	Growth Inhibition Endpoint (ppm)		
	R. phaseoli	A. beijerinckii	T. viride
PYDRIN	>1000	>1000	>1000
Etheril	100-1000	100-1000	—
Pentachlorophenol	~100	10-100	10-100

Table 2. EFFECT OF PYDRIN BLENDED WITH SOIL AT 1X AND 4X RECOMMENDED FIELD DOSAGES ON THE FORMATION OF ROOT NODULES AND GERMINATION OF PINTO BEANS

Product	Dosage	Percent Reduction in Root Nodule Formation			Percent Germination
		Rep 1	Rep 2	Average	
PYDRIN[a)]	1X	0	0	0	100
	4X	80	0	50	75
Etherel[b)]	1X	80	100	88	75
Pentachlorophenol[c)]		100	100	100	100

a) 1X Dosage of PYDRIN at 0.2 lb/acre (a.i.) is equivalent to 0.2224 mg/qt soil based on weight of soil at 3.5×10^6 lb/acre (the product being incorporated in the top 3.5 inches). This is also equivalent to 0.2 ppm in the soil.

b) Ethrel was used at 10 ppm in the soil.

c) Pentachlorophenol was used at 100 ppm in the soil.

The effect of PYDRIN on the decomposition of cellulose in the soil is given in Table 3.

Table 3. EFFECT OF PYDRIN ON THE DISINTEGRATION OF COTTON CLOTH IN TREATED SOIL

Compound	Dosage	Effect on Cloth
PYDRIN	1X Dosage in Soil	Cloth completely disintegrated.
	4X Dosage in Soil	Cloth completely disintegrated.
Pentachlorophenol	100 ppm	60 lb+ tensile strength.
Control in Soil		Completely disintegrated.
Control Not in Soil		60 lb+ tensile strength.

Conclusion

Observation of nodule formation in legumes is not an acceptable method for measuring effects on nitrogen fixation. Free-living nitrogen fixing bacteria rather than symbiotic organisms should be used. Controls were not run. Table 2 shows that replicate 1 showed 80% reduction in root nodule formation while replicate 2 showed none at 4x dosage rate. The difference between these 2 replicates is too large to be acceptable.

Decomposition of cellulose in soil is an acceptable study showing that PYDRIN did not affect cellulolytic organisms. Toxicity tests, showing no growth inhibition at 71000ppm PYDRIN, are ancillary.

Reviewer Sampson

IV. Impact of Commercial Shell Products on Microorganisms in the Soil-Effect on Nodulation on Pinto Beans and on the Nitrogen Fixation Bacteria. W. E. Rader and J. W. Love. Acc. #09638, Tab 8, P902923, TIR-22-112-77

Conclusions

This is a repeat of Tab 8.

Reviewer Sampson

3.4.2 II. Determination of Antimicrobial Activity of Selected Pyrethroid Compounds. J. P. Salanitro, Acc.# 096386, Tab 7, page 02917, TIR-76-033-76

Experimental Procedure

A non-rumen anaerobe growth screen was used to test the antimicrobial activity of six pyrethroid analogues (WL 41517, WL 41706, WL 43467, WL 43479, WL 43775, and WL 44749) on four anaerobic bacteria, Clostridium perfringens, Bifidobacterium adolescentis, Fusobacterium necrogenes, and Bacteroides fragilis as well as on four facultative bacteria, Lactobacillus casei, Streptococcus faecalis, E. coli, and Salmonella typhimurium. Anaerobes were grown in pH

glucose while faculative organisms were grown in Tryptic soy broth treated with 2.8, 8.3, 25 and 75ppm of the 6 pyrethroid analogues and the four antibiotics penicillin, chlorotetracycline, lin..omycin, and bacitracin. Inhibition of growth was visually observed after 24 hours incubation at 37°C. No inhibition of growth was noted with any of the test analogues while the four antibiotics did suppress growth.

Conclusion

This is an unacceptable study to measure the effects of pesticides on microbes. The following deficiencies are noted:

1) Visual observation of growth is not an acceptable quantitative technique. There was no attempt to measure population or numbers of bacteria in these studies.

2) What were the conditions for incubations?

3) Studies should be continued for more than 24 hours. One sampling point is not sufficient to measure pesticide effects on microbes.

4) Most of the organisms used in this study are animal pathogens and indicators of fecal pollution. More appropriate organisms would include free-living, nitrogen-fixing bacteria and blue-green algae such as Azotobacter, Nostoc, and nitrifiers such as Nitrosomonas and Nitrobacteria. Other acceptable organisms include Bacillus, Pseudomonas, Arthrobacter, Cellulomonas, Cytophaga, Streptomyces, Aspergillus, Chaeto··ium, and Fusarium.

5) Were controls run for each organism at each concentration? There is no mention of controls in this experiment.

Reviewer Sampson

3.5 Effect of soil micro-organisms on the pesticide

3.5.1 Metabolic Fate of Fenvalerate in Rats, Soil, Soil Micro-organism and an Aquatic Model Ecosystem.
H. Ohkawa, K. Nambi, H. Haneko, R. Kikuchi. Acc # 096386, Tab 6, pg 02895,

3. Fenvalerate Metabolism in Soil Micro-organisms and on Active Sludge.

Experimental Procedure

Three types of "Live" soil and "active" sludge were added to fungal and bacterial media followed by addition of 1 ppm ^{14}C-CN and CO-labeled fenvalerate. The inoculated flasks were incubated aerobically at 30°C with shaking for 2 weeks. $^{14}CO_2$ was trapped in a 0.5N NaOH solution and on the polyurethene plug. Controls with sterile soil and sludge sealed under N_2 in glass flasks were run. The number of organisms added to each flask are listed below:

soil of sludge	fungi	bacteria
Kodaira soil (2 g)	1.24×10^5	5.94×10^7
Azuchi soil (2 g)	1.77×10^5	2.36×10^8
Katano soil (2 g)	3.10×10^5	1.77×10^8
Active sludge (30 oom)	1.07×10^3	3.00×10^7

Analytical Method

After 2 weeks incubation the reaction mixture was centrifuged and analyzed by TLC.

Conclusion

1. After 2 weeks fenvalerate was metabolized to a greater extent in the bacterial media than in the fungal media and more in soils than in the active sludge. Whereas 48% of the radioactivity was fenvalerate in fungal media, only 16-32% was parent compound in bacterial media. More than 90% was unchanged in sterile controls. $^{14}CO_2$ from CN-labeled fenvalerate varied from 16-43% of the total radioactivity and only 1-3% from CO-labeled fenvalerate. The major metabolite identified in the CO-labeled experiments was CI-VA (69-11%). Other minor metabolites included COOH-fenvalerate, $CONH_2$-fenvalerate, desphenyl fenvalerate, 4'-OH-fenvalerate, and desphenyl $CONH_2$ - fenvalerate.

Table 8. Fenvalerate Metabolism in Soil Microorganisms and an Active Sludge in Medium I(for fungi) and Medium II(for bacteria)

	% of administered radiocarbon																	
	Kodaira Soil						Azuchi Soil						Katano Soil				Active Sludge			
	M-I			M-II			M-I			M-II			M-I			M-II				
	CN[a]	CN	CO	CN[a]	CN	CO	CN[a]	CN	CO	CN[a]	CN	CO	CN[a]	CN	CO	CN[a]	CN	CO	CN[a]	CN	CO
Volatile (NaOH trap)	1.1	40.3	1.1	0.7	43.3	2.1	0.2	43.0	1.6	---	39.5	2.2	0.1	36.6	2.3	0.1	37.1	1.3	1.0	16.1	2.6	0.4	29.3	1.8
Organosoluble																								
Fen.	92.3	47.4	48.6	88.5	19.6	15.9	94.8	45.8	38.3	93.0	29.1	32.0	95.0	47.0	48.7	94.6	22.3	17.7	95.0	75.1	63.9	96.8	47.8	48.7
Cl-VA	---	---	34.0	---	---	67.5	---	---	45.5	---	---	59.4	---	---	41.5	---	---	68.9	---	---	11.2	---	---	34.5
4'-OH-Fen.	---	0.1	0.1	---	0.1	1.3	---	0.1	0.2	---	0.9	1.2	---	---	0.1	---	1.7	2.0	---	1.0	2.1	---	2.1	2.0
b)	---	0.1	0.2	---	0.2	0.4	---	0.1	0.1	---	0.2	0.3	---	0.2	0.2	---	0.3	0.4	---	0.5	0.6	---	---	0.1
Others	0.3	2.9	8.4	0.2	10.5	10.6	0.4	4.0	7.8	2.0	8.1	4.0	2.1	5.2	7.2	2.6	7.4	11.9	0.4	5.7	17.3	0.5	6.4	7.6
Subtotal	92.6	50.5	91.3	87.1	31.3	95.7	95.2	50.0	91.9	95.0	38.3	96.9	97.1	52.4	97.7	97.5	31.7	100.9	95.4	82.3	95.1	97.3	56.3	92.9
Aqueous Sol.	0.4	0.1	---	2.3	10.3	0.1	---	0.3	---	---	11.4	0.3	---	0.3	0.2	0.9	18.5	0.2	1.2	1.4	0.1	0.7	2.6	0.1
Residues	1.5	8.5	2.0	1.3	10.4	2.2	0.4	9.7	2.2	0.1	10.2	2.2	0.1	12.2	2.1	0.3	4.3	1.2	---	1.7	1.4	---	2.3	0.9
Total	95.6	99.4	94.4	91.4	95.3	100.1	95.8	103.0	95.7	95.1	99.4	101.6	97.9	101.5	102.3	98.1	91.6	103.6	97.6	101.5	99.2	98.4	90.5	95.7

a) ; sterilized

b) ; a fraction containing $CONH_2$-Fen., desphenyl Fen., 4'-OH-Fen. and desphenyl $CONH_2$-Fen.

--- ; < 0.1%

2. This is a combination of a microbial degradation study and an activated sludge study.

3. An activated sludge study should be performed under a continuous or semi-continuous process. The effect of fenvalerate on the activated sludge process must be monitored by an acceptable analytical technique under both continuous or semi-continuous and shock loading conditions. Effluent and influent quality should be measured by BOD, COD, etc. Pesticide concentration should be monitored in the influent and effluent. An acceptable protocol is as follows:

   Synthetic sewage (nutrients) and radio labeled active ingredient are added to activated sludge and aerated in a closed system for 23hr, allowing the sludge to settle for 30'. A liter of supernatant (effluent) is removed for pesticide residue analysis including a material balance. Fresh synthetic sewage and test compound are added to the remaining sludge, and the cycle is repeated. Dosage should start at 0.1ppm and increase by increments to 100 ppm. Effects on microbial population must be determined by daily total counts of viable organisms in the sludge or by an acceptable alternative procedure.

4. Reviewer Sampson

3.6 Leaching

Leaching Studies of SD 43775 and Selected Reference Pesticides by Soil Thin-layer Chromatography. R. L. Merritt. TIR-22-102-77. Acc. No.096386; Tab 10, pgs. 02942-02947.

Experimental Procedure

Leachability of PYDRIN (C^{14} - labelled chlorophenyl ring) compared to dieldrin, Supona, Azodrin, Planavin, and Bladex by soil TLC. Soils: Hanford sandy loam, Iowa silty clay loam, Tujunga agricultural sand, and Walla Walla silt loam. Unscreened soil analysis results given. 4 replicates of each soil type spotted and developed; patterns determined from radioautograms.

Analytical Methods

Soil thin-layer chromatography. Soils analyzed by Nelson Labs, Stockton, California (Bibliography of methods used. Soils sieved in preparation for TLC. Eluant was glass-distilled deionized water. Plates air-dried before exposed to X-ray film.

Results:

Mobility Data for each Soil Type.
(Average ± Std. Dev.) (Frontal Rf's)

Soil Type	SD43775 Pydrin	SD15418 Bladex	SD11831 Planarrin	SD7859 Supona	SD9129 Azodrin	SD3417 Dieldrin
Walla Walla	0.0±0.0	0.705±0.01	0.20±0.014	0.2±0.041	0.925±0.029	0.0±0.0
Hanford	0.0	0.60±0.056	0.188±0.056	0.203±0.047	0.810±0.101	0.0
Iowa	0.0	0.583±0.021	0.25±0.0	0.213±0.025	0.. ±0.	0.0
Tujunga	0.0	0.755±0.080	0.125±0.104	0.158±0.054	1.00±0.0	0.0

Conclusions.

PYDRIN was immobile in all 4 soils

See also first study - Tab 9.

Reviewer Blalock

Leaching

3.6.2 Degradation of Fenvalerate (Sumicidin) in Soil Hideo Okawa and Kenja Nambu. Acc. # 096386, Tab 5, pg 02873, code # AM-70-0036.

Note: Also same data in Tab 6

Experimental Procedure

Soil columns 20 cm depth. Soil was incubated 1 month under aerobic upland conditions (see aerobic). Column eluted with 300 ml H_2O. All 4 soils used and treated with 1.0 ppm ^{14}C-CN or ^{14}C-CO. column size 2.5 cm I.D. x 30cm.

Soil was divided into 0-5, 5-10, 10-15 and 15-20cm. Also rapid leaching study

Analytical Method

1. Soil total ^{14}C

2, Effluents extracted 3 times with ether at pH 1-2 and analyzed by TLC

Results

	% of Total ^{14}C-CN or ^{14}C-CO							
	^{14}C-CN				CN	CO	CN	CO
	LC	SCL	SL	S	LC	LC	SCL	SCL
0-5cm	.3	.2	.2	2.7		1.7	.2	.7
5-10cm				1.6		1.1		.7
10-15cm				1.1		.9		.6
15-20cm				1.6		.3		.5
Effluent			.05	.06		.4	.6	1.2
Total ^{14}C	94.4	93.3	96.9	90.5	52.7	69.1	70.9	60.5

Conclusion

1. The registrant states one degradate 2-(4-chlorophenyl) isovaleric acid was eluted from the soil.

2. ^{14}C-CN or ^{14}C-CO degradates do not leach but moieties of chlorophenyl and dipheny ethers are not determined.

3. The study is unacceptable

4. No recovery data

5. The study may be acceptable if ring label studies are carried out, but by itself they are not.

6. Complete anayltical methodology is not given.

Reviewer Ney

Aged Leaching

3.6.3 The Leaching Behaviour of WL 43775 in Laboratory Soil Columns.
Group Research Report. WKGR.0130.76. (Shell, London) C. Jackson and T. R. Roberts. Nov. 1, 1976. Acc. No. 096386; Tab 9; pg. 02931-02941.

Experimental Procedures.

Sample of WL-43775 labelled in benzyl ring. Glass columns (400x45mm id) were filled with a sandy loam soil (800 g) to approximately 320 mm, and water-conditioned.111 u added to surface of each of 2 columns; 1 column stored for 4 weeks. After 45-day leaching period, leachate and soil sections were analyzed.

Analytical Methods

Column eluate samples analyzed by liquid scintillation counting. Residual soil samples combusted and radiocounted. Soil extract samples separated by TLC on silica gel plates.

Results:

Total radioactivity from eluate of 2 columns was 1.63% (stored) and 0.89% (unstored). No further examination made.

1. The distribution of radioactivity was similar in both columns. About 92% was found in the first 2-cm section.

2. Unchanged compounds we found in the 0-2cm and 2-8cm soil samples by TLC. An unidentified compound was found in the 2-8cm layer (SD 36750,(SD 44607), unknown and bound).

3. Parent and/or degradates did not leach.

4. Soil characteristics not described. Texture not given. Since we do not know soil texture in this study we cannot really determine potential for residues to leach. The study is unacceptable.

5. Reviewer Blalock

3.7 Adsorption

3.7.1 Sorption of SD 43775 on Soils by P. E. Porter. Acces. No. 096385, tab 4, 01209, TIR-14-101-77.

Experimental protocol.

SD 43775 was added to one-gallon glass bottles containing 3500ml water and 5 g Hanford sandy loam. The bottles were shaken for 2h and allowed to settle overnight. Water and soil samples were extracted with heptane and analyzed by LLC.

Results.

SD 43775 is strongly sorbed from aqueous solutions onto soil. Kp or sorption coefficient between soil and water was found to be greater than 15,000 and sorption is only slowly reversible.

Reviewer: Sampson

3.7.2 Sorption of SD 43775 on Soils. P. E. Porter. Acc. No. 09 36; Tab 13; pp. 02957_8. TIR-14-101-77.

Experimental Procedures

3 glass bottles: control, 5 g soil, 10 g (Hanford sandy loam). Used 5 ml of 1.0ug/ml. soln. and shaken. Filtered-water and bottle contents analyzed separately. (Heptane-extracted.)

Analytical Methods.

Analysis by liquid-liquid Chromat (LLC) microporosil col., 4% ether, heptane mobile phase. Recoveries were poor.

Results:

Table 1
EQUILIBRATION OF SD 43775 WITH WATER AND SOIL IN GLASS BOTTLES

Bottle	Additive	SD 43775 Found, ug		% Recovery
		Water Phase	Bottle Contents	
1	None	4.07	1.58	114
2	5 g Soil	2.30	2.12	89
3	10 g Soil	2.78	1.05	77

Conclusions

1. Results uncertain d to poor recovery, but Kp calculated greater than 15,000. (Related to amount of soil used and extracted). Sorbed from water to soil.

2. Reviewer Blalock

3.7.3 Sorption of SD 43775 by Glass and Teflon Surfaces from Aqueous Solutions. J. C. Potter . TIR-22-103-75. Acc. No. 09836; Tab 12; pg 02956.

Experimental Procedures

Chlorophenyl ring-labelled PYDRIN solns studied in teflon and Erlenmeyer flasks; and in glass and polypropylene bottles. At time intervals, aliquots taken for analysis.

Analytical Methods.

Liquid scintillation counting of aliquots taken.

Results.

The following concentrations found after 24-hr interval (calc'd as % of nominal conc.):

glass flask	52
teflon flask	32
glass bottle	10
polypropylene bottle	≤ 2

Conclusions

1. All materials - glass, teflon, and polypropylene - strongly adsorb PYDRIN from aqueous soln, with polypropylene at the greatest rate - at a constant after 3 hours.

2. Reviewer Blalock

3.7.4 Fish Toxicity Studies with SD 43775 Tab 25, Page 03105 Accession No. 096386

Two artificial 'ponds' containing six inches of Hanford sandy loam soil (0.5 to O.M) and 36 inches of water were used for testing. One pond was treated at the rate of 0.1 lb ai/acre with SD 43775. Based on the gallonage in the pond and assuming complete solubility, the applied dosage would be 33.5 Cages of catfish were placed in each pond at intervals up to 55 days after treatment. Analyses of water and mud were made for SD 43775 and fish toxicity was noted.

Surface residue in the treated pond declined from 135 ppb at treatment to about 8 ppb at 14 days. Water residues at 12 inches below the surface peaked at about 10 ppb at 4 days and declined to about 5 ppb at 14 days.

Data on SD 43775 residues in mud are given below:

Sample Analyzed[a]	SD 43775 Found, PPB
Bottom Mud (Untreated Pond)	<10.0
Bottom Mud (Treated Pond)	79.0
Water Line Mud (Treated Pond)	370.0

a) Samples taken 14 days after application

Conclusion

(1). Toxic affects were noted in fish introduced into the treated pond at 14 days. No effects were noted in fish placed in the pond at 55 days after treatment. We defer this to ES Section.

(2). Fenvalerate adsorbs to bottom mud and more highly to water line mud when the pesticide is applied to the surface of a simulated pond.

(3). This is a useful study.

(4) Reviewer Schlosser

3.7.5 Toxicity of Fenvalerate to Killifish (Oryzios latipes) in an aquarium containing soil H. Ohkawa, R. Kikuchi. Tab 24, Page 03099, Accession 09386

Two types of test were conducted with killifish in tanks containing soil. A sandy loam rice field soil was treated with fenvalerate at 20-160 PPM and spread on the bottom of a glass aquarium. 10 liters of water were added to the 1.25 kg of treated soil. After 5 days, concentrations of fenvalerate in the aqueous layer were measured and killifish were introduced. In a second test, fenvalerate was applied to the aqueous layer of the aquarium containing 10 liters of water and 1.25 kg of soil. The aqueous layer was stirred for 5 min. Fish were added at intervals.

In the case where treated soil was added to water the concentration of fenvalerate in the aqueous phase reached 0.070 to 1.311 PPM after 5 days. When fenvalerate was added to aquariums containing soil, the concentration in the aqueous layer decreased to 1/10 to 2/5 of the initial levels 3 hours after addition and 1/50 to 1/5 of the initial levels after 24 hours.

Fish toxicities based on fenvalerate concentrations were noted that were significally lower than that found under standard assay procedures were noted during this experiment.

Conclusion:

(1) Fenvalerate is adsorbed from aqueous solution to soil and/or glass, and is desorbed from treated soil to water.

(2) The toxicity of fenvalerate to fish appeared to be lower in the systems studied here than under standard bioassay procedures.

(3) Reviewer Schlosser

3.7.3 Runoff Study-Field Trial at BSRC. (To Collect residue samples of runoff water and soil following a simulated rain on soil treated with SD 43775). Test SD 43775. 76-1. Western District. Acc. No. 09386; Tab 11, pgs. 02984-54.

Experimental Procedures

Study done 1/23/76 in Modesto, California on Hanford sandy loam by J. J. Skelsey. Used 2.4EC (Code 5-2-8-5), 0.8 lb ai/acre (broadcast application). Band 20ft. long x 6" wide across raised end of inclined (8% slope) bed. A pipe with 5 nozzles simulated rain; averaging 1700 ml/min. The 5 catch basins were the following distances: 12", 36", 56", 72", and 97". One pint samples (water + mud) taken after 30 minutes; 2 check plots similarly watered.

Analytical Methods.

Samples homogenized; 2 aliquots taken, one filtered. Each aliquot partitioned with hexane/ethyl acetate and centrifuged. GLC-ec(SC^3H). The MDC (min. detect. conc.) was as follows: filtered water - 0.5 ppb; unfiltered - 2.0 ppb.

Results.

In recovery studies, 120% recovered in both sample types.

The sample analyses are as follows:

Sample	SD 43775 Dosage, lb a.i. per Acre	Length of Run, Inches	Sd 43775 Residue Found, PPB
Filtered Water	None	12	0.5
" "	0.8	12	0-5
" "	"	36	1.0
" "	"	56	0.5
" "	"	97	0-5
Unfiltered Water	None	36	2.0
" "	0.8	12	310.0
" "	"	36	170.0
" "	"	56	37.0
" "	"	72	6.0
" "	"	97	3.0

Conclusions

1. This study is not required. It does give an indication that PYDRIN will runoff with soil particles.

2. Reviewer Blalock

Conclusion:

(1) SD 43775 is strongly sorbed from aqueous solutions onto soil surface. The reaction appears to be only slowly reversible.

(2) Data indicate that SD 43775 would run off from treated area with soil particles.

(3) In artificial ponds, fenvalerate adsorbs to bottom mud and more highly to water line mud when the pesticide ? ? ?

3.8 Field Dissipation Studies

3.8.1 Dissipation of SD 43775 in Soil at Wenatchee, Washington, Report No. TIR-24-312-75. Tab 14 Pg.02959, Acc. No. 096386

Experimental Procedure:

The 2.4 EC formulation of SD 43775 was applied at rates of 0.5 and 2.5 lbs ai/acre by a hand gun at low pressure using water as a carrier to 20' square plots of bare soil. One application was made to a soil textured at 65% sand, 25% silt, and 10% clay. Paraquat had been applied to this soil three weeks prior to the PYDRIN application at a 0.25 lbs ai/acre rate.

One-inch core samples were taken from a 0 to 3 inch depth at 0, 7, 12, 29 and 90 day intervals frozen.
Analytical Method:
Samples were extracted with a Braunsonic ultrasonic generator in the presence of a hexane-dimethylketone solution. Aliquots were subjected to Florisil Column chromatography for clean-up and GLC with a scandium tritide EC detector for quantitation.

Results

Analyses of soil samples (0.3 inch depth)

SD-43775 dosage lb ai/acre	Days after Application	SD 43775 Residue Found in ppm	
.05	0	0.25	
0.5	7	0.17	$T_{1/2}$=35 days
0.5	14	0.19	
0.5	29	0.13	
0.5	90	0.	
2.8	0	2.50	
2.5	7	1.50	$T_{1/2}$= 5 days
2.5	14	0.99	
2.5	29	1.20	
2.5	90	0.12	

Conclusions:

The study showed SD 43775 dissipating in the first 3" of soil after 90 days to 0.08 ppm for the 0.5 lb ai/acre application and 0.1 ppm for the 25 lb ai/acre application.

1. Soil Samples were not taken in increments to a depth of 12 inches - only to 3 inches.

2. One cannot tell if the residue data have been corrected to reflect the variation in recovery from the analytical method which ranged from 71-105%.

3. No explanation is given for the loss on 0 day for the 0.5 lb/acre application. a 50% loss. No crops were present. On the 90th day at this concentration 0.08 ppm is less than a 90% loss (0.05 ppm).

0.5 lbs ai/A was applied and 0.25 lbs ai/A was recovered,

The test should have been run for a longer period of time.

4. Although the above deficiencies were noted, they do not need to be corrected in that this study cannot be accepted because the mode of application does not reflect actual use patterns (0.05-0.2 lbs ai/acre x 10 applications (year). The study was conducted in Washington which is not a typical cotton growing area. Analyses were not made for degradation products.

3.8.2 Dissipation of SD 43775 in soil at Monroe, La., Report No. TIR-23-127-75, Pg. 02970, Tab. 15, Acc. No. 096386.

Experimental Procedure:

The 2.4 EC formulation of SD 43775 was applied to bare soil at rates of 0.5 and 2.5 lbs. ai/acre by broadcast spray to a random block test plot (8 rows by 50 feet). One application was made to a silt loam soil. No other chemical had been applied. Eight subsamples were taken from the 0-3 inch depth and composited at 1,8, and 19 day intervals and frozen.

Samples were extracted with a Braunsonic ultrasonic generator in the presence of a hexane-dimethyl ketone solution. Aliquots were subjected to Florisil Column chromatography for clean-up and GLC with a scandium tritide ED detector for quantitation.

Results:

Analyses of soil samples (0.3 in. depth)

SD 43775 dosage lb ai/Acre	Days after Application	SD 43775 Residue Found in ppm
0.5	1	0.32
0.5	8	0.14 $T_{1/2}$=12 days
0.5	19	0.11
2.5	1	1.5
2.5	8	0.95 $T_{1/2}$=24 days
2.5	19	0.86 (extrapolated value)

Values ranged from 81-104% from spiked sample analyses to test recovery from the analytical method.

Conclusions

1. This study showed SD 43775 dissipating in the first 3 inches of silt loam soil after 19 days to 0.11 ppm for the 0.5 lb ai/acre application and 0.86 ppm for the 2.5 lb. ai/acre application. The decline curves showed a $T_{1/2}$=12 days for the 0.5 lb/acre concentration and $T_{1/2}$=24 days for the 2.5 lb/acre concentration. The latter was a predicted $T_{1/2}$ since it is greater than the maximum test-time interval. Its validity should be carefully evaluated.

2. Soil samples were not taken in increments to a depth of 12 inches - only to 3 inches.

3. One cannot tell if the residue data have been corrected to reflect the variation in recovery from the analytical method which ranged from 81-104%.

4. Although the above deficiencies were noted, they do not need to be corrected in that this study cannot be accepted because the mode of application does not reflect actual use patterns (0.05-0.2 lbs. ai/acre x 10 applications/year.)

5. Reviewer Garner

3.8.3 One-Year Study of the Fate of ^{14}C-SD 43775 in Soil, H. Y. Fan, Rept. No. TIR-22-107-77, Pg. 02989,Tab 17, Acc No. 096386

Experimental Procedure

Chlorophenyl-ring-labeled ^{14}C-SD 43775 in an aqueous emulsion was applied to Hanford sandy loam soil at a rate of either 0.125 lbs ai/acre 4 times at 4 week intervals or once at 0.25 lbs ai/acre. The soil contained in 5-gallon glazed crocks with bottom outlets was placed in an outdoor enclosure. Samples of 0-3, 3-6, 6-9 and 9-12 inches were taken at various time intervals (4,8,12,16, and 21 weeks and 7 and 11 or 12 months) and frozen until analyses.

Analytical Method:

Soxhlet extraction with methanol for 48 hours was used for all soil extractions. Aliquots of the methanolic extracts were chromatographed on Silica Gel thin layer in solvent systems of hexane: EtOAc: THF (80:16:4 v/v)and hexane: $CHCl_3$ and acetic acid (90:10:5). Radioautography was employed. Unextractable ^{14}C residues in soil were combusted. GLC-MS was used to analyze for SD 43775 and its metabolites. A total of 7.36 inches of rainfall was recorded during the experimental period, and approximately 16.5 inches of water was used for irrigation during the growing season.

Recovery of Radioactivity at Various Time Intervals and Soil Levels in 0.125 and 0.25 lbs/acre Applications Expressed as %-age of Originally-Applied ^{14}C-SD 43775.

Time Intervals	Soil Level: 0-3 Inches		3-6 Inches		6-9 Inches		9-12 Inches	
	Dose: 0.125	0.25	0.125	0.25	0.125	0.25	0.125	0.25
4 Weeks	93.1	75.9	0.0	9.0	0.0		0.0	0.0
A 2)	73.4	73.3						
B 3)	8.6	7.5						
8 Weeks	70.7	68.3	2.4	1.5	0.2	0.0	0.5	0.6
A	61.4	55.6						
B	13.9	13.8						
12 Weeks	68.6		1.0		0.1		0.1	
A	39.5							
B	22.3							
16 Weeks	56.2	43.3	1.0	2.4	0.2	0.2	0.1	<0.1
A	32 4	24.1						
B	24.8	21.4						
21 Weeks	34.4		15.0		10.3		1.8	
A	22.5		10.4		8.2			
B	10.5		6.1		2.8			
7 mos(0.125) 8 mos(0.25)	27.9	31.2	9.7	2.6	1.8	0.7		0.3
A	12.9	13.7	5.9	1.4	1.1			
B	15.3	17.9	3.5	1.3	0.7			
11 mos.	22.0		4,6		2.7		0.6	
A	9.8		0.9		1.5			
B	13.4		3.5		1.4			
12 mos.		28.1		1.3		0.4		0.1
A		8.7						
B		16.4						

1) Radioactivity of soil before MeOH extraction

2) Radioactivity of MeOH extract from soil

3) Radioactivity of soil left after MeOH extraction

Conclusions:

1. With a few exceptions, as noted in the table, nearly all of the ^{14}C left in the soil was in the top 3 inches indicating that there is very little movement of SD 43775 or its metabolites in soil. Some ^{14}C leached to lower soil levels in the latter part of the experiment for both application rates; however, since only a very small amount of leaching was found in the 0.25 lb/acre trial, the higher leaching rate for the 0.125 lb/acre application may be partly attributed to a channeling effect.

2. The extraction efficiency of ^{14}C from soil treated with MeOH decreased with the increasing age of the ^{14}C-treated soil from over 85% down to 30% over the 12-month period for the 0.25 lb/acre application.

3. Half lives of SD 43775 in soil were approximately 6 weeks for the 0.125 lb/acre application and 4 weeks for the 0.25 lb/acre application. After soil exposure for 1 year 5% of the applied material was the parent compound.

4. Diastereoisomers of SD 43775 of equal intensity were resolved using GLC-MS.

5. Based on the estimated %-age of originally applied radioactivity to soil it was found that about 1.48% of the material had the same R_f value as the Amide, SD 47117, after 12 months. The author concluded from co-chromatography that diastereoisomers formed for the amide also.

6. Although soil characteristics were given for the Hanford sandy loam soil, this study is unacceptable in that the amounts of material applied did not reflect actual use patterns, and sampling times did not include pre-application, day of application, or immediately, post-application for multiple applications. Tests

were not run in # agricultural use areas.

Reviewer Garner

3.8.4 1977 - Residue Data for SD 43775 in Soil Resulting from Ten Applications of SD 43775 to Cotton Plants, a Texas Study, Report No. TIR-24-232-77, Pg. 02979, Tab 16, Sec. No. 096386.

Experimental Procedures:

The 2.4 EC formulation of SD 43775 was applied to cotton at the squaring stage at rates of 0.1, 0.2 and 0.4 lbs ai/acre by a tractor boom sprayer. Ten applications were made at weekly intervals. The test plot of sandy loam soil containing 8 rows 50 feet long had been previously sprayed with Treflan herbicide at 0.5 lbs. ai/acre prior to planting.

Ten soil cores (0-3 inches) were taken from each of 2 replicates to form a composite sample immediately after the 10th spraying. Soil was sandy loam (<1%om).

Analytical Method:

Samples were extracted with a Braunsonic ultrasonic generator in the presence of an acetone/hexane (1:1) solution. Aliquots were subjected to Florisil column chromatography for clean-up and GLC with an EC detector for quantitation.

67-75% was recovered from samples spiked with 0.05 and 0.1 ppm SD 43775 respectively to monitor the analytical method.

Results:
Analyses of Samples (0-3 in. cores)

SD 43775 dosage lb. ai/acre	Days after final treatment	SD 43775 Residue Found in ppm
0.1	0	0.11
0.1	0	0.12
0.2	0	0.18
0.2	0	0.21
0.4	0	0.37
0.4	0	0.43

Conclusion

1. Since cotton plants were being sprayed and less ... material reaches the soil, this study shows some build-up in the soil of SD 43775 after 10 applications (data in table); however, it is not known if the residues found have been corrected to reflect the 67-75% recovery rate noted in monitoring the analytical method.

2. Soil Samples were not taken in increments to a depth of 12 inches - only to 3 inches.

3. The 0.1 and 0,2 lbs ai/acre x 10 applications/year do reflect actual use patterns; however, soil samples were not taken at post-application intervals to determine a T½.

4. This is not considered a dissipation study.

5. Reviewer Garner

3.8.5 1977 - Residue Data for SD 43775 in Soil of a Cotton Field Resulting from One Foliar Application to the Cotton, a California Study, Rept. No. TIR-24-256-77, Pg. 03034, Tab. 19, Acc. No. 096386.

Experimental Procedure:

The 2.4 EC formulation of SD 43775 was applied to cotton plants 3 feet high at rates of 0.2 and 0.4 lbs. ai/acre by spray delivered from a Hahn Hi-Boy with

800067 T-jet nozzles operated at 55 psi. A single application was made to a Hanford sandy loam soil test plot containing 16 rows 55 feet long. No other chemical had been applied to the soil.

Twenty core samples per application rate were taken within one hour of application. Cores consisted of a 2.5" deep x 1" diameter glass vials containing approximately 42 g. soil placed in rows and furrows prior to application. 6 or 7 replicate cores were combined to form a composite sample.

Analytical Method:

Samples were extracted with a Braunsonic ultrasonic generator in the presence of an acetone/hexane (1:1) solution. Aliquots were subjected to Florisil column chromatography for clean-up and GLC with an EC detector for quantitation.

100-97% was recovered from samples spiked with 0.05 and 0.1 ppm SD 43775, respectively to monitor the analytical method.

Results:

Analyses of Samples (Application made to the cotton plants)

SD 43775 dosage lb ai/acre	Days after Final treatment	SD 43775 Residue Found in ppm
0.2	0	0.03
0.2	0	0.05
0.2	0	0.02
0.4	0	0.06
0.4	0	0.10
0.4	0	0.08

Conclusion:

The only value of this study is the conclusion that very little PYDRIN reaches the soil when 3 feet tall cotton plants are sprayed; therefore, the study is supportive only.

This is not considered a dissipation study.

3.9 Rotational Crops

3.9.1 1976 - Residue Data for SD 43775 in Rotation Crops (Onions and Sorghum) Following Eight Applications of SD 43775 the Previous Year to Cotton. A Texas Study. Acc # 096386, Tab 20, Pg. 03041, TIR-24-125-76.

Experimental Procedure:

Sandy loam soil (1%OM) treated with 0.2 or 0.4 lbs A/A eight times with 2.4 EC formulations.

Onions (yellow Granex) and Grain sorghum (Acco 109) Onions planted 10/22/75 and sorghum on 3/16/76. Last application on 7/29/75 at cotton squaring. Onions sampled 3/13/76 and sorghum 7/12/76 all at full maturity. Onions 228 d and sorghum 349 d after last treatment.

Analytical Method

MMS-R-456-1 Determination of SD 43775 Residues in Crops Election Capture G S Chromatographic Method. Blend with hexane/IPA. Remove IPA with H_2O, column clean on Florisil and elute with hexane/ethyl acetate.

Results

	Treated area 8 applications at 0.2 UsA/A PH±	ppm Found(Parent)	0.4 lbs A/A ppm Found
Onion Tops	228	∠0.01	∠0.01
Peeled Onion	228	∠0.01	∠0.01
Whole onion	228	∠0.01	∠0.01
Sorghum Heads	349	∠0.01	∠0.02
Sorghum Stalks	349	∠0.01	∠0.02

1. Onions 85 days from treatment to planting - planting to harvest 228 days

2. Sorghum 231 days treatment to plant and planting to harvest 119 days.

Conclusion:

1. A crop rotation restrictions of 1 year will be needed on the label based on this study.

2. Applications of 8 times a year at 0.2 and 0.4 lbs A/A are supported by 1 year rotational crop restriction.

3. Analysis only for parent compound. We need residue metabolism studies to support that only parent is unavailable to crop. Only parent compound was considered by Chemistry Branch.

4. No soil characteristics submitted .

5. Complete analytical method not submitted.

6. We need to know the amount of residue in soil .

3.9.1 1977 - Residue Data for SD 43775 in a Rotation Crop (Wheat and Vetch) Following Nine applictions of SD 43775 the Previous Year to Cotton, A California study Acc. # 096386, Tab 21, Pg 03069, TIR-24-145-77.

Experimental Procedure

Hanford sandy loam (0.5-1% OM) treated at 0.2lbs A/A 9 times with 2.4 EC formulation. Wheat and Vetch as a cover crop were rotated. India 66R(Wheat) and purple vetch.

The first application to cotton was 8/4/76 and last application 9/10/76. On 5/10/76 Treflan (0.5lbs/A was also applied. Wheat and vetch were planted 11/18/76 and harvested 4/14/77.

Analytical Method

MMS-R-456-1. This method has the same MMS-R-456-1 number as method under Tab 20.

This is an ECGC method (Ni^{63} detector)

Results

	lb Ai/A	Last App. To Plant	Plant to Harvest	SD 43775 PPM
Wheat/Vetch	.2x9=1.8	69	147	.01

crop 3 feet, wheat in bloom

Conclusion

1. Residues of parent (SD 43775) were not found in wheat/vetch cover crop plant 69 days after last treatment and harvest 147 days after planting.

2. Soil characteristics not given.

3. Complete analytical method not given.

4. It assumes spring wheat PHI is closer to cotton agricultural practice.

5. We need to know the amount of residue in soil.

3.9.3 Residues Studies in Rotation Crops in ^{14}C-SD 43775 - Treated Soils. Hy. Y. Fan. Acc # 09386, Tab 18 pg.03620 Shell TIR -22-113-77.

Experimental Procedure

Hanford Sandy Loam
^{14}C-chlorophenyl and ^{14}C-phenoxyphenyl ring compound used.
Treatment 1 lb/A.

Analytical Method

1. LS for ^{14}C-chlorophenyl

2. GLC with EC ^{63}Ni detector
   Table beets extracted methylene chloride and then CH_3CN combined, taken to dryness, extracted with hexane.
   Beet tops extracted with hexane and isopropanol, H_2O extract to remove isopropanol.
   Beets and tops cleaned up and chromatographed.

Results	lbs/A	Treatment to Planting	Treatment toHarvest	^{14}C-Chloro-phenyl ppm as SD 43775	^{14}C-phenc phenyl ppm as SD 43775
Crop					
Sugar Beet Tops	1	1 mo.	4 mo.	.017	
Peel	1			.01	
Beet				.005	
Alfalfa	1	11 mo.	4 mo.	.02 (GLC GLC-MS ^{14}C)	
Table Beets Tops	2	120 d	8 mo.	.064(.019 .013 .008)	
Beet				.122(.01 .03 .014)	
Wheat Kernel	2	120 d	8 mo.	.011	
Bran				.011	
Straw				.044	
Broccoli	2	120 d	4½ mo.	.022	
Table Beets Top	1	120 d	8 mo.		.04
Beet					.04
Wheat Kernels	1	120 d	8 mo.		.004
Bran					.005
Straw					.008
Broccoli	1	120 d	4½ mo.		.004

The 2 lb/A rate is the 1 lb rate and one year later another 1 lb/A rate. Sugar beets and table beets were 1 month old seedlings when planted

Conclusions:

1. Residues appeared to increase in rotational crops from one year to the next. This is indicated in the ^{14}C-choroplenyl study were soil was treated at 1 lb/A and 11 months later another 1 lb. Crop plant 120 days later and harvested 4 and 8 months- Beet crops and higher residues. Hexane extraction and analysis of residues in beets by GLC, GLC-MS and ^{14}C showed very little SD 43775 <.019 ppm and ^{14}C extractable <0.01 The remainder must have been tied in plant. The registrant had no data on that.

2. Crop maturity was not realistic to agricultural practice.

Crop	Maturity	Not
Broccoli	60-75 day	4½ mo.
Sugar beets	160-215	8 ,
Table Beets	50-100	8 mo.
Alfalfa	Seed 130-200, Hay 85-130	4 mo.
Wheat	Spring 110-170, Winter285-310 D.	8 mo.

3. The ^{14}C-phenoxyphenyl did not present a problem. Residue of this moiety are not likely to appear in rotational crops.

4. Soil characteristics were not given.

5. The complete analytical method is not submitted.

6. Recovery data was not submitted.

7. We need to know the amount of residue in soil. Without this we do not know that the chemical or its degradates are present.

3.9.4 1975 - Residue Data For SD 43775 in Rotation Crops (Alfalfa, Potatoes, Wheat, and Soybeans) From a simulated Rotation Study. A California Study, Acc #096-386, Tab 27, Pg 03148, TIR-24-201-75.

Experimental Procedures

Sandy loam soil (<1%) treated with 0.1 or 0.5 lbs/A in gal/A with 2.4 EC formulation 1 time. Dalthol was applied at 6 lb/A in 1972. Application made 5/8/75; crops rotated (planted) 6/5/75; harvested 7/29/75 and 9/11/75

Analytical Method

1. Method number not given this time. Samples extracted with hexane, partition in CH_3CN, column clean on florisil and determined by EC GLC with Ni63 detector. Appears to be same method as in Tab 21

Results

Alfalfa rotated in areas treated at 0.1 and 0.5 lbs Ai/A was planted 28 days after treatment and harvest

52 days later. Residue less than 0.01 ppm SD 43775.

Potatoes, wheat and soybeans also rotated 28 day after last application and harvest 98 days later. Residues in potato (pulp and peel), wheat head and soybean (beans, pod and vines) was less than 0.01 ppm SD 43775.

Conclusion

1. This study does not represent actual use pattern.

2. The study does show residues were not taken up by one application.

3. The complete analytical method is not given as referenced.

4. Soil characteristics were not given.

5. We need to know the amount of residue in soil.

3.9.5 1977 - Residue data for SD 43775 in rotation crops (Sugar Beets, soybeans and Sorghum) following nine applications of SD 43775 the previous year to cotton. A California Study Accession No. 09700, Tab 14, Page 00251 TIR-24 145-77-B

Sugar beets, soybeans, and sorghum were grown in soil in 1977 that had been planted to cotton in 1976 and 1975. The plot received 11 applications of SD 43775 at 0.2 lb ai/acre between 7/17 and 9/26/75. Nine applications were made at the same rate in 1976 on the following dates 8/4, 8/9, 8/13, 8/18, 8/23, 8/17, 9/1, 9/7 and 9/10. The formulation was 2.4 EC; and the location of the plots was Modesto, California. Soil texture is indicated as Hanford sandy loam with 0.5 to 1.0% Organic matter.

Planting date for all crops is given as June, 1977. Sampling date 10/4/77. Growth stage at sampling indicated as 'harvest'.

Estimated interval between last application and planting - 9 months.

Analytical Method

Analysis was for SD 43775 only. Initial extraction of representative sample in presence of hexane/IPA using high speed blender is followed by filtration, solvent partitions, column chromatography on activated Florisil and quantitation by GLC with EC detection.

Recovery data are given below:

Sample	SD 43775 Fortification Level, ppm*	%Recovered by Analysis
Sugar Beet Roots	0.05	110
" " Tops	0.1	93
Soybeans	0.05	110
Soybean Vines	0.1	94
Sorghum Stalks	0.1	110

*The SD 43775 was added to portions of sample before extraction and analyses were performed to monitor the analytical method.

Analytical Results:

Residues were <0.01 PPM SD 43775 for all plant samples reported. These include sugar beet roots, sugar beet tops, soybeans, soybean vines, Sorghum heads and sorghum stalks.

Typical chromatograms given on pages 00271 to 00277 show single peaks for SD 43775 in some cases and double peaks in others. This should be explained. Sample calculations using data from these chromatograms are needed.

Conclusions:

(1) It appears from the data submitted that there were no detectable residues of SD 43775 (0.01 PPM) in sugar beets, soybeans and sorghum planted in areas previously treated with PYDRIN 2.4 EC. Interval from last application to planting was 9 months. Maximum dosage rates and numbers of repeat applications were reflected in this study.

However the presence of double and single peaks in typical chromatograms needs to be explained. Sample calculations based on these chromatograms are also needed .

(2) Residue data are for parent compound only. No data are given for possible residue of metabolites or degradations products in the rotational crops studied.

(3) Soil residues at time of planting are not given.

3.10 Fish Residue Accumulation:

3.10.1 Residues of ^{14}C and SD 43775-^{14}C in fish exposed to SD 43775-^{14}C J. C. Potter Tab 22, Page 03085, TIR-22-105-76 Accession No. 096386

Residues of ^{14}C and SD 43775-^{14}C in fish exposed to SD 43775-^{14}C J.C. Potter Tab 23, Page 03090, TIR -22-105-76. This is an addendum to the study cited above (Tab 22) and contains additional experimental details, data presentations and explanations.

Experimental Procedure:

Rainbow trout were exposed to water containing SD 43775 -^{14}C (locked in the chlorophenyl ring) at 0.20-0.27 PPB for periods as long as 35 days. This was followed by exposure to untreated water for 33 days. Water pH is given as 7.9 tc 8.5. During the exposure period water was aerated continuously and fish were transferred every three or four days to freshly treated water.

Analytical Method

The edible portion only (skin, head and viscera removed) of the fish were analyzed for total ^{14}C and SD 43775 by GLC (EC-tritium detector). Fish were macerated, extracted with CH_3CN, partitioned between CH_3CN and acetone, column cleaned on Florosil and quantitated by EC-GLC. The complete method is not given. Some of the data are tabulated below:

TOTAL ^{14}C RESIDUES IN FISH

Days	Fish	Total ^{14}C Residues: Group I — ppm Equivalents ± Probable Error of Mean [a,b]	Group II — No. of Fish	Group II — ppm Equivalents ± Probable Error of Mean [a,b]
Exposure Period:				
1	1	0.0037 ± 0.0002	--	--
3	1	0.0062 ± 0.0004	--	--
5	2	0.017 ± 0.0004 [c]	--	--
10	2	0.022 ± 0.0003 [c]		
15	1	0.024 ± 0.002	--	--
20	3	0.053 ± 0.002 [c]	--	--
30	1	0.057 ± 0.004	--	--
35	2	0.055 ± 0.007 [d]	2	0.087 ± 0.005 [d]
Clearing Period:				
1	--	--	1	0.071 ± 0.0006
3	--	--	1	0.062 ± 0.0004
9	--	--	1	0.058 ± 0.0002
19	--	--	4	0.038 ± 0.006 [d]
33	3	0.030 ± 0.002 [d]	--	--

a) Mean of duplicate analysis; probably error of mean of replicate analysis
b) Counting efficiency = 22,675 cpm/ug (P.E.M. = 105 cpm/ug; 17 determinations) or 0.7817 (ratio cpm to dpm); background = 31-32 cpm.
c) Fish carcasses composited prior to analysis.
d) Each fish analyzed separetely; mean ± probable error of mean of replicate fish.

COMPARISON OF ^{14}C RESIDUES AND SD 43775 IN FISH

Days	^{14}C Residues [a], ppm Equivalents	SD 43775 Residues [b] PPM
Exposure Interval:		
5	0.017 ± 0.0004	0.017
10	0.022 ± 0.0003	0.019
20	0.050 ± 0.002	0.041
35	0.055 ± 0.007 [c]	0.050
Clearing Period:		
19	0.038 ± 0.006 [c]	0.031
33	0.030 ± 0.002 [c]	.029

(Continued from table on last page)

a) Mean ± Probable Error of Mean.
b) Determined by GLC equipped with electron capture detector.
c) Each fish analyzed separately prior to being composited for GLC analysis.

Table 1. TOTAL ^{14}C RESIDUES IN WATER IN PPB EQUIVALENTS ± P.E.M.

Experiment I			Experiment II		
Treatment Day	Tank A	Tank B	Treatment Day	Tank C	Tank D
0		0.29 ± 0.03	0		0.20 ± 0.007
1		0.15 ± 0.001			0.28 ± 0.01
2		0.10 ± 0.002			0.22 ± 0.006
3	1.4 ± 0.38	0.09 ± 0.14	3	0.23 ± 0.001	0.19 ± 0.001
5	0.11 ± 0.01				
10	0.24 ± 0.008	0.11 ± 0.003	10	0.26 ± 0.008	0.16 ± 0.002
15		0.17 ± 0.01	15		0.17 .01
20	0.21 ± 0.011		20	0.18 ± 0.002	
30		0.14 ± 0.007	24.	0.32 ± 0.008	0.20 ± 0.001
			30	0.22 ± 0.004	→
35	0.14 ± 0.007		34	0.18 ± 0.001	
			35	0.21 ± 0.01	

Some calculated Bioaccumulation Ratios for edible tissue are given below: (PPB equivalents in tissue/PPB equivalents in water)

	Exposure period	Ratio
Group I	5 days	154
	10	91
	15	141
	20	252
	30	407
	35	392
Group II	35	414

Conclusions:

(1) SD 43775 accumulated in edible tissue of rainbow trout to approximately 400X the nominal concentration in water after about 30 days of exposure.

(2) Fish residues were roughly 90% parent compound as indicated by GLC analyses.

(3) Depuration was relatively slow with about 40-60 of residual activity remaining after 33 days of withdrawal, virtually all as intact parent compound.

(4) No radioassay or chemical analyses was done on other edible portions of the fish tissue. Treated water was not chemically analyzed.

310.2 ^{14}C and SD 43775 residues in catfish exposed to a water/soil suspension treated with SD 43775-^{14}C. J. C. Potter, G. F. Barber, and C. R. Sauls. TIR-22-102-78 Page 00216 Tab 13, Accession No. 097000.

Hanford sandy loam was treated with SD 43775-^{14}C (chlorophenyl labeled) at nominal concentrations of 0.01 and 1.0 PPM. The soil was moistened and aged for 30 days in an outside environment. Aged soil was added to stainless steel tanks and water added at a ratio of one part by weight of soil to 99 parts by weight of water. Catfish were placed in the tanks and held for periods as long as 30 days followed by a depuration period in clean water for up to 76 days. During exposure, water in each tank was aerated continuously. To avoid the accumulation of excretion products about one-half of the water was removed from the tanks and replaced with fresh water after exposures for 7, 14, and 21 days. Fish samples were taken at intervals, combusted and ^{14}C residues were determined. A few selected samples of fish tissue from the 1.0 PPM soil treatment were analyzed for SD 43775 by GLC. Some of the data for the 1.0 PPM soil treatment are given below.

TOTAL ^{14}C RESIDUES IN FISH

Total ^{14}C Residues, ppm Equivalents

Treatnent, Day	1.0 ppm Soil Treatment		
	Meat	Carcass	Viscera
5	0.038	0.069	0.11
9	0.034 ± 0.0001	0.056 ± 0.003	0.11 ± 0.02
15	0.030 ± 0.006	0.073 ± 0.001	0.18 ± 0.08
19	0.022 ± 0.001	0.050 ± 0.007	0.14 ± 0.01
20	0.033 ± 0.003	0.047 ± 0.002	0.16 ± 0.04
25	0.026 ± 0.005	0.059 ± 0.009	0.12 ± 0.01
30	0.020 ± 0.002	0.038 ± 0.005	0.17 ± 0.02
Clearing, Day			
5	0.016 ± 0.003	0.041 ± 0.004	0.12 ± 0.01
14	0.017 ± 0.004	0.028 ± 0.003	0.062 ± 0.003
25	0.013 ± 0.003	0.030 ± 0.001	0.13 ± 0.04
35	0.016 ± 0.002	0.027 ± 0.003	0.068 ± 0.012
46	0.005 ± 0.003	0.021 ± 0.0004	0.059 ± 0.004
55	0.006 ± 0.0	0.025 ± 0.001	0.044 ± 0.017
66	0.007 ± 0.003	0.018 ± 0.001	0.022 ± 0.004
76	0.004 ± 0.001	0.018	0.028 ± 0.012
76	0.001	0.012	0.040

Total ^{14}C in Water
1.0 ppm Soil Treatment[a] in ppb Equivalents

	Tank E			Tank F			Tank G			Tank H		
Day	Filtrate	FP +S[c]	Total	Filtrate	FP+S[c]	Total	Filtrate	FP+S[c]	Total	Filtrate	FP+S[c]	Total
1	0.4310.02	0.61	1.04	0.40±0.01	0.49	0.89	0.43±0.01	0.94	1.37	0.5310.04	0.81	1.34
7	0.86±0.01	0.21	1.07	0.80±0.03	0.14	0.94	0.95±0.02	0.24	1.19	0.96±0.01	0.26	1.22
14	0.34±0.003	0.06	0.40	0.30±0.01	0.13	0.43	0.47±0.01	0.28	0.75	0.38±0.02	0.32	0.70
21	0.54±0.02	0.03	0.57	0.63±0.01	0.03	0.66	0.89±0.01	0.10	0.99	0.73±0.01	0.09	0.82
28	0.37±0.001	0.04	0.41	0.42± 0.002	0.03	0.45	0.70±0.01	0.10	0.80	0.55±0.02	0.14	0.69

a) Filtrate mean of duplicate determination; solids single determination.
b)
c) FP+S - Filter Paper + Solids; ^{14}C in solids retained on filter paper.

^{14}C Residues in ppm Equivalents vs. SD 43775 Residues in ppm

		Carcass				Viscera				Meat			
Days	Soil Level, ppm	Total ^{14}C[a] (ppm)	^{14}C in Extract[b] (ppm)	SD 43775 GLC (ppm)	GLC/Total ^{14}C,%[c]	Total ^{14}C[a] (ppm)	^{14}C in Extract[b] (ppm)	SD 43775 GLC (ppm)	GLC/Total ^{14}C,%[c]	^{14}C,%[c] (ppm)	^{14}C in Extract[b] (ppm)	SD 43775, GLC (ppm)	GLC/Total ^{14}C,%[c]
Exposure Days:													
9	1.0	0.056	0.042	0.024	43	0.11	0.049	0.031	28	0.034	--	0.015	45
30	1.0	0.038	0.035	0.022	58	0.17	0.14	0.090	53	0.020	--	0.014	70
Clearing Period in Days:													
76	1.0	0.012	0.015	0.012	100	0.04	0.045	0.035	88	0.003	0.003	0.010	330

a) Total ^{14}C by combustion; see Table 7.
b) Carbon-14 in extract after chromatography on Florisil.
c) Ratio of total residues of SD 43775 to total ^{14}C in percent.

TOTAL ^{14}C RESIDUES VS. SD 43775 RESIDUES

Treatment Day	^{14}C Residues in ppb Equivalents and SD 43775 Residues in ppb[a]		
	^{14}C in Water[b]		SD 43775[c] (GLC)
7	Filtrate	0.89	Filtrate ∠0.05, Solids 0.05[d]
	Filter Paper + Solids	0.21	
	Total	1.10	
21	Filtrate	0.70	Centrifugate 0.045[e]
	Filter Paper + Solids	0.06	
	Total	0.76	
28	Filtrate	0.51	Centrifugate 0.041[e]
	Filter Paper + Solids	0.08	
	Total	0.59	

a) Water from 1.0 ppm soil treatment.
b) Total ^{14}C in water by filtration method from Table 13.
c) SD 43775 determined by GLC.
d) Water and suspended soil separated by filtration.
e) Water and suspended soil separated by centrifugation at 875 g's.

In the case of the 0.01 PPM soil treatment study, all total ^{14}C Residues (PPM Equivalents) in fish were below 0.001 except in one case, (the 14th day of clearing) where a residue of 0.0012 ± 0.0009 PPM was found in the carcass. Failure of airconditioning on day 19 of exposure was claimed to be the cause of the death of 10 fish at this time. Calculated ^{14}C residues (PPM equivalents) in whole fish are reported as follows: Treatment day 15, 0.067; day 20, 0.051 and day 30, 0.044; clearing day 5, 0.040; day 46, 0.020 and day 76, 0.014.

Analytical Methods:

Soil - Initial Soxhlet extraction with acetone. A liquid-solid chromatography step using Florisil absorbent is included. SD 43775 only is determined by GLC-EC using a 63Ni detector. Water - Initial extraction with hexane, liquid-solid chromatography using Florisil absorbent and determination of SD 43775 by GLC-EC using the same instrumental parameters as for soil. Fish - Homogenized sample is blended in the presence of hexane/IPA. After reextractions with acetonitule and hexane and cleanup on Florisil, SD 43775 is determined by GLC-EC with the same instrumental parameters as for soil and water. Limts of detection are reported as 0.01 PPM for fish and soil and 0.05 PPB for Water. Using data for water residues on treatment day 28 and fish residues at day 30 the following bioaccumulation ratios are calculated. Water residues: Filtrate 0.51 ppb equiv., total 0.59 ppb equiv., SD 43775 (GLC) - 0.041 ppb. Bioaccumulation Ratios

Basis	Carcass	Viscera	Meat
SD 43775	536	2195	341
^{14}C Equivalents (Water Filtrate)	74	333	39

Registrant gave the following accumulation factor based on residues in whole fish:

Total ^{14}C = 52/0.836 = 62
SD 43775 = 24.5/0.05 = 490

Conclusions:

(1) Essentially no ^{14}C residues were found in fish or water in the system using soil treated with SD 43775 - ^{14}C at 0.01 PPM.

(2) The following conclusions are made concerning the exposure systems using soil treated with SD 43775-^{14}C at 1.0 PPM.

(a) Residues accumulated in catfish to a nominal level of 0.05 PPM (^{14}C equivalents) based on whole fish: A plateau at this level appears to have been reached in 5 days.

(b) Bioaccumulation factors for'whole fish' are reported as 62 (based on Total ^{14}C residues) and 490 based on SD 43775 residues found in fish and water.

(c) Of total ^{14}C residues found in fish tissues, 50-70% were identified as SD 43775 at 30 days while only about 7% of total ^{14}C residues found in water at 28 days were identified as SD 43775.

(d) Residues found in viscera were about 7X those found in meat.

(e) The 'half-life' for clearance of total ^{14}C residues from whole fish is indicated as 46 days. At day 76 of clearance, total ^{14}C Residues in whole fish were reported as 0.014 PPM, essentially all of which were identified as parent compound.

(f) Only the chlorophenyl ring, indicated by the ^{14}C label, and parent compound are accounted for in this study. Metabolites or breakdown products which do not include the chlorophenyl ring would be undetected in fish tissue. The occurence of considerable amounts of these breakdown products in water is suggested by the fact that only about 10% of the ^{14}C activity in water is due to parent compound.

3.10.3 Chronic Txicity of SD 43775 to the Fathead Minnow (Pimephales promelae) Report # BW-78-1-018 Accession No. 097000, Tab 9, Page 00124.

Although this study was designed to evaluate the long-term effects of SD 43775 on the fathead minnow, data are reported on residue buildup in the tissues of exposed fish which are of interest to environmental chemistry. That part of the data which deals with the effects on exposed fish will not be discussed in this review.

Fish were exposed in a flow-thru system for up to 260 days. Nominal target levels of SD 43775 in water ranged from 0.013 to 0.2 PPB. Fish tissue were analyzed for parent compound only.

Analytical method

Water - Samples were extracted three times with ethylene chloride. Extract was concentrated by evaporation, taken up in hexane, cleaned-up on a Florisil column, and ultimately determined by GLC with Ni63 electron capture detection.

Fish samples: Analyzed by method MMS-R-456-1 "Determination of SD 43775 Residues In Crops - Electron - Capture Gas Chromatographic Method". Initial extraction is with hexane/IPA using high speed blending. Extract is partitioned with water to remove IPA. Partition hexane with CH_3CN, exchange back to hexane and column chromatograph using activated Florisil adsorbent and hexane/ethyl acetate eluant. Quantitation is by GLC with EC detection. Minimum detectable concentration of SD 43775 in fish is reported as 0.01 PPM.

Some of the residue data are tabulated below:

Sample	Target Conc. of SD 43775 in Water, ppb	Amount (ug) of SD 43775 Added per Liter of water (ppb)	Exposure Interval, Days	SD 43775 Residue Found, ppm
Whole Fish		-	-	
" "	0.1	-	168	0.67
" "	0.05	-	"	0.25
" "	0.025	-	"	0.11
" "	0.013	-	"	0.07
Fish Muscle		-	-	
" "	0.1	-	168	0.37
" "	0.05	-	"	0.13
" "	0.025	-	"	0.1
" "	0.013	-	"	0.06
Whole Fish			260	
" " (Male)	0.1	-	"	0.32
" " (Female)	0.1	-	"	0.81
" " (Male)	0.05	-	"	0.09
" " (Female)	0.05	-	"	0.40
" " (Male)	0.025	-	"	0.06
" " (Female)	0.025	-	"	0.13
" " (Male)	0.013	-	"	0.03
" " (Female)	0.013	-	"	0.07

Some calculated bioaccumulation factors based on target concentrations of SD 43775 in Water and SD 43775 residues found in fish are given below

Exposure interval 168 days

	Water conc. PPB	Accumulation factor
Whole fish	0.1	6700
	0.05	5000
	0.025	4400
	0.013	5384
Fish muscle	0.1	3700
	0.05	2600
	0.025	4000
	0.013	4615

Exposure interval 260 days

Whole fish	Water cone PPB	Accumulation factor
Male	0.1	3200
Female	0.1	8100
M	0.05	1800
F	0.05	8000
M	0,025	2400
F	0.025	5200
M	0.013	2307
F	0.013	5384

Conclusions:

(1) Accumulation factors in the range 1800 to 8100X were calculated for SD 43775 in the fathead minnow under exposure conditions of the study. Accumulation for female whole fish is significantly higher than for males. An average accumulation for whole fish for both sexes and exposure times and water concentrations of 0.013 to 0.1 PPB is about 3500.

(2) Residues found in whole fish were in the range of 0.03 to 0.81 PPM.

(3) This study differs from the type recommended in the guidelines mainly in its duration of 168 and 260 days vs. 30 for the recommended study. Also, there was no depuration period.

3.10.4 Metabolic Fate of Fenvalerate in Rats, Soil, Soil Microorganism and an Aquatic Model Ecosystem. H. Ohkawa, K. Nambu, H. Kancko, R. Kikuchi. Acc. # 096386, Tab 6, pg 02895

Fenvalerate Metabolism in an Aquatic Model Ecosystem.

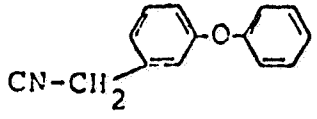
Experimental Procedure

Sandy loam soil treated with 0.3 ppm. ^{14}C-fenvalerate was placed in an aquarium and the tank was filled with 100 l water. After 7 days, carps and daphnids were added. The water was sampled for intervals up to one month.

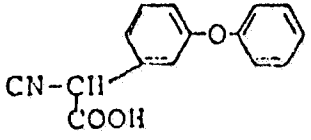
Table 9 Bioaccumulation Ratios and Metabolite Proportions of ^{14}C-CN-(±)-Fenvalerate in Organisms 30 Days after Addition of Organisms to an Aquatic Model Ecosystem

	% of the applied ^{14}C				
	Soil	Aqueous layer	Fish	Daphnids	Algae
Organosoluble ^{14}C	74.4	0.72	0.13	0.05	2.11
Fenvalerate	73.5	0.22	0.10	0.05	2.02
FOCN[a)]	----	0.10	----	----	----
$CONH_2$-Fenvalerate	0.02	----	----	----	0.04
4'-OH-Fenvalerate	0.71	0.04	0.01	----	----
Unknown I	----	----	<0.01	----	----
Unknown II	----	0.01	----	----	----
PMA[b)]	----	<0.01	----	----	----
Unknown III	----	----	----	----	0.02
Others	0.17	0.35	0.02	----	0.03
Residual ^{14}C	14.7	----	0.07	<0.01	0.10
Total ^{14}C	89.1	0.72	0.20	0.05	2.21
Bioaccumulation ratio[c)]			213	1771	2310

a) FOCN;



b) PMA;



c) Concentration of fenvalerate in an organism / Concentration in aqeous layer(filtrate)

Analytical Method

Fish, daphnids, algae, and soil were extracted with methanol and analyzed by TLC.

Conclusion:

Fenvelerate concentration decreased from 0.15 ppb at 7 days to 0.05 ppb at one month. After one month, 74% of the applied radioactivity was found in the soil, 0.7% in the water, and 0.1, 0.05, and 2.1% in the fish, daphnids, and algae respectively. The fenvalerate concentration was 11.1 ppb in fish, 92.1 ppb in daphnids, and 120.1 ppb in algae. The bioaccumulation ratios in daphnids and algae (1771X and 2310x) were higher than in fish (213x). Minor metabolites identified were $CONH_2$-fenvalerate, 4'-OH-fenvalerate, POCN, and PMA.

Bioaccumulation occurs in daphnids and algae. This is an ancillary study.

3.10.5 An Investigation of the Short Term Effects on and Residues in the Aquatic Environment Resulting from Pesticidal Applications of PYDRIN INSECTICIDE to cotton in Mississippi. Terrence C. Majure Accession No. 09700, Tab 7, Page 00078

Two sites in Holmes County, Mississippi were treated with SD 43775 as the 2.4 EC formulation.

Site 1 - 42 acres located on the banks of a lake with cotton rows running parallel to the lake. All rows drained into the east end of the lake.

Site 2 - 60 acres abutting a different lake. Cotton rows ran at approximately 45° from the lake shore and drained directly into the lake. Rate of application is given as 0.1 lb (ai)/ acre.

Dates of application: Site 1 -(1.0 gal/acre) on 8/16 and 8/24/77. Site 2 - (1.0 gal/acre) on 8/2 and 8/9/77 and 2.0 gal/acre on 8/22 and 9/11/77. Samples of fish, water and algae were collected on 8/3, 9/13 and 9/15/77. Rainfall at Site 2 was reported as ½ inch on August 4 (two days after Treatment I) and 3/4 inch on Aug. 23 (one day after Treatment 3). Three species of fish were sampled: gizzard shad, bluegill, and yel-

low-bullhead. Samples of algae were collected from trees and stumps standing in the water.

Analytical Method

'MMS-R-456-1' Determination of SD 43775 Residues in Crops - Election Capture Gas - Chromatographic Method". Whole fish were found in a large meat grinder and homogenized prior to sampling. Samples were blended in the presence of hexane/IPA. After solvent partition, extraction and clean-up on Florisil, ultimate quantitation was done by GLC using an EC detector. A minimum detectable concentration for SD 43775 is reported as 0.01 PPM for fish and algae. For Water samples, initial extraction was with hexane/ethyl acetate, as clean-up on Florisil is included and final determination is by GLC with EC detection. The Minimum Detectable Concentration for SD 43775 in Water is reported as 0.03 - 0.04 PPB.

Some results are tabulated below: (on next page)

Analyses of Water Samples

Code No.	Source of Sample	Site No.	No. of Applic.a)	Interval, Final Treatment To Sampling, Days	SD 43775 Residue in Unspiked Sample, ppb	SD 43775 Residue in Sample Spiked at 0.8 ppbb)
22	PBK, Surface	1	2	19	< 0.03	--
23	"	"	"	"	-	0.08
24	PBK, 18"	1	2	19	< 0.03	-
25	" "	"	"	"	-	0.07
17	HRSH, Surface	2	4	2	< 0.03	-
18	" "	"	"	"	-	0.03
19	HRSH, 18"	2	4	2	< 0.03	-
20	" "	"	"	"	-	0.05
33	HRSH, Surface	2	4	4	0.03	-
34	HRSH, 18"	2	4	4	0.05	-

a) SD 43775 was applied to the cotton field at 0.1 lb a.i. per acre per application. At Horseshoe Lake (HRSH) the final application included overspraying of the lake itself.

b) Samples spiked in the field at the time of sampling. Analysis of the solution used to spike the samples four months after the spiking showed only 12% of the original SD 43775 remained. Examination of the chromatogram (copy shown in Typical Chromatographic Data Section) shows the presence of probable degradation products.

Site No.	Sample	Lake	SD 43775, Dosage, lb a.i. per Acre Per Application[a] (To Cotton Field)	No. of Applications	Interval, Treatment to Sampling, Days	SD 43775 Residue Found
1	Algae	Pbk	0.1	2	19	0.01
1	Bluegill	Pbk	None	-	-	<0.01
1	"	"	0.1	2	19	<0.01
1	Gizzard Shad	"	None	-	-	<0.01
1	" "	"	0.1	2	19	<0.01
1	Bullhead	"	None	-	-	<0.01
1	"	"	0.1	2	19	<0.01
2	Algae	Hrsh	0.1	4	2	<0.01
2	"	"	0.1	4	4	<0.01
2	Bluegill	"	0.1	1	1	<0.01
2	"	"	0.1	4	2	<0.01
2	"	"	0.1	4	4	<0.01
2	Gizzard Shad	"	0.1	1	1	<0.01
2	" "	"	0.1	4	2	<0.01
2	" "	"	0.1	4	4	0.01
2	Bullhead	"	0.1	4	2	<0.01
2	"	"	0.1	4	4	<0.01

a) At Horseshoe Lake, final application includes overspraying of the lake itself.

Conclusions:

(1) Detectable residues of SD 43775 at 0.01 PPM were found in only two samples, algae and Gizzard Shad, under conditions of the study. Residue in 2 other algae samples and 13 fish samples were below this minimum detectable concentration (0.01 PPM)

(2) Detectable residues of SD 43775 were found in 2 water samples in site 2 at 0.03 and 0.05 PPB. This was the site that received overspraying.

(3) This is an ancillary study and not of the type required for environmental chemistry.

3.10.6 Intensive study of the Environmental Effects and Residues Resulting from Practical Alplications of PYDRIN INSECTICIDE TIR-24-635-77 Accession No. 097000, Tab 6, Page 00046

A field run-off type study and field residue studies were carried out in a Louisiana test site, a 37 acre field of cotton situated along the banks of a lake. The field drains directly into the lake which contains several species of fish. Two 55 gallon barrels were placed in the field as catch basins for run-off water. One in the main field drainage ditch which served about 33 acres and the other located to catch run-off from a small area (0.3 acre). Rainfall was recorded as follows:

7/28	1.7 inches
8/23	0.8 inches
8/25	0.5 inches
8/27	0.2 inches
9/06	0.5 inches
9/19	2.0 inches
9/29	0.1 inches

Water samples from the catch barrels were sampled as follows:

7/14 (Pretreatment) - from barrel draining large area
8/24 (after 1st application) - from both barrels.
8/26 - from barrel draining small area.
8/30 - from barrel draining small area.
9/06 - from barrel draining small area.
9/09 - from barrel draining small area.
9/29 - from barrel draining small area.

Water was sampled from the barrel draining the small area when run-off was sufficient to overflow the other barrel.

PYDRIN was applied at 0.1 lb ai/acre. Dates of application were 8/22, 8/26, 8/31, 9/5, 9/9, 9/14, 9/19, 9/23 and 9/29/77.

Soil samples were taken 7/14 pretreatment) and 9/29 after last application.

Fish and water samples from the lake were taken: pretreatment 7/14, after first treatment 8/24 and after last treatment 10/4. Algae samples were collected at the same sites and same frequency as fish. Bird samples were also taken by shotgun.

Some duplicate samples of water were spiked in the field with SD 43775 to track residue breakdown prior to analyses.

Analytical Method:

MMS-R-4561 'Determination of SD 43775 Residues in Crops - Election -Capture Gas Chromatographic Method"

Algae, Fish and Birds - Macerated in the presence of hexane/IPA using a high speed blender. Soil was subjected to high frequency vibration in presence of acetone/hexane (1:1) for 2 minutes. All samples were solvent partitioned subject to clean-up on Florisil and quantitated by GLC using EC detection.

Sample	Sampling Location	SD 43775 Dosage lb a.i. per Acre Per Application	No of Applic. Prior to Sampling	Sampling Date	Interval Last Application To Sampling, Days	SD 43775 Residue Found, ppm
Soil Cores, Pretreat	Farm	0	0	7/14	-	<0.01
Soil, 3" Cores From Drill	Farm	0.1	1	8/22	0	<0.01
Soil, 3" Cores From Middle	Farm	0.1	1	8/22	0	<0.01
Soil, 3" Cores From Middle	Farm	0.1	9	9/29	0	0.06, 0.04[a]
Algae	Lake	0	0	7/14	-	<0.01
Algae	Lake	0.1	1	8/24	2	<0.01
Bluegill	Lake	0	0	7/14	-	<0.01
Bluegill	Lake	0.1	1	8/24	2	<0.01
Bluegill	Lake	0.1	9	10/4	5	<0.01
Shad	Lake	0	0	7/14	-	<0.01
Shad	Lake	0.1	1	8/24	2	<0.01
Shad	Lake	0.1	9	10/4	5	<0.01
Catfish	Lake	0.1	1	8/24	2	<0.01
Catfish	Lake	0.1	9	10/4	5	<0.01
Bass	Lake	0.1	9	10/4	5	<0.01
Redwing Blackbird	No. of Ferriday, IA	0	0	7/11	-	<0.01
Indigo Bunting Bird	In Area of Treatment	0.1	9	10/9	10	<0.01
Indigo Bunting Bird	In Area of Treatment	0.1	9	10/9	10	<0.01

a) Duplicate subsample of a single sample analysed separately.

Analyses of Field Spiked Samples

Sample Source	Sampling Date	Nominal Spiking Level, ppb[a]	SD 43775 Found in Spiked Sample, Expressed as Equiv. ppb in Total Sample			SD 43775 Found in Unspiked Sample, ppb
			Supernatant Water[b]	Sediment[c]	Total	Total
Lake, Surface	7/14	0.4	<0.03	0.13	0.13	<0.06
" 12"	"	0.4	<0.03	0.18	0.18	<0.06
" 24"	"	0.4	<0.03	0.08	0.08	<0.06
" Surface	8/24	0.4	0.03	0.20	0.23	<0.06
" 12"	"	0.4	<0.03	0.22	0.22	<0.06
" 24"	"	0.4	0.03	0.17	0.20	-
" Surface	10/4	0.4	0.06	0.14	0.20	<0.06
" 12"	"	0.4	0.06	0.14	0.20	<0.06
" 24"	"	0.4	0.09	0.06	0.15	<0.06
Farm, Large Area	7/14	0.04	0.05	0.06	0.11	<0.06
" " "	"	0.4	0.05	0.22	0.27	<0.06
" " "	8/24	0.04	0.03	3.6	3.6	2.4
" " "	"	0.4	0.03	3.9	3.9	2.4
" " "	9/29	0.04	0.17	8.5	8.7	8.1
Farm, Small Area	8/24	0.04	0.10	6.5	6.6	4.0
" " "	"	0.4	0.08	5.5	5.6	4.0
" " "	8/26	0.04	0.04	0.54	0.58	0.74
" " "	8/30	0.04	0.09	2.6	2.7	1.9
" " "	9/6	0.04	0.40	3.4	3.8	5.2
" " "	9/9	0.04	0.18	1.5	1.7	1.2

a) Spiked at time of sampling.
b) Residue of SD 43775 dissolved or suspended in "clear" portion of water sample.
c) Residue of SD 43775 sorbed on sediment portion of sample, expressed as equivalent ppb in total water sample.

Source of Sample	No. of Applic. Prior to Sampling	Sampling Date	Interval, Last Applic. to Sampling, Days	SD 43775 Residue Found Expressed as Equiv. ppb in Total Sample		
				Supernatant Water[b]	Sediment[c]	Total
Lake, Surface	0	7/14	Pretreat	< 0.03	< 0.03	< 0.06
" 12"	"	"	"	< 0.03	< 0.03	< 0.06
" 24"	"	"	"	< 0.03	< 0.03	< 0.06
Lake, Surface	1	8/24	2	< 0.03	< 0.03	< 0.06
" 24"	"	"	"	< 0.03	< 0.03	< 0.06
Lake, Surface	9	10/4	5	< 0.03	< 0.03	< 0.06
" 12"	"	"	"	< 0.03	< 0.03	< 0.06
" 24"	"	"	"	< 0.03	< 0.03	< 0.06
Large Area	0	7/14	Pretreat	< 0.03	< 0.03	< 0.06
" "	1	8/24	2	0.09	2.3	2.4
" "	9	9/29	0	0.07	8.0	8.1
Small Area	1	8/24	2	0.22	3.8	4.0
" "	2	8/26	0	0.08	0.66	0.74
" "	2	8/30	4	0.08	1.8	1.9
" "	4	9/6	1	0.08	5.1	5.2
" "	5	9/9	0	0.12	1.1	1.2

a) SD 43775 was applied to the cotton field at 0.1 lb a.i. per acre per application.
b) Residue of SD 43775 suspended or dissolved in "clear" supernatant portion of water sample.
c) Residue of SD 43775 sorbed on sediment portion of water sample, expressed as equivalent ppb in total sample.

Conclusions:

(1) Residues of SD 43775 in the range of 0.74 to 8.1 PPB were found in runoff water from treated cotton fields.

(2) No detectable residues were found in fish, birds and algae under conditions of this study.

(3) Residues in the range of 0.04 to 0.06 PPM SD 43775 were found in 3" soil samples after 9 applications of SD 43775 at 0.1 lb ai/acre.

(4) This is an ancillary study and not of the type required by environmental chemistry.

3.11 Animal Metabolism

3.11.1 Metabolic Fate of Fenvalerate in Rats, Soil, Soil Microorganisms and an Aquatic Model Ecosystem H. Ohkawa, K. Nambu, H. Kaneko, R. Kikuchi. Acc # 09638, Tab 6, pg. 02895. Also see review of Tab 5

Fenvalerate Metabolism in Rats

Experimental Procedure

Male rats were treated with one oral dose of CO-, CH - and CN-^{14}C-labeled fenvalerate at the rate of 8.4mg/Kg, held for 6 to 14 days in cages, and sacrificed for radioanalysis of urine, feces, expired air, and tissues.

Analytical Method

Metabolites were identified and quantitated by TLC and radioautography.

Results

The major metabolites found in the urine and feces were 4'-OH-fenvalerate, phenoxybenzoic acid, 4-OH-phenoxybenzoic acid (free and as the SO_4).

Conclusion

This is an ancillary study.

3.11.2 Metabolism of WL 43775 by Rat Liver Enzymes Part I and II. by A.C. Boyer. Tab 5 and 6. Acces. No. 096385, 01211 and 01218. TIR-22-115-76 and TIR -22-117-76.

The mixed function oxidase activity of the liver microsomal - plus supernatant incubated with ^{14}C-WL 43775 was studied by measuring the 0-demethylation of p-nitro-anisole. Minor metabolites identified on TLC included 3-phenoxybenzaldehyde, 3-phenoxy-benzenemethanol, 3-(4-hydroxy-phenoxy)-Benzoic acid, and 4-chloro- -(1-methylethyl) - benzeneacetic acid. A major metabolite which accounted for as much as 44% of total radioactivity was 3-phenoxy-benzoic acid. Volatile compounds were not found after the reaction mixture was eluted from Tenax columns and analyzed by GC-mass spectroscopy.

This is an encillary study.

3.11.3 Residues of ^{14}C in Tissues of Rat Fed SD 43775-^{14}C by J. C. Potter and Residues of ^{14}C in Tissues of Rats Fed SD 43775-^{14}C for 28 days by J. C. Potter and D. L. Arnold. Acces. No. 096385
Tab 7 and 8, 01222 and 01234; TIR-22-106-76 and TIR-22-118-77.

In the first experiment rats were given feed containing 21 ppm of SD 43775-^{14}C(chlorophenyl ring labelled) for 24 hrs. The rats were then given clean feed for 1, 3, and 7 days and sacrificed. The highest residues were found in the fat of rats - 0.15 to 0.48 ppm. The kidney, liver and muscle were found to contain $\leq$ 0.09 ppm.

In the second experiment rats were given feed containing 20 ppm of SD 43775-^{14}C (phenyl ring labelled) for 7, 14, and 28 days and then some of the rats were placed on clean feed for 1, 7, 14 and 28 days. Rats were sacrificed at each interval. Again fat tissues contained the highest residues (2.9 ppm) after 28 days.

Residues in Fat Tissues from Rats Fed ^{14}C-SD 43775. 01290 TIR-22-103-77 Tab 12.

The nature of the radioactive residue found in fat from rats fed 20 ppm ^{14}C-SD43775 (above experiment) was 93% unchanged parent compound. This is an ancillary study.

3.11.4 Metabolites in Livers of Rats Fed ^{14}C-SD 43775 by A. C. Boyer. 01265, TIR-22-105-77. Tab 9 Identification of Metabolites in the Livers of Rats Fed ^{14}C-SD 43775. 01265, TIR-22-105-77. Tab 10. Carbon-14 Bound Residues from Livers of Rats Fed ^{14}C-SD 43775. 01287, TIR-22-118-76. Acces. No. 096385 Tab 11.

Rats were fed 20 ppm SD 43775-^{14}C for various feed-on/feed-off periods of time. Analysis of liver macerates showed not more than 1.0 ppm during the feed-on portion of the experiment (0-28 days), declining to 0.06 ppm after 7 days of feed-off.

TLC, HPLC and MS were used to characterize metabolites from liver extracts taken from rats fed for 28 days. 3-phenoxybenzoic acid and 3-(p-hydroxyphenoxy) benzoic acid constituted about 35 and 43% of total ^{14}C applied to the TLC plate. It was found that 7.4% of the original radioactivity was bound to the particulate material but 75.2% of the bound residue could be liberated by treatment with base. This is an ancillary study.

3.11.5 Identification of Metabolites Found in the Urine of Rats Fed ^{14}C-SD 43775 by A. C. Boyer. 01304, tab 13, TIR-22-109-77. Identification of Metabolites found in the Feces of Rats Fed ^{14}C-SD 43775, 01325. TIR-22-110-77. Acces. No. 096385, tab 14

Urinary metabolites found in rats fed 20 ppm ^{14}C-SD 43775 for 28 days were characterized by TLC autoradiography. These metabolites included 3-phenoxybenzoic acid (10%), 3-(p-hydroxyphenoxy) - benzoic acid (42%), and 3-(p-hydroxyphenoxy) - benzoic acid o-sulfate 45%).

Of the ^{14}C found in feces, 16.5% was 3-(p-hydroxyphenoxy) benzoic acid, 16.7% was benzeneacetic acid, 4-chloro-α-(1-methyl-ethyl)-cyano-3-(p-hydroxyphenoxyphenyl) methyl ester, 27.5% was benzeneacetic acid and 23.6% was 3-(p-hydroxyphenoxy) benzoic acid o-sulfate. This is an ancillary study.

3.11.6 Cow Feeding Studies 31

(1) Residues of ^{14}C in Milk and tissue From Cows Fed SD 43775-^{14}C. J. C. Potter, Acc # 093690, Tab 5, pg 00072, TIR-22-102-76

(2) Residues of Carbon - 14 in Milk and Tissue From Cows Fed SD 43775-^{14}C. J. C. Potter, Acc # 093690, Tab 6, pg 00094, TIR-22-112-76

(3) Residues of ^{14}C in Milk and Tissue From Cows Fed SD 43775-^{14}C. J. C. Potter and D. L. Arnold. Acc. # 093690, Tab 7, pg 00127, TIR-22-111-77.

(1) Tab 5. Cows Fed 21 days at 0.11 ppm equivalent /^{14}C chlorophenyl.

(2) Tab 6. Cows fed 28 days at 0.15 ppm equivalent /day of ^{14}C-CN.

(3) Tab 7 Cows fed 28 days at 10.7 ppm equivalent /day of ^{14}C-CN.

	Tab 5 ^{14}C - Chlorophenyl		Tab 6 ^{14}C-CN		Tab 7 ^{14}C-CN	
	PPM Equ.	%	PPM Equ.	%	PPM Equ.	%
Milk	.0018		.0017	.6	.133	.7
Cream	.017		.022		.938	
Skim Milk					.01	
Brain	.01		.004		.04	
Bone			.007		.17	
Subcutaneous Fat	.02		.008		.68	
Mesteric Fat	.02		.014		.79	
Kidney	.01		.004		.18	.01
Liver	.01		.006		.34	.06
Lung	.01		,004		.05	.01
Quadriceps Muscle	.01		.004		.06	
Gastronemius Muscle	.01		.004		.04	
Plasma	.0024		.0014		.09	
Whole Blood			.003		.07	
Urine		33.3	.061	20.3	7.0	25.7
Feces		36.1	.042	33.4	4.8	34.3
Unrecovered Exereta Est.				10		

(Table continued)

	Tab 5 ^{14}C - chlorophenyl		Tab 6 ^{14}C-CN		Tab 7 ^{14}C-CN	
	PPM Equ.	%	PPM Equ.	%	PPM Equ.	%
Carcass				5		
Rumen					2.17	2.9
Small Intestine					.44	
Large Intestine					.79	
Washings						27.9
Total % recovered				72%		92%

3.11.7 Residue of ^{14}C In Eggs and Tissues From Laying Hens Fed SD 43775-^{14}C. J. C. Potter. Acc # 093690, Tab 9, pg 00170, TIR-22-103-76

Chicken fed for up to 32 day with ^{14}C-chlorophenyl labeled SD 43775 at a level of 0.03 ppm.

	ppm equivalents for different feedings 33 days	7 day	32 day
egg whites	0.002		
egg yolks	0.001		
Blood		.004	.004
Fat		.008	.008
Gizzard		.004	.004
Heart		"	"
Liver		"	"
Dark Meat		"	"
Light Meat		"	"
Skin		.008	.008
Carcass	.01		
droppings	93.5 % applied here.		

These are ancillary studies.

3.12 Analytical Method

3.12.1 Determination of SD 43775 Residues in Crops. Electron - Capture Gas Chromatographic Method. Pgs. 00193 - 00202; Tab 11. Acc. No. 096390 Shell-Modesto Method Series MMS-R-456-1, October 1976

A GLC method, using the electron-capture (EC) detector, is described for determining residues of the pyrethroid insecticide SD 43775 in crops. The minimum detectable concentration (MDC) is about 0.01 milligram per kilogram or 0.01 ppm.

Samples are extracted with hexane/isopropanol (3:1) and the isopropanol removed by water partitioning. The hexane extracts of oily crops are partitioned with acetonitrile to separate lipids from the SD 43775. The acetonitrile is exchanged back to hexane which is water washed and cleaned up by liquid-solid chromatography through the activated Florisil column. Hexane extracts of non-oily crops are cleaned up directly without acetonitrile partitioning. The isolated SD 43775 is quantitated by GLC-EC (Ni63)

Precision and accuracy data are compiled from recovery results that have been determined in this laboratory.

Compound	Samples Analyzed	Fortification Range, ppm	No. of Observations	% Recovery Mean	% Recovery Std. Dev.
SD 43775	Crops[1)]	0.02-40	70	94.5	13.3

1) Crop samples used for statistical evaluation included: alfalfa (green and dried), apples (whole, peel, pulp, wet pomace, and juice), sweet corn (kernels, stover, and whole ear), cabbage, potatoes (whole), lettuce, sorghum (grain), broccoli, cucumbers, peas (pods and hay also), green peppers, snap beans (and hay), tomatoes, and squash.

3.12.2 Determination of SD 43775 Residues in Animal Tissues, Milk, Milk Fat, Creamy Hair, Eggs, and Gauze Patches. Electron-Capture Gas Chromatographic Method. MMS-R-447-2. August, 1977. Shell's BSRC, Modesto, Calif. Modesto Method Series. Pgs 00203-00219. Tab 12, Acc. No. 096390

EC-Ni^{63}

Min. Detect. Cone, 0.02 ppm

(a) Animal tissues are extracted with hexane and the SD 43775 is partitioned from the hexane extract into acetonitrile. The acetonitrile phase is washed with hexane. The washed acetonitrile is exchanged to hexane and cleaned up by liquid-solid chromatography through an activated Florisil column. The isolated SD 43775 is quantitated by GLC-EC.

(b) Egg Samples are extracted with a two-phase solvent system consisting of hexane and acetonitrile. The hexane phase, containing fat-soluble interferences, is discarded. The acetonitrile phase, containing extracted SD 43775 residues, is processed as in s(a)

(c) Hair samples, which usually contain high residue levels of SD 43775 (above 10 ppm), are extracted with 5%v/v ethyl acetate in hexane. The extract is directly injected into the gas chromatograph for quantitation of SD 43775 content.

(d) Gauze patches are extracted with a 1:1 misture of acetone and hexane. The extract is taken to dryness and the residue is taken up in hexane, cleaned up by liquid solid chromatography through an activated Florisil column and analyzed by GLC-EC.

(e) Milk, cream or milk fat is extracted with CH_2Cl_2 followed by an acetone extraction of the milk solids. The acetone extract is exchanged to hexane and the hexane and CH_2Cl_2 extracts combined and solvent is removed. The fat is weighed and then solubilized with hexane and partitioned with CH_3CN. The CH_3CN is washed with hexane, and then diluted with NaCl solution. The NaCl/CH_3CN solution is extracted with hexane, the hexane concentrated, then cleaned up by liquid solid chromatography through an activated Florisil column and analyzed by GLC-EC.

Sample	% Recovery Number	Mean	Std. Dev.	Rel. Std. Dev.	95% Conf. Reproducibility
All analyses					
All levels	177	87	14	16	38
All operators					

3.12.3 SD 43775-Gas Liquid Chromatographic Interference Study. pp 00220-22, TIR-24-603-76. Tab 13. Acc. No. 096390

Standards of following common pesticidal compounds prepared for comparison: MeParathion, Azodrin, Toxaphene, Galeuon, Nudrin, dieldrin, aldrin, capton, Guthion, 10.0 ug/ml ethylacetate solns. and/or 1.0 ug/ml 10%et ac/hex soln.

AFID evaluation - P-sns, alk flame ionz. EC eval. - EC-scandium tritide.

Results.

1) 20. ug of each compound did not interfere with 16 ug of SD 43775 (yielding 20% FSD response) using the AFID.

2) 2.0 ug of each compound did not interfere with 0.1 ug SD 43775 (yielding 20% FSD response)using the EC detector.

Compound	Retention times (min) 220°C	200°C	Relative retention times 220°C	200°C
Aldrin	0.50	0.83	1.00	1.00
Dieldrin	0.86	1.6	1.74	1.87
SD 43775 (isomer 1)	8.0	21	16.0	24.9
SD 43775 (isomer 2)	8.7	23	17.6	28.0

Conclusions

PYDRIN elutes beyond retention time of most other pesticides analyzed by GLC- using either EC or AFID detectors.

3.12.4 Residue Determination of SD 43775 in Cottonseed and Leaves of Cotton Plants. GLC/Alkali Flame Ionization Detector. Modesto Method Series. MMS-R-423-1, April, 1975. Tab 15, pgs 00227-00232, Acc No. 096390

Minimal Detectable residue approximately 0.1 ppm.

(a) Cottonseed samples are extracted with acetonitrile which is washed with hexane. The washed acetonitrile is exchanged to hexane. Hexane extracts are cleaned up by liquid-solid chromatography on an activated Florisil column. SD 43775 is quantitated by GLC/AFID.

(b) Cotton leaves are prerinsed with hexane to determine surface residues, then extracted with acetonitrile and processed as in 2. (a).

Commodity	ppm SD 43775 Added	Percent Recovery
Cottonseed	0.5	95
"	0.5	95
"	0.5	90

Stated that number of recoveries analyzed to date are insufficient for statistical purposes.

3.12.5 Determination of SD 43775 Residues in Cottonseed. Electron-Capture Gas Chromatographic Method. Shell-BSRC, Modesto, Calif. MMS-R-439-1, Jan. 1976. Tab 16, pgs 00233-00239. Acc. No. 096390

Min. Dectect. Cons. (MDC) is approximately 0.01 mg/k or 0.01 ppm.

Cottonseed samples are extracted with hexane and the SD 43775 is partitioned from the hexane extract into acetonitrile. The acetonitrile phase is washed with hexane. The washed acetonitrile is exchanged to hexane which is water washed and cleaned up by liquid-solid chromatography through an activated Florisil column. The isolated SD 43775 is quantitated by EC-GLC.

Detector: EC-Ni^{63}

Compound	Samples Analyzed	Fortification Range, ppm	No. of Observations	% Recovery Mean	% Recovery Std. Dev.
SD 43775	Cottonseed	0.025-0.2	25	85	10

3.12.6 Determination of SD 43775 Residues in Crops Electron-Capture Gas Chromatographic Method. Acc. # 096648, Tab. 4, pg 88146, MMS-R-456-1

Analytical Procedure

Samples are extracted with hexane/isopropanol, isopropanol is removed with H_2O partitioning. Hexane extract is partition with CH_3CN. The CH_3CN is exchanged back to hexane and H_2O washed and cleaned by LSC through Florisil Column. Wash column with hexane and discard. Add ethylacetate to hexane and elute SD 43775. An aliquot is taken for ECGC-Ni^{63} detector.

Recovery for crops is 94.5%±13.3 at 0.02 to 40 ppm.

3.12.7 Thin-Layer Chromatography of SD 43775 Treated Cotton Leaves. J. E. Loeffler Acc # 096648, Tab 1, pg 88101, TIR-22-113-76

TLC plates Silica Gel 60F254. Develops Tetrahydrofuran, ethyl acetate and hexane.

Spot determined by Berthold TLC scanner with ratemeter Nonradioactive SD 43775 illuminated with UV.

3.13 Plant Residue + Metabolism

3.13.1 Identification of Non-Polar Metabolites From ^{14}C - SD 43775 - treated Cotton Fibers. A. Ehmann. Acc # 096390, Tab 4, pg 00067 TIR-22-114-77

Cotton treated at open boll stage with 260.64 g of ^{14}C-chlorophenyl or ^{14}C-phenoxphenyl (0.25 lbs/A) and harvest 8 weeks later.

Fiber contained 30.95 ug of ^{14}C-chlorophenyl and 67.64 ug of ^{14}C-phenoxyphenyl.

Residues of ^{14}C chlorophenyl and ^{14}C-phenoxyphenyl.

Residues of ^{14}C chlorophenyl and ^{14}C-phenoxyphenyl

Nonpolar		
SD 43775	82%	85%
SD 53036	5%	4.5%
SD 54597	2%	2%
Polar	11%	8.5%

3.13.2 Investigation of the Transport of ^{14}C - (chlorophenyl)-SD 43775 From Treated to Untreated Leaves on Cotton Plants J. E. Loeffler Acc # 096390, Tab 1 pg00059, TIR-22-110-76

Summary

"Neither ^{14}C-SD 43775 nor any possible ^{14}C-containing metabolites are transported either in the xylem or in the phloem out of a cotton leaf treated with ^{14}C-(chlorophenyl)-SD 43775."

3.13.3 Fate of SD 43775 Applied to Open Cotton Bolls. A. Ehmann. Acc # 096390, Tab 3, pg 00062, TIR-22-117-77.

Cotton was treated with 0.25 lbs/A at the open boll stage with single dose of ^{14}C-chlorophenyl labeled SD 43775. Seeds harvest 8 weeks later.

Conclusion

Total ^{14}C is 0.253 ppm of which 95.2% was SD 43775 and at least 3 polar compounds in trace amounts.

3.13.4 The Metabolism of the Pyrethroid Insecticide WL 43775 In Apple Fruit and Foliage Under Outdoor Conditions. M. E. Tanden. Acc # 096648, Tab 2, pg 88105, SBL 12/77/I/AC 407.

This is a ^{14}C-benzyl or ^{14}C chlorophenyl label study.

	% ^{14}C-present			
PHI	^{14}C benzyl	^{14}C Chloroph.	^{14}C-benzyl	^{14}C-Chloro
	Leaves 304 week		Peel 22 days	
WL 43775	75	83.7	86.7	92.6
WL 43774	.9	.4	-	.5
WL 47117	.1	.6		
WL 48838	.8	.7		
SD 36750	.3	-		
Non-Polar	1.3	1		
Polar A	11.3	6.1		
Polar	6.3	5.3		
UnxTreated	4.1	2.2		
RF .05		-	3.3	0.7
RF .25			2.1	1.1
Hydrophilic Polar			2.5	2.8

Less than 1.3% ^{14}C-benzy + 1.8% ^{14}C-chlorophenyl in fruit

2.13.5 The Metabolism of the Pyrethroid Insecticide WL 43775 (Belmark) in Lettuce and Soil Under Outdoor Conditions. E. J. Hitchings. Acc # 096648. Tab 3, wk 3/I/AC 304. pg 88425

This is a ^{14}C-benzy or ^{14}C-chlorophenyl label study

	WL 43775 equiv. mg/kg	
Lettuce 12 day PHI	^{14}C benzy	^{14}C-Chlorophenyl
WL 43665	.94	.80
Wl 10944	nd	.03
Unidentified	nd	.01
SD 36750	.01	nd
$Polar_{EA}$	.04	.07
$Polar_{AQ}$	.13	.15
Unextracted	.05	.05

Soil had unchanged parents 4366J

3.13.6 Residue Determination of SD 43775 In Cottonseed and Leaves of Cotton Plants. Acc #096648, Tab 7, pg 88161, MMS-R-423-1

This was GLC/Alkali Flame Ionization Detector Cottonseed is extracted with CH_3CN which is washed with hexane. The washed CH_3CN is exchange in hexane. Hexane extract is cleaned by LSC on Florisil column. Ethyl acetate and hexane are used to elute through

column. An aliquot is taken for GLC analysis.

Cotton leaves are extracted with hexane for surface residues and CH_3CN of absorbed residues. The hexane extract is L C on Florisil and procede as above. The CH_3CN extract is described above.

Recovery is 90-95% in cottonseed at 0.5 ppm. I quote, "an insufficient number of recovery samples have been analyzed to date with this procedure to make a statistical evaluation of precision and accuracy.

3.13.7 Determination of SD 43775 Residues In Cottonseed, Acc. # 096648, Tab 8, Pg 88167, MMS-R-439-1.

Electron-Capture Gas Chromatographic Method.

Cottonseed samples are extracted with hexane, the SD 43775 is partitioned from hexane into CH_3CN. The CH_3CN is washed with hexane. The washed CH_3CN is exchanged to hexane which is H_2O washed and cleaned on LSC through Florisil. Elute with ethyl acetate and hexane. An aliquot is taken for ECGC analysis using Ni^{63} detector.

3.13.8 Carbon-14 content of cottonseed after Single and Multiple Treatment of Squares with ^{14}C-(chlorophenyl) - SD 43775. J. E. Loeffler. Acc #096390, Tab 2, pg 00060, TIR-22-107-76

Conclusion

Cottonseed harvested 95 and 106 day after one treatment had 0.05 ppm ^{14}C equivalent SD 43775. Seeds from untreated bolls had 0.02 ppm equivalent. Maybe $^{14}CO_2$ given off and taken up.

Seeds harvested 56 days after 2 treatments with 26 days. The 56 day is after first treatment. The seed had no detectable residue.

Seeds harvested 90 days after first treatment from plant receiving 3 treatments had no significant residues.

3.14 Vaporization

3.14.1 Vaporization and Sorption of SD 43775 from Water Solutions. J. C. Potter, TIR-22-103-75 Acc. No. 096386; Tab 12; pgs 02955-56.

Experimental Procedures

C^{14}-PYDRIN (chlorophenyl ring) used; all samples counted in liquid scintillation counter. Lab air drawn through 3 gas scrubbers; middle one containing compound, last one toluene. Extracts from both analyzed.

Analytical Methods

Liquid scintillation counting.

Results

Total C^{14} recovered (from last 2 bottles) was 83.3-91.3%. Less than 2.0% from toluene bottle alone.

Conclusions

Little or no vaporization from aerated water suspensions.

3.14.2 Vaporization and Sorption of SD 43775 from Water Solutions by J. C. Potter. Acces. No. 096385 tab 3 01207, TIR-22-103-75.

Experimental Protocol:

Chlorophenyl labelled 14C-SD 43775 was added to aqueous solutions to study vaporization and sorption to glass and teflon surfaces. Air was drawn through 3 gas scrubbers connected in series for 5 hours. The first scrubber contained tap water, the second contained a 0.35 ppb solution of SD 43775-^{14}C and the third scrubber contained toluene. Extraction of the scrubbing bottles with ethanol and toluene showed little vaporization or loss of SD 43775.

Sorption of SD 43775 was studied by adding this chemical to aqueous solutions in teflon and glass flasks and ploypropyles.

Results

Very little vaporization of SD 43775 was found from aerated water solutions. SD 43775 adsorbs strongly to glass, teflon, and polypropylene.

3.15 Effects of a synthetic pyrethroid, SD 43775 on non-target organisms when utilized as a mosquito larvicide. T. Mima and R. Tolshaski Tab 26, Page 03113, Accession No. 096386

This report does not contain environmental chemistry-type data.

4.0 Conclusions:

Hydrolysis: The half-life of SD 43775 in 10% ethanol/90% water solution at 38°C is reported as 100 hrs. at PH 1.1 (buffered), 570 hours at PH 7.2 (tap water) and 70 hours at PH 9.1 (buffered). Hydrolysis products are not chemically identified.

Photolysis: SD 43775 photodegrades on the surface of a sandy loam soil with 68% of parent compound remaining after 28 days. Degradation of the 'dark' control also occurred (12% during the same time period.) Photoproducts were not chemically identified.

In water a formulation of SD 43775 exposed to sunlight showed approximately 53% photodegradation of parent compound in 28 days. The presence of 2% acetone approximately doubled the photodegradation rate in water. Photoproducts were more polar than parent compound but were not chemically identified.

Aerobic Soil Metabolism: The half-life of extractable SD 43775 in Hanford sandy loam (0-3" depth) is less than 4 weeks. At least 14 chlorophenyl ring containing metabolites were tentatively identified. SD 53065, SD 47117, SD 10944, SD 55886, SD-54597, SD 47116, SD 39009 and SD 43774 were considered major metabolites. SD 52666 and/or SD 53919,SD 52617 and/or SD 53405, SD 44546, SD 45329 and SD 48838 are found in lesser amounts.

Anaerobic soil metabolism: There is no significant difference in 14C loss when chlorophenyl ring labelled SD 43775 is incubated in soil under aerobic or anaerobic conditions. When 14C-CN labelled material is used, the rate of loss of 14C activity is significantly less under anaerobic conditions. $CONH_2$-fenvalerate (SD 47117) is identified as a soil degradation product under anaerobic conditions.

Effect of soil microorganisms on the pesticide:

(1) Comparative studies using chlorophenyl ring labeled SD 43775 in sterile and non-sterile soils indicated that microorganisms participate in the degradation of SD 43775. Degrading microorganisms are not identified.

(2) Soil bacteria appear to be more active than soil fungi in degrading SD 43775. The acid Cl-VA is indicated as a major product for both types of organisms.

Effect of the pesticide on soil microorganisms: SD 43775 did not inhibit cellulolytic organisms in soil as indicated by the disintegration of cotton cloth. Effects on nitrogen fixation, nitration, protein and carbohydrate degradation are not demonstrated.

Leaching: Parent compound and degradation products show only slight tendency to leach in soil.

Adsorption: SD 43775 is sorbed strongly from aqueous solutions onto soil. The reaction is slowly reversible.

Field dissipation: The half-life of extractable SD 43775 in field soils is approximately 4 weeks. Approximately 25% of applied active ingredient reaches the soil at time of application to three foot high cotton plants. The amide SD 47117 is a minor soil metabolite. Data submitted were minimal. Proposed use directions were not fully reflected.

Residues in Rotational Crops: Chemically identified residues of SD 43775 were taken up into table beets (0.019 PPM tops and 0.010 PPM beets) from treated soil (last treatment 1 lb/acre 120 days earlier). Other studies indicated equivalent SD 43775 residues of 0.005 to 0.020 PPM in sugar beets and alfalfa planted approximately one year after application at 1 lb/acre. Data are lacking on plant metabolism, soil residues, soil characteristics and analytical methods. Based on the data submitted, a crop rotation restriction of one year will be needed.

Fish Residue Accumulation: In a dynamic-type study nominal accumulation in edible tissue of rainbow trout was approximately 400 X. About 90% of the residues were identified as parent compound. Depuration was relatively slow with about 40-60% of residual activity remaining after 33 days of withdrawl. No radioassay chemical analyses was done on other than edible portions of fish tissue.

In a model ecosystem using treated soil the bioaccumulation ratio in carp was calculated as 213, based on concentration of SD 43775 in the fish/concentration in aqueous layer (filtrate) 4'-OH-fenvalerate was also identified in fish tissue. Accumulation ratios in exposed daphnids and algae calculated as 1771 and 2310, respectively.

In a static type study in which catfish were exposed to a system containing soil treated with pesticide, an accumulation factor of 490 was found based on SD 43775 residues in fish and water (whole fish basis). Total residues were at the nominal level of 0.05 PPM (14C equivalents). Of the total 14C residues found in fish 50-70% were identified as SD 43775.

In a flow-thu study on fathead minnows carried out for 168 and 260 days, an average accumulation factor of about 3500 X was estimated based on SD 43775 identified in 'whole fish' tissue and nominal water concentrations of the pesticide. Residues in female fish were significantly higher than those found in moles at the same exposure level.

5.0 Recommendations:

5.1 We cannot concur with the uses of PYDRIN 2.4 EC on cotton and PYDRIN TECHNICAL for formulating use.

5.2 Directions for use for the PYDRIN 2.4 EC formulation do not include a maximum cumulative dosage per growing season. This is needed for a full evaluation of the data.

5.3 The following comments are made on the data submitted.

5.3.1 Hydrolysis:

(1) Hydrolysis products are not identified.

(2) Material balance data are not given.

(3) Data are needed for hydrolysis at pH5.

(4) The temperature of 38°C is out of proportion with soils.

(5) It is not clear from the data whether the study was done in the dark.

(6) No recovery data are given for analytical extractions.

5.3.2 Photodegradation:

(1) Photoproducts formed in water and on soil surfaces are not chemically identified. Products comprising 10% or more of applied radioactivity should be identified.

5.3.3 Aerobic - Anaerobic - Sterile

(1) 'Degradation of 14C- (chlorophenyl) SD 43775 During exposure to soil Under Aerobic, Anaerobic and Sterile Conditions' TIR-22-108-76

(a) Recovery data are not given

(b) We do not know soil characteristics

(c) The complete analytical methodology has not been submitted for LC and TLC.

(d) We would like photographs if available of the TLC.

(e) The study was not carried out long enough to determine T½ in soil.

(2) 'Degradation of Fenvalerate (Sumicidin) in Soil' AM-70-0036

(a) None of the studies account for the chlorophenyl or the diphenyl ether portion of the molecule.

(b) Analytical procedures are not given in full detail and no recovery data submitted.

(c) We do not have adequate information on exact % - ppm to determine the points or the curves.

(3) 'One-year study of the Fate of 14C-SD 43775 in soil' TIR-22-107-77.

(a) The diphenyl ether linkage is not accounted for.

(b) The complete detailed analytical methods have not been submitted.

(c) Raw data and recovery data have not been submitted.

(4) One-year study of the fate of 14C-SD 43775 in soil H. Y. Fan. TIR-22-107-77 Addendum #2

(a) The fate of the phenoxphenyl moiety is not demonstrated in the study.

(b) The study does not account for residues below the 3 inch soil level.

5.3.4 Effect of the pesticide on soil microorganisms:

(1) 'Impact of PYDRIN INSECTICIDE on microorganisms in the soil environment' TIR-22-108-77

(2) Determination of Antimicrobial Activity of Selected Pyrethroid Compounds TIR-76-03376

(a) The effect of SD 43775 on populations of specific soil microorganisms or the effects on microbial functions such as nitrogen fixation, nitration, and protein and carbohydrate degradation are not demonstrated.

(b) In study (1) above free living nitrogen fixing bacteria rather than symbiotic organisms should be used. Controls were not run.

(c) In study (2) above most of the organisms used in this study are animal pathogens and indicators of fecal pollution. No attempt was made to measure population or numbers of bacteria in these studies. Conditions for incubation are not given and there is no mention of controls. One sampling point is not sufficient to measure pesticide effects on microbes.

5.3.5 Leaching

(1) Degradation of Fenvalerate (Sumicidin) in Soil AM-70-0036

(a) Recovery data and complete analytical methodology is not given.

(b) The study may be acceptable if ring label studies are carried out since moieties of chlorophenyl and diphenyl ethers are not determined.

(2) The Leaching Behaviour of WL 43775 in Laboratory Soil Columns. Group Research Report WKGR 0130 76.

(a) Soil characteristics are not given.

5.3.6 Field Dissipation: Data are needed for actual use conditions in four typical cotton growing areas which reflect maximum dosage rates and the maximum number of repeat applications.

5.3.7 Rotational Crops

We cannot determine a time interval when residues would be absent in rotational crops or the amount of residues that would be present in rotational crop because:

(1) 1976 Residue Data for SD 43775 in Rotation Crops (onions and Sorghum)

(a) Analyses were only made for parent compound. residue metabolism studies to support that only parent is available to crop.

(b) Soil characteristics were not submitted

(c) The complete analytical method is not submitted.

(d) We need to know the amount of residue in soil.

(2) 1977 - Residue Data for SD 43775 in a rotation Crop (Wheat and Vetch).....TIR-24-142-77

(a) Soil characteristics are not given

(b) Complete analytical method not given.

(c) We need to know the amount of residues in soil

(3) Residue Studies in Rotation Crops in 14C-SD 43775 - treated soils. TIR-22-113-77

(a) Soil characteristics are not given

(b) The complete analytical method is not submitted

(c) Recovery data has not been submitted

(d) We need to know the amount of residue in soil

(4) 1975 - Residue Data for SD 43775 in Rotation Crops. (Alfalfa, Potatoes, Wheat and Soybeans) From a Simulated Rotation Study TIR-24-201-75

(a) This study does not represent actual use pattern

(b) The complete analytical method is not given or referenced

(c) Soil characteristics are not given

(d) We need to know the amount of residue in soil.

(5) 1977 - Residue data for SD 43775 in Rotation Crops (Sugar Beets, Soybeans, and Sorghum) following nine applications of SD 43775 the previous year to Cotton. A California Study TIR-24-145-77-B

(1) The presence of double peaks and single peaks for SD 43774 (in chromatograms) must be explained. Sample calculations based on these chromatographic data are needed.

(2) Complete soil characteristics are not given

(3) Soil residues at time of planting of rotational crops are not given.

(6) Data are needed to show that residues other than parent compound (SD 43775) are not present in rotational crops under conditions of maximum dosages and multiple applications. If other residues are found they should be quantitatively estimated.

5.3.8 Activated Sludge: This study is required to support products manufactured or formulated in the U.S. if such is discharged into a waste water treatment system. The data submitted in the study "Metabolic Fat of Fenvalerate (Sumicidin) in rats, soil, soil microorganisms and an aquatic model ecosystem" do not meet this requirement in that this study was not performed on a continuous or semi-continuous process. An outline of an acceptable protocol is given below:

Activated sludge metabolism. For assessment of this potential contamination of the aquatic environment, a laboratory study of effects of pesticides on the waste-

water treatment process is required to support the registration of all manufacuring-use products and all formulated products which are indirectly discharged into wastewater treatment systems. Some pesticides discharged into these systems, if toxic to microorganisms, may disrupt the treatment process by killing the microorganisms responsible for normal wastewater treatment. Pesticides subsequently entering the affected systems are therefore not transformed by the disrupted wastewater treatment process and consequently are discharged directly into the aquatic environment. Synthetic sewage (nutrients) and the radiolabeled active ingredient should be added to activated sludge and aerated in a closed system for 23 hours, allowing the sludge to settle for 30 minutes. A liter of supernatant (effluent) should then be removed for pesticide residue analysis including a material balance. Fresh synthetic sewage and the active ingredient should then be added to the remaining sludge and the cycle repeated. Dosage should start at 0.1 ppm and increase by increments to 100 ppm. Effects on microbial population must be determined by daily total counts of viable organisms in sludge.

Note to PM. We defer to the Environmental Safety section to determine the significance of results of the fish residue accumulation studies and the need for further studies of this type. Accumulation of 400X was noted in rainbow trout 213X in carp, 490 in catfish and 3500 in fathead minnow.

PM: Note: Toxicology Branch has indicated that reentry data will not be needed for the use of PYDRIN on cotton. See attached memo.

PM: Note: This is the second completed review put into one review. Shell made 2 submissions for this review 10/5/77 and 3/22/78. We will have to redue this review because of a third submission from Shell in EC dated 5/4/78

Ronald E. Ney Jr. 5/11/78
EEE Branch
Environmental Chemistry Section

Arthur O. Schlosser 7/11/78 PGS 7/11/78
Arthur O. Schlosser 5/8/78
Karen Sampson Karen Sampson 7/11/78
Charlotte Blalock
Willa Garner

PM: NOTE: If a meeting is requested at any time all reviewers must be present as the submission was divided among the following reviewers:

Ms. Garner
Mrs. Blalock
MS. Sampson
Mr. Schlosser
Mr. Ney

Each review will have to support their comments.

Some reports for which we cannot identify at this time list compound by SD number which do not appear to agree with compounds listed on pages 02 27, 02828, 02829 and 02830. For example: SD 53038 or SD 53036 and SD 36750 and SD 44607. Submit a list of the compound that agree with those in your reports. Also list with said compounds where they are found, for example: in plants, in soil, by photodegradation in water, etc.

Mr. Hobson was informed of methodology defficiency on 1/11/78 and made no response to date. The PM Mr. Mitchell was notified by review format 1/12/78