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Cyfluthrin Persistence in Soil as Affected by Moisture, Organic Matter, and Redox Potential

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Cyfluthrin [(*RS*-α-cyano-4-fluoro-3-phenoxybenzyl(1*RS*,3*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] (CYFLU) is a synthetic pyrethroid insecticide with agricultural (Baythroid 2™, formerly Bay FCR 1272) and household, hygienic, and turf/ornamental (Tempo™, Solfac™) uses. CYFLU is nonsystemic and is particularly effective against chewing insects, but is extremely toxic to fish and bees [Mobay Corporation (now Miles, Inc.), material safety data sheet, May 1985; Baythroid 2™ technical data brochure, June 1988]. Published degradation/persistence studies with CYFLU are limited. Noble and Hamilton (1985) reported that CYFLU used in grain storage breaks down slowly over a 52-week period under normal conditions of moisture and temperature. At higher moisture levels and temperatures, CYFLU loss is faster. Residues of CYFLU on strawberries (*Fragaria* sp.) 7 days after the last of 3 weekly applications at 0.015 kg a.i. ha^{-1} were reported to be less than the acceptable maximum tolerance of 0.1 mg kg^{-1} (McEwen et al., 1986). In a study designed to determine the effects of acid rain and ozone on insecticidal efficacy against gypsy moth larvae [*Lymantria dispar* (L.)] on tree seedlings, CYFLU appeared to be more resistant to degradation from atmospheric deposition than trichlorphon [dimethyl (2,2,2-trichloro-1-hydroxyethyl)phosphonate] (Dylox™) (Barger and Cannon, 1987). Preiss et al. (1988) reported the partial purification of an esterase from tomato (*Lycopersicon lycopersicum* L.) cell suspension cultures capable of degrading CYFLU. The metabolism of CYFLU by the mites *Rhizoglyphus robini* and *Tetranychus urticae* was recently reported by Capua et al. (1990) as was the resistance to CYFLU of the beetle *Tribolium castaneum* (Collins, 1990).

Information on CYFLU degradation/persistence in soil is proprietary (*Dr. John Murphy, Mobay Chemical Corporation, 1988, personal communication*). Because CYFLU showed promise in field trials for controlling *Heliothis* spp. in cotton (*Gossypium hirsutum* L.) (Micinski and Graves, 1987) and sugarcane borer [*Diatraea saccharalis* (F.)] in sugarcane (*Saccharum officinarum* L.) (Showler et al., 1987), we investigated the persistence of CYFLU in the laboratory in a heavy clay soil under anaerobic conditions. Intermittent anaerobic soil conditions frequently occur in Mississippi River delta cotton fields and south Louisiana sugarcane fields during the cool, rainy season (late fall, winter, and early spring). CYFLU remaining after summer applications could be subjected to anaerobic conditions.

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MATERIALS AND METHODS

Sharkey clay soil (very fine, montmorillonitic, nonacid, thermic Vertic Haplaquepts) (0- to 7.6-cm depth; pH 6.8; 4% sand, 37% silt, 59% clay, 2.4% organic matter), obtained from a site on the Louisiana State University Ben Hur Farm in Baton Rouge, Louisiana, was used throughout this study. The soil (no history of CYFLU application) was air-dried, passed through a 2-mm sieve, and determined by gas chromatography (GC) to be CYFLU-free. One hundred-gram samples (94.04 g on an oven-dry weight basis) of soil (contained in 300-cm^3 wide mouthed amber glass bottles) were fortified with technical grade CYFLU at 0.5 ppm ($\mu g\ g^{-1}$) applied in 1 mL hexane from a freshly prepared stock solution, on an oven-dry soil weight basis. After the soil was thoroughly mixed and the solvent was allowed to evaporate (10 h), the soil was either left unamended or amended (with organic matter, OM) by additional thorough mixing with cotton plant residue (composed of stalks, petioles, and leaves; 0.95% total nitrogen and 43.4% organic carbon; oven-dried at 65°C and ground to pass a 20-mesh screen). Plant residue (2.82 g) was added based on 3% of the oven-dry soil weight.

These soil samples were moisturized to either -0.3 bar (26.5%) or -1.0 bar (20.2%) water potential, then tightly sealed, and incubated in the dark at 25°C in a plant growth chamber for 31, 73, 115, and 140 d. A completely randomized block design was used, with three replications for each pesticide treatment [amended (+OM) and unamended (-OM), -0.3 bar and -1 bar] for each incubation period. The soil samples that were incubated for 140 d were all fitted with combination platinum/calomel electrodes for periodic redox potential (Eh) determinations throughout incubation.

After 31, 73, 115, or 140 d incubation, 10.00 g soil was Soxhlet-extracted with 200 mL of a 41:59 (v/v) hexane-acetone azeotropic solution for 3 h. The extract was placed in a separatory funnel, washed with distilled water to remove the acetone, dried over anhydrous sodium sulfate, and brought to an appropriate volume for GC analysis. Mean CYFLU extraction efficiency was about 92±8%. A second 10.00 g soil was used for soil moisture determination.

During the early phases of the study, aliquots (5 μL $injection^{-1}$) of the hexane extracts were analyzed for CYFLU using a Micro Tek model DSS-162 gas chromatograph, upgraded with a solid-state temperature programmer and a dual-channel electrometer and equipped with a high-temperature ^{63}Ni electron capture detector and a Hewlett-Packard model 3388A plotting integrator. A coiled Pyrex glass column, 1.2 m long x 6 mm OD x 4 mm ID, packed with 3% SP2401 on 100-120 mesh Supelcoport was used. The carrier gas (filter-dried N_2, 99.995% minimum purity) flow rate was 180 cm^3min^{-1}. The column oven, detector, and inlet temperatures were 210, 270, and 245°C, respectively. Under these GC conditions, CYFLU gave three partially resolved peaks, with retention times of 7.7, 8.8, and 9.6 min, representing four enantiomeric pairs of optical isomers. Total CYFLU was determined by combining the peak areas. The limit of quantitative detection was 0.005 $\mu g\ g^{-1}$, and recovery was corrected for extraction efficiency. Technical grade CYFLU (emulsifiable concentrate containing 200 g a.i. L^{-1}) was obtained from the Louisiana State University Entomology Department courtesy Mobay Chemical Corporation.

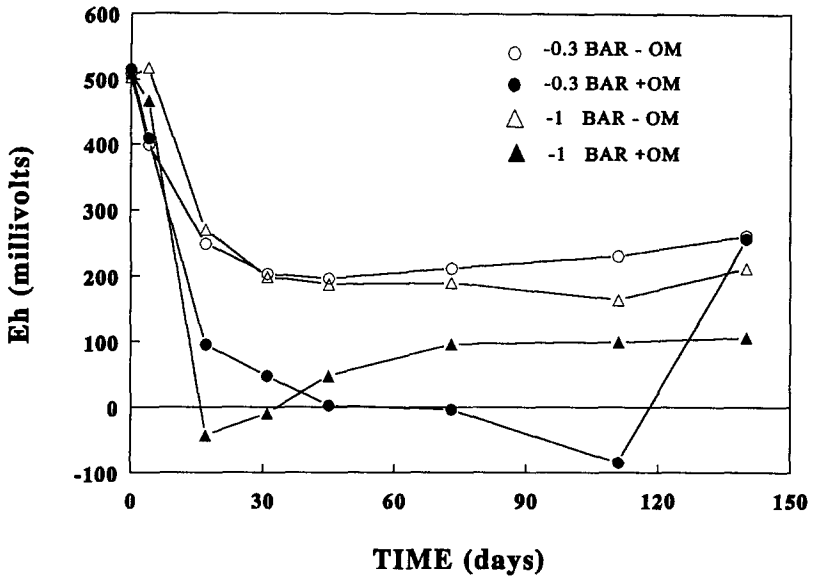

Figure 1. Changes in mean redox potential (Eh) in amended and unamended soil at -0.3 bar and -1.0 bar moisture.

During the later phases of the study, aliquots (2 µL injection^{-1}) of CYFLU extracts were analyzed using a Tracor Model 540 gas chromatograph equipped with a ^{63}Ni electron capture detector, a Dynatech Precision GC-411V autosampler for unattended sample injection, and a 15 m X 0.53 mm J & W Scientific DB 210 (1.0 µm film thickness) column. The carrier gas was ultra-high purity helium at 12.3 cc min^{-1} and the column makeup and detector purge gas was ultra-high purity nitrogen at 50 and 5 cc min^{-1}, respectively. Column oven, inlet, and detector temperatures were 215, 240, and 350°C, respectively. Under these GC conditions, retention times were 10.3, 11.6, and 12.6 min. A PE Nelson 2700 chromatography data system, consisting of a model 970 interface, Turbochrom 3™ software, and a microcomputer with color printer, was used for automated quantification and reporting of pesticide peak data including gas chromatograms. A multilevel calibration procedure was used with standards and samples injected in triplicate. Calibration curves were updated every tenth sample.

RESULTS AND DISCUSSION

Figure 1 shows the change in mean redox potential (Eh) in the various soil systems (unamended and amended, -0.3 bar and -1 bar moisture) that were sealed and incubated for up to 140 d. During the first two weeks, soil Eh decreased more rapidly in the amended systems than in those left unamended, an indication of greater microbial activity in the amended systems. After about 2 weeks, Eh values generally remained lower in the amended versus unamended systems. Oyamada and Kuwatsuka (1988) reported strikingly

similar changes in redox potentials in 6 Japanese soils amended with various organic substrates (cellulose, glucose, and rice straw) and incubated under waterlogged conditions. The changes in soil Eh values observed in the present study were also similar to those reported by Parr and Smith (1976) and Smith and Willis (1978) in their moist (-0.3 bar), anaerobic (nitrogen atmosphere) soil systems. We have no explanation for the rise in Eh in these sealed systems toward the end of the present study. This phenomenon has been observed by others (Parr and Smith, 1976; Oyamada and Kuwatsuka, 1988), also without explanation.

Mean recoveries of CYFLU from these soil systems incubated for 31, 73, 115, and 140 d are presented in Table 1. CYFLU disappearance was very rapid during the first month of incubation with recoveries of only 35-50 % after just 31 d. Some of the rapid disappearance during the first few days of incubation

TABLE 1. Recovery of cyfluthrin (CYFLU) from soil after anaerobic incubation

Treatment	Recovery, %[a]			
	31 d	73 d	115 d	140 d
-0.3 bar				
unamended	50.8±4.5a[b]	27.9±3.1a	14.8±2.9a	15.0±2.6a
amended[c]	35.2±2.3c	20.9±1.3b	14.4±1.7a	9.4±2.5b
-1 bar				
unamended	42.2±2.1b	31.1±1.6a	17.5±2.2a	11.0±0.6b
amended	38.4±1.2bc	22.0±2.6b	14.6±1.4a	9.2±1.2b

[a]Mean±standard deviation of three replicates; corrected for extraction efficiency.
[b]Values within the same column followed by a common letter are not significantly different at P=0.05 according to the New Duncan Multiple Range Test (SAS Institute, Inc., 1985).
[c]Plant residue added equivalent to 3% of the oven-dry soil weight.

may have been due to aerobic degradation (Eh about +400-+500mV). Between 31 d and the end of incubation (140 d), disappearance of CYFLU slowed substantially, resulting in terminal recoveries of 9-15 %. Roberts and Standen (1977) observed a similar degradation pattern for cypermethrin [(±)-α-cyano-3-phenoxybenzyl(±)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate] under waterlogged, anaerobic soil conditions. In their study, almost 70 % of the cypermethrin had disappeared from soil after only about 35 d. Between 35 d and 160 d, cypermethrin disappearance increased only an additional 20 % (to 90 %). Cypermethrin and CYFLU have almost identical basic chemical structures, the difference being that CYFLU has a fluoro group at the 4 position on the benzyl ring.

In the present study, CYFLU disappearance was generally more rapid in the amended systems than in the unamended systems. An exception was at 115 d, where there was no statistical difference (P=0.05) in mean recovery values

among the treatments. CYFLU disappearance in the amended systems was about the same at -0.3 and -1.0 bar moisture. The unamended systems behaved similarly, indicating that the difference in moisture level (-0.3 bar vs. -1.0 bar) was not important in this study. Overall CYFLU disappearance ranged 85-90% after 140 d incubation.

Best-fit linear regression equations for CYFLU disappearance are shown in Table 2. Comparison of regression lines were made according to Snedecor and

TABLE 2. Best-fit linear regression equations for cyfluthrin (CYFLU) disappearance from soil

Treatment	Equation	DT_{50}[a]	*r*
-0.3 bar			
unamended	ln R[b]=4.4535-0.0140t[c]	39	-0.96
amended[d]	ln R =4.3251-0.0154t	27	-0.96
-1 bar			
unamended	ln R=4.4411-0.0144t	37	-0.98
amended	ln R=4.3702-0.0156t	29	-0.97

[a]Estimated 50% disappearance time (days).
[b]CYFLU recovery, %.
[c]Incubation time (days).
[d]Plant residue added equivalent to 3% of the oven-dry soil weight.

Cochran (1980) and revealed heterogeneous variances. At P=0.10, the slope of the regression line for the -0.3 bar, amended treatment was different from that of the regression line of the -0.3 bar, unamended treatment. Slopes of the regression lines for the two -1.0 bar treatments were also statistically different at P=0.10, a further indication of faster CYFLU disappearance under amended anaerobic vs. unamended anaerobic soil conditions.

A probable initial pathway for CYFLU anaerobic degradation in soil is shown in Figure 2. The two metabolites shown, 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (**II**) and 4-fluoro-3-phenoxybenzoic acid (**III**), are the result of hydrolysis of CYFLU at the ester linkage by microbial esterase enzyme systems. Such hydrolysis is common to most pyrethroid insecticides in soil as well as in plants, insects, and arachnids. Roberts and Standen (1977, 1981), for example, showed that cypermethrin initially degraded aerobically and anaerobically via ester hydrolysis to **II** and 3-phenoxybenzoic. They also noted the accumulation of 3-phenoxybenzoic acid under anaerobic but not aerobic conditions. Preiss et al. (1988) isolated an esterase from tomato cells which hydrolyzed CYFLU into **II** and **III** plus 3-phenoxy-4-fluorobenzaldehyde and 3-phenoxy-4-fluorobenzylalcohol. By using esterase inhibitors in their study of pyrethroid degradation by two mite species, Capua et al. (1990) concluded that hydrolytic cleavage at the ester linkage appeared to be the major metabolic pathway.

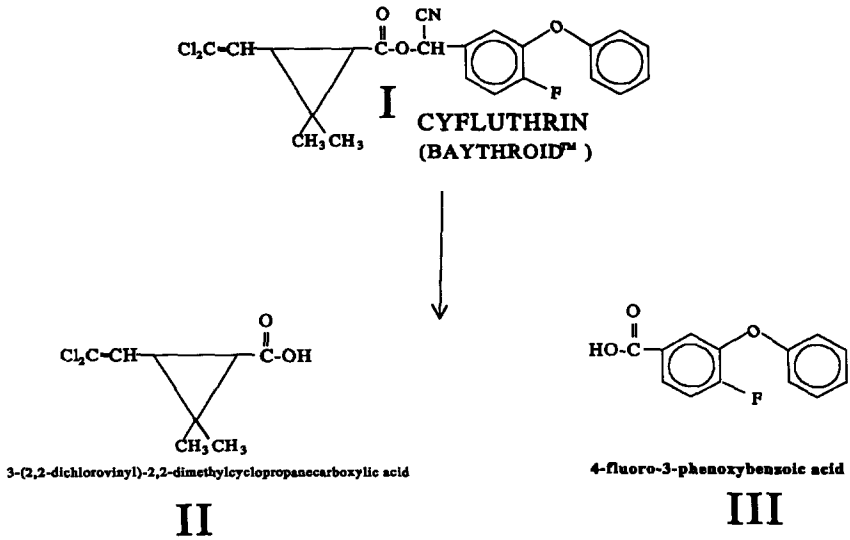

Figure 2. Probable initial pathway for cyfluthrin (CYFLU) anaerobic degradation in soil.

Under the conditions of this study, CYFLU persistence in soil was affected by organic matter and redox potential and appeared unaffected by soil moisture. The added organic matter (crop residue) served to rapidly reduce the soil redox potential. When molecular O_2 is limiting and organic matter is readily available, facultative anaerobic microorganisms indigenous to the soil can shift from aerobic respiration (utilization of molecular O_2 as the electron acceptor) to either anaerobic respiration (utilization of inorganic compounds as electron acceptors) or fermentation (utilization of organic compounds as electron acceptors)(Parr et al., 1970). Placing a crop residue in a soil environment can also alter the residue's indigenous microflora (including bacteria, fungi, actinomycetes, and protozoa), resulting in stimulatory effects on overall microbial activity (Parr and Papendick, 1978).

The results of this study suggest that since pyrethroid insecticides such as cyfluthrin can also dissipate readily under biologically-active anaerobic soil conditions, a practical means of reducing or eliminating pyrethroid carryover from one cropping season to the next could be by flooding cropland between harvest and planting. A project involving controlled flooding of large fields in the Mississippi Delta has recently been proposed *(Drs. F. D. Shields and C. M. Cooper, USDA-ARS, Oxford, MS, 1992, personal communication)*. Such controlled flooding should not only result in anaerobic soil conditions conducive to pesticide degradation but also in reduced sediment production (soil erosion) from the fields due to the water cover.

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All programs and services of the U. S. Department of Agriculture are offered on a nondiscriminatory basis without regard to race, color, national origin, religion, sex, marital status, or handicap. Mention of a pesticide in this paper does not constitute a recommendation for use by the U. S. Department of Agriculture nor does it imply registration under FIFRA as amended. Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U. S. Department of Agriculture.

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