Degradation of Fluazifop-butyl in Soil and Aqueous Systems

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The degradation of fluazifop-butyl was studied in sterile buffered water, in sterile soil, and in nonsterile soil with different moisture contents. Fluazifop-butyl was stable in sterile buffered water at pHs 4 and 7, with more than 90% of the initial amount remaining in solution after 21 days. At pH 9 fluazifop-butyl degraded following a pseudo-first-order kinetics with a half-life of 2.5 days. Fluazifop-butyl was used at a concentration of 10 mg kg^{-1} soil in studies of soil degradation. In air-dried soil 40% of the applied fluazifop-butyl remained in the soil 21 days after treatment. However, with a higher soil moisture content, less than 5% of the applied fluazifop-butyl was present after 7 days. There was a slower dissipation rate in sterile soil than in nonsterile soil, indicating that microflora play a role in fluazifop-butyl degradation. The degradation of fluazifop-butyl in soil and water proceeded mainly by hydrolysis, with fluazifop as the major product.

Fluazifop-butyl [butyl 2-[4-[[5-(trifluoromethyl)-2-pyridyl]oxy]phenoxy]propionate] is a herbicide used for postemergence control of graminaceous weeds in soybean (*Glycine max* L. Merr.) and in other dicotyledonous crops (Palmieri et al., 1982; Buhler and Burnside, 1984). The chemical, physical, and toxicological properties of fluazifop-butyl have been described by Horellou et al. (1982). When applied under greenhouse and field conditions, it is rapidly absorbed by plants and converted to its major acid metabolite, fluazifop [2-[4-[[5-(trifluoromethyl)-2-pyridyl]oxy]phenoxy]propionic acid] (Carr, 1986; Hendley et al., 1985; Kells et al., 1984). Parker et al. (1985) detected fluazifop residues in cucumbers (*Cucumus sativus* L.) and sweet potato (*Ipomoea batatas* L.) harvested 25 and 55 days after application, respectively.

In soil, fluazifop-butyl can be rapidly converted to fluazifop (Horellou et al., 1982). Arnold et al. (1982) reported that fluazifop-butyl and fluazifop had half-lives of less than 3 days and 12 weeks, respectively, in soil. Bewick (1986) studied the metabolism of fluazifop-butyl in soil. He detected a stereoselective inversion of the optical configuration of the free acid resulting from hydrolysis.

In order to obtain more information on the degradation behavior of fluazifop-butyl we have investigated the following: (a) the hydrolysis rates of fluazifop-butyl at different pHs in water; (b) microbial involvement in soil degradation; (c) the effect of soil water regimes.

EXPERIMENTAL SECTION

Chemicals. All commercial solvents and chemicals were used as supplied. Authentic samples of fluazifop-butyl and fluazifop were gifts from ICI Plant Protection Division, Milan, Italy. Deionized and Milli-Q (Millipore, Waters, Milan, Italy) filtered water were used for the hydrolysis experiments.

Hydrolysis. Aliquots of standard fluazifop-butyl solution (500 mg L^{-1}) in acetonitrile were diluted with sterile buffer solutions, pH 4 (phthalate buffer), 7 (phosphate buffer), or 9 (borate buffer), to give final concentrations of 1.2 or 2.5 mg L^{-1}. Portions (50 mL) of the herbicide solutions were placed in 250-mL sterile Erlenmeyer flasks, closed with cotton wool plugs covered with Parafilm, and kept in the dark at a constant temperature (25 °C). All operations were performed under sterile conditions, in a horizontal laminar flow sterile hood.

At selected time intervals three replicate samples of solutions of each pH were analyzed for fluazifop-butyl and fluazifop.

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Soil Degradation Studies. All experiments were conducted with a soil sampled to a depth of 0–25 cm, dried to 10% water content (w/w), sieved to obtain a <2-mm fraction, and stored at room temperature in black PVC bags. The soil used was a sandy loam containing 7.8% clay and had a cation exchange capacity of 5.9 mequiv/100 g. The organic matter content was 1.72%, the pH in water was 6.1, and the maximum moisture capacity (MMC) was 33% (w/w) (field moisture capacity 16.8%).

Apparatus. The incubation system used for the soil degradation studies was based on that described by Laskowsky et al. (1983). Each incubation system consists of a two-compartment apparatus. The soil sample is placed in the first compartment, and 75 mL of 0.5 M NaOH is placed in the second compartment to absorb any carbon dioxide evolved. The incubation system is carefully closed and connected to an O_2 supply to replace the O_2 consumed in the respiratory processes. This apparatus maintains the desired soil humidity and allows quantitative evaluation of CO_2 evolved (Gennari et al., 1986).

Soil Treatment with Fluazifop-butyl. A standard solution of fluazifop-butyl in acetone (1 mL, 1000 mg L^{-1}) was added to 3 g of air-dried soil contained in a 10-mL wide-mouthed glass vial. The vial was closed with a cotton wool plug and the acetone evaporated at room temperature under vacuum in a desiccator. The treated soil was then introduced into the incubation system, diluted with 97 g (dry weight) of soil, and stirred manually for 5 min. The final concentration of fluazifop-butyl in the soil was 10 mg kg^{-1} based on the dry weight of the soil.

Effect of Soil Moisture Content. Soil samples were treated with fluazifop-butyl as described above, and distilled water was added dropwise to obtain moisture levels of 20%, 35%, and 50% of the MMC. A test with air-dried soil was also performed. Incubation was conducted in the dark at 25 °C. Triplicate samples were taken for analysis for fluazifop-butyl and fluazifop content immediately after application of fluazifop-butyl and after 1, 3, 7, and 21 days.

Microbial Involvement in Fluazifop-butyl Degradation. To determine the role of microorganisms in fluazifop-butyl degradation, one series of soil samples was treated with ethylene oxide (EO) as described below. Air-dried soil (97 g) was weighed in polyethylene bags of BARD Sterile peel (7.5 cm) packaging system type and then exposed to an EO (10% in CO_2) atmosphere for 8 h (pressure 4×10^5 Pa; relative humidity 65%; temperature 40 °C). This treatment causes complete elimination of viable microbial cells (Gennari et al., 1987).

The sterile soil was transferred to the incubation system that had been previously sterilized by autoclaving for 15 min at 120 °C. Soil (3 g) used for the application of

0021-8561/88/1436-1319$01.50/0

fluazifop-butyl was dry-sterilized in the 10-mL glass vial with a cotton wool plug at 160 °C for 10 min. This soil was treated as described above. The moisture content of the soil was adjusted to 50% of MMC with sterile water and the soil kept in darkness at a constant temperature of 25 °C. All operations were carried out under a horizontal laminar flow sterile hood working under sterile conditions.

Immediately after preparation of the samples for incubation and after 1, 3, 7, and 21 days, triplicate samples were analyzed for fluazifop-butyl and fluazifop contents.

Analysis. The extraction procedures and the HPLC analytical conditions for fluazifop-butyl and fluazifop determination in soil and water have been reported elsewhere (Nègre et al., 1987).

RESULTS AND DISCUSSION

Hydrolysis Experiments. Parts a and b of Figure 1 show plots of log [concentration] versus time for the disappearance of fluazifop-butyl from buffered-sterile water at pH 4, 7, and 9 and show that hydrolysis occurred very slowly at pH 4 and 7. At pH 9 degradation followed pseudo-first-order kinetics, and curve fitting yielded a rate constant of 3.18×10^{-6} s^{-1} ($r^2 = 0.95$) for the initial concentration of 1.2 mg L^{-1} and 3.21×10^{-6} s^{-1} ($r^2 = 0.97$) for the initial concentration of 2.5 mg L^{-1}, corresponding to half-lives of 2.5 days in both cases. Hydrolysis of fluazifop-butyl in water showed direct degradation of the herbicide to the corresponding free acid fluazifop. The fluazifop formed was stable at all pHs tested.

Microbial Involvement in Fluazifop-butyl Degradation. The fluazifop-butyl concentration decreased with time in both sterile and nonsterile soils (50% of MMC in Table I). The half-life values of the fluazifop-butyl in nonsterile and sterile soils were <1 and 3 days, respectively. In sterile soil the data for disappearance of parent fitted a pseudo-first-order decay curve well ($r^2 = 0.99$). The more rapid loss of fluazifop-butyl in sterile soil than in water at pH 4 or 7 indicates that hydrolysis was catalyzed by the soil. Soil adsorption sites may catalyze nonbiological degradation of pesticides. For example, catalytic degradation of carbaryl on montmorillonite has been observed by Fusi et al. (1986), and Armstrong et al. (1967) found that atrazine hydrolysis was catalyzed by adsorption.

In sterile soil the recovery (expressed as fluazifop-butyl and fluazifop) was 101.4 ± 0.9 for the first 7 days and then slowly declined. After 99 days from treatment, 84% of the chemical applied to the soil was still extracted as fluazifop. In nonsterile soil the acid formed was soon degraded, the recovery being less than 100% as early as 1 day after the start of the test.

These results suggest that bacterial flora contribute to the degradation of this product. Our results are in line with those reported by Martens (1978) in an examination of the degradation of another phenoxyalkanoic herbicide, diclofop-methyl [methyl 2-[-(2,4-dichlorophenoxy)phenoxy]propionate], in soil. Martens observed rapid hydrolysis of the ester into the corresponding acid, diclofop, under aerobic and anaerobic conditions. The diclofop formed was much more persistent in anaerobic than aerobic conditions and proved sensitive to biotic degradation. The involvement of bacterial flora in the degradation of phenoxyalkanecarboxylic acids was also noted by Burgher et al. (1962). These authors have shown that susceptibility to such degradation is influenced by the specific structure of the molecule.

The reduced recovery of fluazifop may be due in part to a binding or complexing of the acid to the soil as indicated by Smith (1977, 1985) for diclofop and haloxyfop.

Table I. Hydrolysis of Fluazifop-butyl to Fluazifop in Nonsterile Soil at Different Moisture Levels and in Sterile Soil (Average from Triplicate Samples)[a]

	nonsterile														sterile: 50% satd		
	air-dried			20% satd			35% satd			50% satd							
time, days	FB	F	FB + F	FB	F	FB + F	FB	F	FB + F	FB	F	FB + F	FB	F	FB + F
0	100	0		100	0		100	0		100	0		100	0	
1	97.9	5.1	2.1	0.3	100.1	4.9	47.1	5.7	48.0	5.6	95.1	2.1	22.2	3.4	62.3	2.4	84.5	3.9	24.9	3.2	65.5	1.7	90.5	1.4	74.8	1.7	26.6	0.4	101.4	1.7
3	91.8	2.7	10.3	1.1	102.1	1.7	14.2	0.8	76.1	1.0	90.3	1.5	8.5	0.6	67.8	3.1	76.3	2.5	10.6	2.3	73.0	1.6	82.0	1.3	49.8	1.7	50.8	1.4	100.6	3.0
7	80.0	5.9	18.9	2.1	98.9	4.9	3.3	1	84.5	2.3	87.7	1.2	3.5	0.9	66.7	2.2	70.2	1.4	3.3	0.3	64.0	1.1	66.7	1.0	20.5	7.3	81.9	8.6	102.4	1.6
21	39.5	1.9	51.5	2.0	91.4	2.6	<1		76.1	2	76.1	2	1	0	47.7	3.5	48.7	3.5	<1		46.1	0	46.1	0	1.35	0.1	93.9	0.8	95.2	1.1
42	C		C				C		C				C		C				<1		92.6	1.1	92.6	1.1						
99	C		C				C		C				C		C				<1		84.4	1.4	84.4	1.4						

[a] Key: FB = ester as ester equivalent (%) (±SD); F = acid as ester equivalent (%) (±SD); C = not determined.

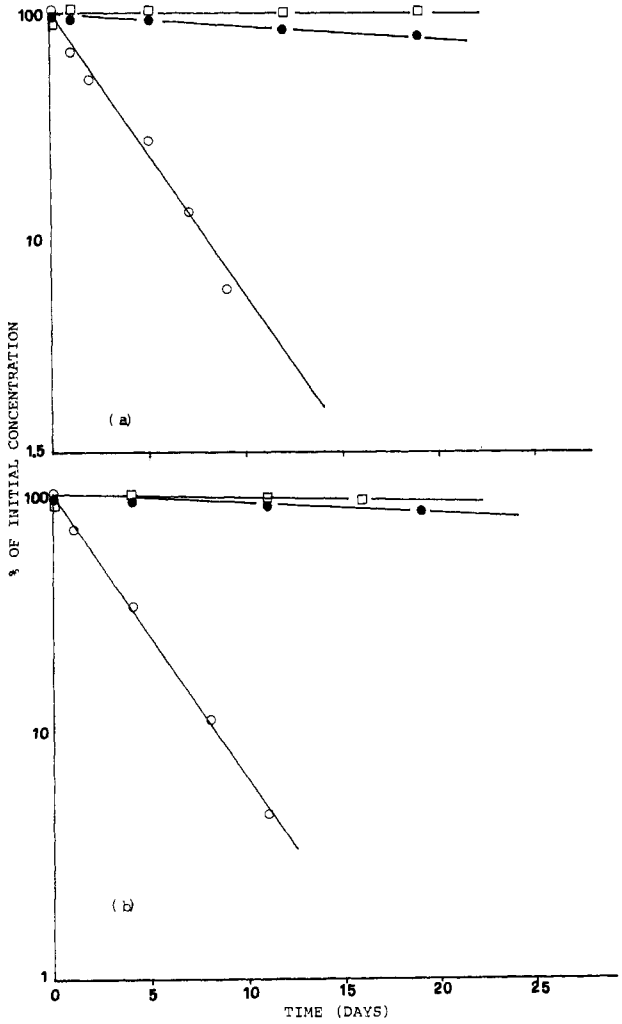

Figure 1. Hydrolysis degradation rates of fluazifop-butyl at pH 9 (○), pH 7 (●), and pH 4 (□). Initial concentrations: 1.2 mg L^{-1} (a); 2.5 mg L^{-1} (b). Average from triplicate samples. Standard deviation <6%.

Effect of Soil Moisture Content. The data in Table I show that fluazifop-butyl degradation was independent of soil moisture content in the range 50–35% of MMC. A reduction in soil moisture to 20% of MMC resulted in a slower rate of degradation only during the first 3 days after treatment. In air-dried soil the herbicide was found to be more persistent: about 40% of the applied fluazifop-butyl remained in the soil 21 days after treatment. These results are in agreement with those reported for diclofop-methyl (Smith, 1977) and haloxyfop-methyl [methyl 2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]-propionate] (Smith, 1985), which are also degraded more slowly in drier soils. The kinetics of degradation of fluazifop-butyl in moist soils was greater than first order. In air-dried soil, it followed zero-order kinetics ($r^2 = 0.98$) with a half-life of 17 days, showing that hydrolysis is by different mechanisms according to the soil moisture content. Zero-order kinetics are observed in heterogeneous reactions such as the reaction of gases on solid surfaces (Glasstone, 1959). The water present in air-dried soil is associated with the surface of the soil particles as adsorbed moisture and can move only in the vapor phase (Brady, 1974). Thus, in air-dried soil, it is possible that fluazifop-butyl hydrolysis could occur on the soil surface by heterogeneous reaction.

Soil moisture appeared to have more influence on the dissipation rate of fluazifop (Table I) than on fluazifop-butyl. The recovery (expressed as fluazifop-butyl and fluazifop) was higher in soil at 20% of MMC than in soil with higher water content. In air-dried soil recovery was less than 100% only after the third day from treatment.

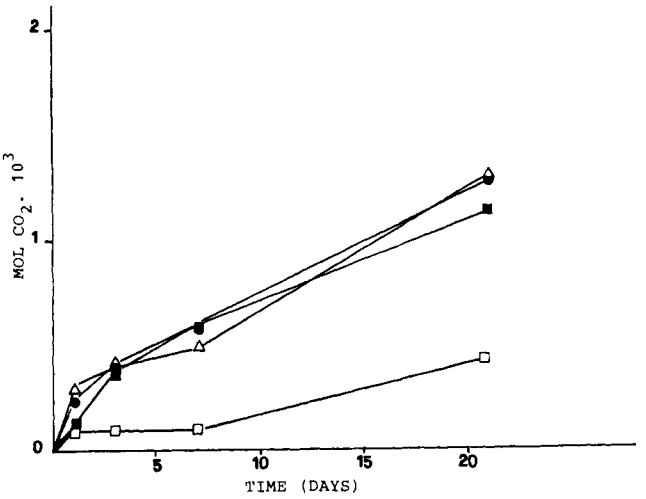

Figure 2. Production of carbon dioxide by soils moistened to 50% (△), 35% (●), and 20% (■) of maximum moisture capacity and by air-dried (□) soil. Average from triplicate samples. Standard deviation <8%.

In order to observe whether a reduction in soil moisture content affected the microbial activity of the soil, the CO_2 evolved by the soils was measured (Figure 2). There was no difference in the production of carbon dioxide from soil with a 20–50% range of MMC, indicating that under these conditions no quantitative changes in microbial population occurred. However, low-water regimes may cause such changes (Birch, 1958), and those may greatly influence the course of decomposition of pesticides in soils (Hill and Arnold, 1978).

Carbon dioxide production in air-dried soil was significantly lower than in the moist soils, indicating reduced microbial activity. These data together with those of Table I provide substantial evidence that the degradation of fluazifop-butyl and fluazifop is partly related to microbial activity.

ACKNOWLEDGMENT

This work was supported by grants from Regione Piemonte Assessorato Sanità (Contributions 115–116) and CNR (Contribution 86.00840.06 del 23/9/1986).

Registry No. Fluazifop-butyl, 69806-50-4; fluazifop, 69335-91-7.

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Received for review January 28, 1988. Accepted April 25, 1988.

Enhanced Soil Degradation of Alachlor by Treatment with Ultraviolet Light and Ozone

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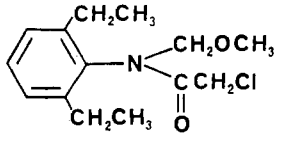
Photolytic ozonation followed by microbial degradation has been considered as a disposal option for agricultural pesticide wastewater. In an effort to better understand and ultimately to optimize the process with respect to alachlor, photolysis and ozonation have been examined separately. Alachlor is dechlorinated upon irradiation and forms a number of intermediates that retain the aromatic ring and carbonyl carbons as determined by labeling studies. These compounds include hydroxyalachlor, norchloralachlor, 2′,6′-diethylacetanilide, 2-hydroxy-2′,6′-diethyl-*N*-methylacetanilide, and a previously unreported lactam. In comparison, ozonation does not readily dechlorinate alachlor but rather oxidizes the alkyl side chain and opens the aromatic ring. Solutions that were subjected to photolysis or ozonation were placed in soil biometer flasks as was untreated alachlor, and the degradation was measured by the release of $^{14}CO_2$. Treated solutions showed rapid metabolism whereas less than 5% of the parent compound was mineralized after 35 days.

Alachlor [2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide] is a widely used herbicide that controls most annual grasses and certain broadleaf weeds. It is esti-



Alachlor

mated that production in 1982 was 38 400 metric tons (Gianessi, 1986). Soil persistence studies indicated relatively rapid breakdown of alachlor. I.e., 30–40 days was required for 90% dissipation (Kearney et al., 1985); however, very little ring-labeled [^{14}C]alachlor was mineralized to $^{14}CO_2$ in soil (Chou and Tiedje, 1973). The soil fungus *Chaetomium globosum* reportedly converted alachlor to a number of ring-intact metabolites, including 2-chloro-2′,6′-diethylacetanilide, 2,6-diethyl-*N*-(methoxymethyl)-aniline, 2,6-diethylaniline, and 1-(chloroacetyl)-2,3-dihydro-7-ethylindole (Tiedje and Hagedorn, 1975). In addition to microbial metabolism, alachlor is subject to photodecomposition on the soil surface. Residues of 67.5%, 54.1%, and 59.4% alachlor were measured on three soil surfaces exposed to sunlight (Fang, 1977). The major photoproducts reported in that study were 2-chloro-2′,6′-diethylacetanilide, 2,6-diethylaniline, 2′,6′-diethylacetanilide, monochloroacetic acid, 2,6-diethyl-*N*-(methoxymethyl)aniline, and 1-(chloroacetyl)-2,3-dihydro-7-ethylindole.

Despite the fact that alachlor is subject to both microbial metabolism and photodecomposition, residues have been detected in well water at certain locations (Cohen et al., 1986). Ultraviolet irradiation in conjunction with ozonation and followed by soil metabolism has been examined as a waste disposal method in an effort to reduce the risk of groundwater contamination from pesticide disposal (Kearney et al., 1984). In a recent survey of 11 major pesticides, formulated alachlor, in the concentration range 10–100 ppm, was shown to undergo rapid decomposition (Kearney et al., 1987).

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