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Flumioxazin Soil Persistence and Mineralization in Laboratory Experiments

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Flumioxazin is an herbicide registered for use in soybean and peanut. However, few published papers concerning the soil persistence of flumioxazin are available. Therefore, laboratory studies were initiated to determine the half-life ($t_{1/2}$) of flumioxazin in Greenville sandy clay loam and Tifton loamy sand soils when incubated at 15 and 25 °C. Results indicated that temperature had little effect on flumioxazin persistence. The $t_{1/2}$ for the Greenville soil was 17.9 and 16.0 days while the Tifton soil was 13.6 and 12.9 days, at 15 and 25 °C, respectively. These data correspond to the greater clay content of the Greenville soil (32%) as compared to the Tifton soil (2%). Therefore, the Greenville soil had greater soil adsorption and less flumioxazin was generally available to be degraded by soil microorganisms. In soils that were heat treated to reduce microbe populations, 99% of initial flumioxazin was accounted for after 16 days. Mineralization of flumioxazin, measured as $^{14}CO_2$ evolution, was also greater in the Tifton soil (2.2% after 64 days) than in the Greenville soil (2.0% after 64 days). From these data, it was concluded that microbes were the most influential factor concerning the degradation of flumioxazin.

KEYWORDS: Flumioxazin; soil degradation; mineralization

INTRODUCTION

Pesticide soil dissipation is the result of several concomitant chemical and biological factors including temperature, pH, soil moisture, microbes present, and the proclivity of the respective molecule for degradation (*1*). Moreover, the degree to which a pesticide is sorbed to soil colloids is inversely proportional to the rate of degradation by soil microbes (*2*).

Increased herbicide persistence can translate into increased weed control with time but can also increase the potential that the herbicide will become an environmental contaminant (*3*). Therefore, it is desirable that a given herbicide persists sufficiently to provide effective weed control, while also degrading at a rate to adequately reduce environmental risk.

Flumioxazin, a *N*-phenyl phthalimide herbicide, is registered for preemergence control of dicotyledonous weeds species in soybean (*Glycine max*) and peanut (*Arachis hypogaea*) (*4*). Currently, limited information exists concerning the environmental fate of flumioxazin. Studies have indicated that flumioxazin has a soil half-life between 11.9 and 17.5 days (*4*). However, soil type, experimental procedures (laboratory or field dissipation), and the conditions of the experiment were not listed.

Because of the spectrum of weeds controlled by flumioxazin, this herbicide has been most commonly used in the peanut growing regions in the southern United States (*5*−*7*). Adsorption coefficients values (K_d) for flumioxazin in the predominant soils in this region have been observed to be between 3.8 and 0.4 (*8*). K_d values near 1 reflect that nearly equal quantities of flumioxazin are sorbed and in solution simultaneously. Therefore, lower K_d values mean that relatively large amounts of flumioxazin are available for degradation by soil microbes. This will impact the persistence of flumioxazin in the environment.

The objective of this research was to determine the half-life of flumioxazin in two commonly occurring soils in the peanut producing regions in the state of Georgia. The influence of incubation temperature and soil microbial population on dissipation of flumioxazin was also investigated.

MATERIALS AND METHODS

Greenville sandy clay loam (scl) (fine, kaolinitic, thermic Rhodic Kandiudults) and Tifton loamy sand (ls) (fine-loamy, kaolinitic, thermic Plinthic Kandiudults) soils were gathered from the top 10 cm of cropping areas that were void of previous flumioxazin application. These soils were chosen because they are representative of those commonly found in the region of Georgia where flumioxazin is most often applied, as well as the fact that these soils vary in their relative clay and sand content (**Table 1**). The soils were characterized by the University of Georgia Soil Testing Laboratory (Athens, GA). The soils were air-dried and passed through a 2 mm sieve. Twenty-five grams of dry soil was placed in plastic bottles and capped (*9*). One milliliter of flumioxazin, dissolved in acetonitrile at a concentration of 100 ng mL^{-1}, was added to each bottle. After the solvent had evaporated, the soil sample was mixed for even herbicide distribution. Water was added to each bottle in order to achieve 70% of field capacity. The samples were incubated at either 15 or 25 °C for 0, 0.25, 0.5, 1, 1.5, 2, 4, 8, 16, and 32 days in the dark. All remaining bottles were opened after 8 and 16 days of incubation to ensure that the environment remained aerobic. Samples were stored at −20 °C until extraction.

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Table 1. Physical Characteristics of the Soils Used for Persistence and Mineralization Experiments

series	pH	CEC	% OC	% sand	% silt	% clay
Greenville scl	6.0	7.6	2.6	58	10	32
Tifton ls	6.1	4.3	1.6	94	4	2

To determine the influence of microbial degradation on the persistence of flumioxazin, the Tifton ls soil was heat treated for 48 h at 90 °C to reduce microbial populations. Wolf et al. (*10*) have shown that heat treatment (HT) reduces microbial populations by 1000-fold, without damaging the structural or chemical integrity of the soil.

Flumioxazin was recovered from each soil using accelerated solvent extraction (ASE) in high-performance liquid chromatography grade acetonitrile (Fisher Scientific, Pittsburgh, PA) as described in Vencill and Ferrell (*11*). ASE conditions were as follows: extraction solvent, acetonitrile (34 mL); temperature, 100 °C; pressure, 11 MPa; 5 min static time; flush volume, 60%; the sample was extracted with one cycle. Hydromatrix was used as the drying agent to mix with soil samples. The acetonitrile extract was evaporated to dryness using a vacuum concentrator (Labconco RapidVap, Kansas City, MO). The samples were then reconstituted with 1 mL of acetontirile, and flumioxazin concentration was analyzed using gas chromatography (HP 6890) coupled with mass spectroscopy (HP 5973) (*11*). The unit was equipped with an HP 6890 auto sampler and a HP-5MS cross-linked 5% PH ME siloxane, 30 m × 0.25 mm × 0.25 μm capillary column. The carrier gas was He with a flow rate of 1.6 mL min^{-1}. The sample was injected in pulsed splitless mode at 250 °C with an injection volume of 5 μL. The inlet temperature and pressure were held constant at 250 °C and 109 kPa, respectively. The oven temperature program was used as follows: injection at 80 °C with a 1 min hold, ramped from 80 to 170 °C at 30 °C min^{-1} with a hold of 4 min, then ramped from 170 to 205 °C at 10 °C min^{-1} with a hold of 1 min, and final ramp from 205 to 210 °C at 30 °C min^{-1} with a hold of 5 min. The total run time was 20.47 min, and flumioxazin eluted at 16.66 min.

Half-lives ($t_{1/2}$) for each temperature were determined, as in Lehmann et al. (*12*), by plotting $\ln(c/c_o)$ vs t and then solving for t using eq 1: $c/c_o = 0.5$. Rate constants were determined from the slope of the linear regression line. The experiment was a completely randomized design with three replications.

Mineralization was measured as $^{14}CO_2$ evolution from Greenville scl and Tifton ls soils incubated at 25 °C in biometer flasks (*13*). Soils were collected from field sites that had no history of flumioxazin application. These soils were air-dried and passed through a 2 mm sieve. Fifty grams of soil was then placed in the biometer assembly and wetted to 40% of field capacity. The soil was then incubated for 14 days prior to the addition of flumioxazin. This procedure was conducted as described by EPA guidelines (*14*).

A mixture of ^{14}C (phenyl-^{14}C, specific activity 12.9 MBq/mg) and formulated (Valor 51% active ingredient, wettable powder; both provided by Valent USA, Richardson, TX) flumioxazin, containing 1650 Bq and 5 mg ai kg^{-1} soil, was carefully distributed to the soil surface. The sidearm of the biometer flask was filled with 10 mL of 0.1 N KOH solution to trap $^{14}CO_2$. The KOH solution was removed after 1, 2, 4, 8, 16, 32, and 64 days; a 1 mL aliquot of the trap solution was counted for activity using liquid scintillation counting spectroscopy (Beckman LS5000, Beckman Instruments, Fullerton, CA). After the 10 mL of KOH was removed, an additional 5 mL of KOH was added and discarded as a rinse. Additionally, when 10 mL of KOH was added and remained in the flask until the next sample time, 10 mL of air was also added in order for the environment within the flask to remain aerobic. This study contained three replications and was conducted twice. The data were plotted as cumulative $^{14}CO_2$ evolution over t (*15*). The means were plotted, and the standard error of the mean was calculated for each data point.

RESULTS AND DISCUSSION

Greenville scl and Tifton ls soils were used. Previous research indicated that the K_d value for flumioxazin was 3.8 and 0.7 for the Greenville scl and Tifton ls soils, respectively (*8*).

Table 2. First Order Half-Lives ($t_{1/2}$) and Dissipation Rate Constants (k) of Flumioxazin at Two Temperatures

soil	temperature (°C)	$t_{1/2}$ (days)	k (days^{-1})	r^2
Greenville	15	17.9	0.038	0.88
Greenville	25	16.0	0.043	0.90
Tifton	15	13.6	0.051	0.93
Tifton	25	12.9	0.053	0.88

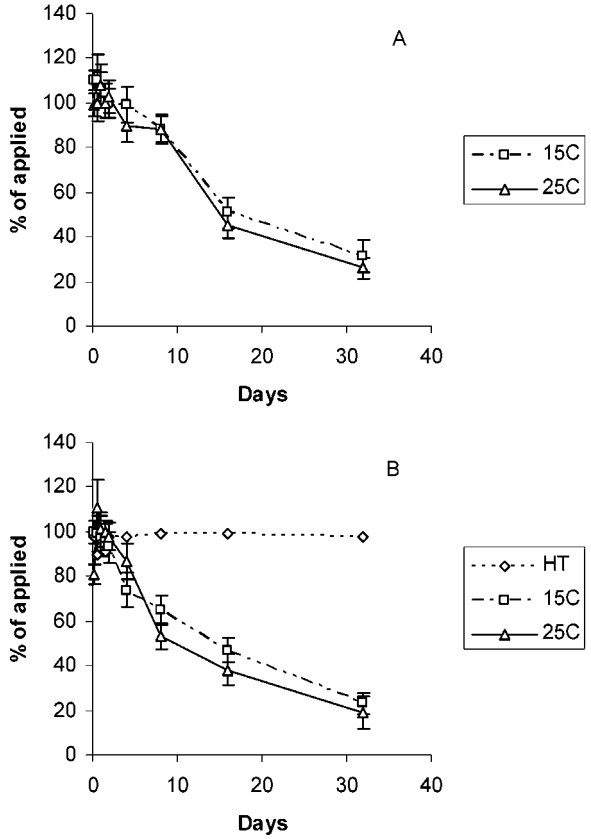

Figure 1. Dissipation of flumioxazin from (**A**) Greenville scl and (**B**) Tifton ls over 32 days at 15 and 25 °C. HT was used to reduce microbe populations within the soils sample. Error bars represent the standard error of the mean.

Flumioxazin Persistence. The results of the flumioxazin dissipation study are summarized in **Table 2**. Incubation temperature had little impact on the dissipation rate of flumioxazin in either soil (**Figure 1**). However, soil microbes were observed to be the predominant factor influencing flumioxazin dissipation. This was indicated by observing the lack of flumioxazin dissipation in the HT soil. After 16 days, the HT soil retained near 99% of the originally added flumioxazin. At 70% field capacity, <1% hydrolysis had taken place after 16 days of dark incubation. Therefore, when soil microbe populations are reduced, flumioxazin dissipation rates are greatly retarded.

The $t_{1/2}$ for the Greenville scl soil was 17.9 and 16.0 days, while the Tifton ls was 13.6 and 12.9 days at 15 and 25 °C, respectively. Temperature had a relatively small impact on flumioxazin degradation. For herbicides with soil half-lives greater than 100 days, such as atrazine and flumetsulam, increases in temperature can have dramatic effects on degradation rates (*9*, *12*). However, in herbicides with half-lives from 10 to 20 days, such as metolachlor, degradation rates have been shown to be less effected by temperature (*12*). Therefore, flumioxazin, with half-lives between 12 and 17 days, was not expected to be greatly influenced by incubation temperature.

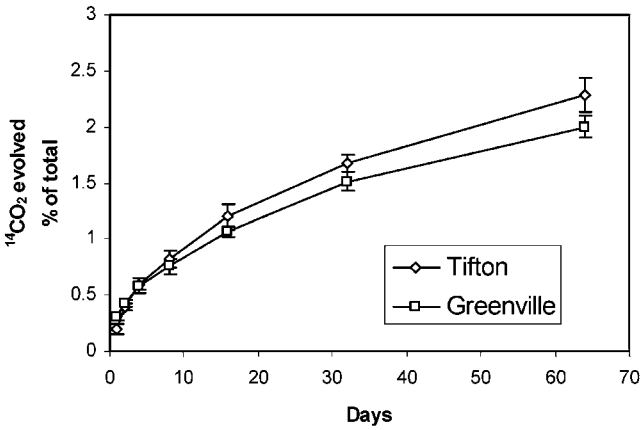

Figure 2. Mineralization of flumioxazin, as trapped $^{14}CO_2$, in two soils incubated at 25 °C for 64 days. Error bars represent the standard error of the mean.

The half-life data for flumioxazin were similar to the previously published dissipation times of 11.9−17.5 days (*4*). The reason for the greater $t_{1/2}$ values with the Greenville scl soil was likely influenced by the increased adsorption by this soil (*8*). Previous papers have stated that pesticides that are sorbed to soil surfaces are not available for degradation by soil microorganisms (*2*, *16*). Flumioxazin sorption in the Greenville scl was greater than that of the Tifton ls (K_d of 3.8 as compared to 0.7); however, the $t_{1/2}$ was only increased by approximately 4 days (*8*).

Flumioxazin Mineralization. Flumioxazin mineralization, as indicated by $^{14}CO_2$ evolution, amounted to between 2 and 2.2% of total flumioxazin applied (**Figure 2**). This rate of mineralization of flumioxazin after 64 days was similar to that of sulfentrazone (2.1% after 77 days) (*17*). Although differences in mineralization rates were detected, these differences were small and the overall mineralization rates were low. Therefore, it is unlikely that mineralization will greatly impact flumioxazin concentrations on a large scale.

Higher rates of mineralization were detected in the Tifton soil as compared to the Greenville scl soil. Comparisons of standard errors detected differences between the Tifton ls and Greenville scl soils. These differences were likely due to less sorption in the Tifton ls soil; thus, more herbicide was available for microbial degradation. Moreover, at 64 days after application, the rate of $^{14}CO_2$ evolution began to level off, as has been reported in some instances with atrazine (*15*). These data, coupled with the dissipation data described above, which included an HT soil, substantiate that microbial degradation of flumioxazin was the primary path of flumioxazin degradation in the soil environment. This agrees with information previously presented data for flumioxazin (*4*).

The laboratory persistence of flumioxazin was found to be relatively short, regardless of soil textural properties. However, soil persistence was positively related to the adsorption coefficient of the given soil. Although flumioxazin dissipation in soil occurred relatively quickly, mineralization rates were much lower. Therefore, the processes of microbial degradation and mineralization of flumioxazin occur at substantially different rates.

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