ACS SYMPOSIUM SERIES **842**

Terrestrial Field Dissipation Studies

Purpose, Design, and Interpretation

Ellen L. Arthur, Editor
Bayer CropScience

Aldos C. Barefoot, Editor
DuPont Crop Protection

Val E. Clay, Editor
Bayer CropScience

American Chemical Society, Washington, DC

Chapter 14

Environmental Fate of Fluometuron in a Mississippi Delta Lake Watershed

Martin A. Locke*, Robert M. Zablotowicz, and Lewis A. Gaston

Southern Weed Science Research Unit, Agricultural Research Service, U.S. Department of Agriculture, P.O. Box 350, Stoneville, MS 38776
***Corresponding author: telephone: 662–686–5272, mlocke@ars.usda.gov**

The Mississippi Delta Management Systems Evaluation (MSEA) Project was established to assess management practices for restoring soil and water quality. This paper reviews part of our research consisting of field-scale characterizations of soil properties and their relation to fluometuron degradation and sorption to soil, the role of best management practices (e.g., vegetative strips, riparian zones) in minimizing off-land fluometuron movement, and herbicide concentrations in surface water. Surface (0-5 cm) soil samples were collected in an oxbow lake watershed (Beasley) (60-m spaced grids, 40 ha). Soils were characterized and fluometuron sorption assessed. Based on characterizations, areas representative of different soil series were sampled to evaluate fluometuron dissipation under field conditions. Geostatistical analysis of soil characteristics showed significant spatial dependence, reflecting variability in the alluvial soils. Fluometuron sorption was correlated positively with organic carbon (OC) and clay, and negatively with sand content. Half-lives for fluometuron dissipation from the surface 0 to 5 cm ranged from 12 to 25 days. Fluometuron dissipation was correlated with both clay (positive) and sand content (negative), but not OC. The primary metabolite, desmethyl fluometuron (DMFM) was observed, usually 2 to 3 weeks after herbicide application and occurred in greater concentrations in clay soil. Both fluometuron and DMFM were observed in lake

water, appearing one month (June) after field application, and were below detectable limits in October. These studies indicate that fluometuron and its major metabolite have limited persistence in both soil and surface water of the watershed studied.

Understanding the interactions among crop management practices, soil characteristics, and the fate of herbicides is a rational approach for minimizing risks of pesticides on the environment. The EPA considers pesticides one of the major classes of chemical contaminants that can affect quality of lakes and streams. More herbicides are used than any other pesticide, making it a high priority for assessing guidelines proposed by EPA and state regulatory agencies setting limits on what constitutes levels of pollutant that impairs surface water bodies (i.e., Total Maximum Daily Load, TMDL). A comprehensive evaluation of herbicide impacts on the environment needs to follow the fate of herbicides from the point of application in the field to entry and dissipation in surface waters.

Soil characteristics determine the quantity of herbicide to be applied and the rate at which that herbicide dissipates. Sorption of many herbicides to soil increases with clay and organic carbon (OC) content (1, 2, 3), thereby reducing herbicide efficacy in controlling weeds (4). However, when considering the environmental risk of herbicides, more restricted movement to non-target sites in soils with higher clay and OC content is beneficial. The spatial variability of atrazine sorption in soils from an Iowa field site was affected by landscape position (5), with the greatest sorption in depression areas. The magnitude of atrazine sorption correlated with OC, pH and to a lesser extent clay content.

The Mississippi River Delta is a major agricultural region devoted primarily to cotton, soybeans, corn, and rice. The Delta region extends along a narrow band on either side of the Mississippi River from Southern Missouri to the coast of Louisiana, and is comprised of approximately 8.5 million hectares. A current dilemma for farmers is to meet environmental concerns while producing a quality product with sustained profitability. Traditional row crop management in the Delta Region includes extensive tillage and pesticide use with little crop or weed residue covering the soil surface during fallow winter months. It is during this period that soils are most susceptible to erosion. In spite of high annual rainfall (114 to 155 cm), water shortages often occur at critical crop growth stages, and there is significant acreage in the Delta that is irrigated, further contributing to soil erosion loss. Increasing public concern and governmental

regulation to minimize soil loss on erodible soils has prompted the development of production practices that conserve natural resources, preserve environmental quality, and sustain agricultural productivity.

An interagency cooperative research and demonstration project (Mississippi Delta MSEA) was established in 1994 with the purpose of assessing how agricultural activities influence Delta Region surface and ground water quality. The project also fits a national priority research objective for improving and restoring water resources. A second overall objective of the project was to increase knowledge about best management practices (BMP's) applicable to the Mississippi Delta region and quantify how they can improve soil and water resources. This project should bring the knowledge obtained from years of experimental plot studies to the farm level. Both environmental and economic benefits need to be quantified to demonstrate to producers how their farms can be improved by using BMP's.

In order to develop a comprehensive evaluation of herbicide dissipation in a Mississippi watershed, research focused on fluometuron [*N*,*N*-dimethyl-*N*'-[3-trifluoromethyl) phenyl urea]. The approach taken for this paper was to evaluate fluometuron dissipation in different settings ranging from the field where it was applied to a nearby water body. Fluometuron is the most widely used herbicide in cotton production in the southern United States. A recent survey of herbicides observed in three Mississippi Delta streams indicated that fluometuron was routinely detected from spring months when herbicides are often applied until early fall (6). Fluometuron is a member of the phenyl urea group of herbicides, and is used to control many broadleaf and grass weed species (7). It is applied to soil, usually before emergence of the cotton crop, but also can be applied in a directed spray on weeds after cotton emergence. The half-life of fluometuron in soil has been measured from 14 to 120 days after application (e.g., 8, 9, 10, 11).

Understanding the fate of metabolites as well as the parent compound is very germane to assessing environmental impacts of herbicides. Metabolite degradation is dependent on both the soil properties and chemical properties of the metabolite. The major metabolite of fluometuron in soil, desmethyl fluometuron (DMFM), results from *N*-demethylation (12). In the study by Coupe et al. (6), DMFM also was detected in the surface water. Further demethylation of DMFM forms trifluoromethyl phenyl urea (TFMPU), which is typically observed in low concentrations. Hydrolysis of either fluometuron or TFMPU will form trifluoro-methylaniline (TFMA), rarely reported in soil, but which has been detected in water samples in Texas (13).

Materials and Methods

Beasley Lake Watershed

The Mississippi Delta MSEA project is centered around three oxbow lake watersheds, i.e., old cut off river channel meanders (14). The approach of using oxbow lakes for the present project was chosen because it allows assessment of an entire, closed watershed. In some other MSEA projects, the watersheds were very large, making it difficult to evaluate how management practices were influencing bodies of water. In an oxbow lake watershed, all water drains into the lake, and lake health can be monitored over time.

The data presented in this paper are from only one of the watersheds, Beasley Lake. Beasley Lake watershed consists of 405 ha, and the lake is 17 ha in size. Beasley Lake is an oxbow lake that was once part of the Sunflower River (Figure 1). The topography of the region is relatively flat, with less than 1% slope toward the lake. A large, forested riparian area drains into the lake. The only improvements installed by researchers in Beasley Lake watershed were slotted board risers and grass filter strips. Slotted board risers are drainage outlets constructed so that during periods of heavy runoff, a board can be installed to slow water movement through the outlet, thus allowing sediment to settle. Vegetative buffer strips (primarily grass) along edges of fields were another physical improvement added at Beasley Lake.

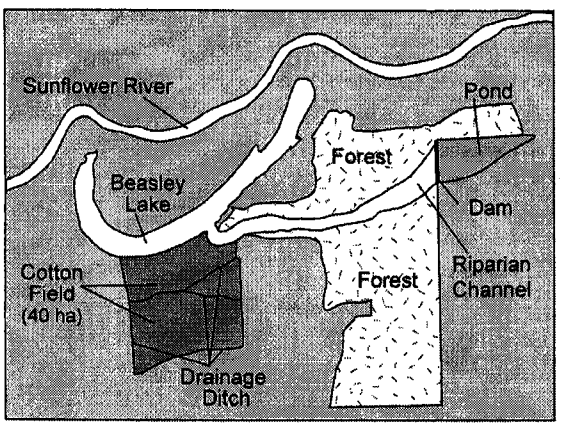

Figure1. Map of Beasley Lake watershed, including 40-ha cotton field where fluometuron dissipation was evaluated, forested riparian channel, and lake.

Study Site and Soil Sampling for Herbicide Dissipation

Cotton and soybean were the predominant crops grown in Beasley Lake from 1995 to 1997, the period of interest for this paper. Overall research objectives for the data presented here were to assess relationships among management practices, herbicide dissipation, soil resources, and lake health. For field dissipation studies, a 40-ha area under cotton production was selected (see outlined area in Figure 1). The area was managed with practices conventional for cotton production in the Mississippi Delta Region, including disking in the spring and fall, forming row beds in the spring, and cultivation after planting.

The study area contained a diverse number of soil types. Soil survey data indicated that Dundee (fine-silty, mixed, thermic Typic Endoaqualfs), Forestdale (fine, smectitic, thermic Typic Endoaqualfs), Dowling (very-fine, smectitic, thermic Vertic Epiaquepts) and Alligator (very-fine, smectitic, thermic Alic Dystraquerts) are major soil series represented. A 60 m by 60 m square grid was established, with column and row ends permanently marked and the grid locations georeferenced (Pathfinder ProXR, Trimble Navigation, Ltd., Sunnyvale, CA). Each grid node was the center of a 2 m x 2 m plot from which soil samples were collected.

At cotton planting in Spring, 1996, fluometuron (0.6 kg ha^{-1}) herbicide was applied to the soil in a band at the top of the row bed. Fourteen sampling sites were selected within the 40-ha area for evaluation of fluometuron dissipation, and each sampling site was centered on a grid node. The sample sites were chosen so that the soil types common to the watershed area were represented. Soil samples were collected from the 0-5, 5-15, and 15-25 cm depths in 1996 just prior to fluometuron application and periodically for four weeks after application. Previous knowledge of the approximate half-life of fluometuron gave an indication of the length of time the soil could be sampled to obtain a relative assessment of dissipation.

Soil Analysis

Soil samples for the fluometuron dissipation study were frozen until extraction and analysis. Field moist soil samples were extracted with methanol (2:1 soil:MeOH w:v). Extracts were centrifuged after a 24-h shaking, filtered with Gelman Acrodiscs (0.25 μm) (Gelman Laboratory, Ann Arbor, MI), and analyzed with HPLC. HPLC conditions included: HPLC System 2690 (Waters, Inc., Milford, MA); Fluorescence Detector 486 (Waters, Inc.); Econosil reverse-phase C18 column (Alltech Assoc., Deerfield, IL); gradient 55:45 water:ACN to

30:70; flow rate one mL min^{-1}; and fluorescence wavelengths Em 329, Ex 294. The chromatograms were assessed for fluometuron and a dominant metabolite, desmethyl fluometuron (DMFM). Standards of fluometuron technical grade and DMFM were obtained from Novartis, Inc., Greensboro, NC.

Fluometuron sorption was evaluated in soil samples from 50 of the grid node points (0-5 and 15-25 cm soil depths). The 0-5 cm soil depth was chosen because it is the depth of the soil profile that will likely have the most influence on herbicide dissipation. The 15-25 cm depth was selected as the interface between where mixing due to tillage occurred and the relatively undisturbed subsoil. Batch methods were used to assess fluometuron sorption. Fluometuron used for analysis included ^{14}C-labelled (98% purity) and technical grade (Novartis, Inc.). One fluometuron concentration (11.5 μM, 42 Bq mL^{-1}) in 0.01 M $CaCl_2$ was used, with three replications, and the experiment was repeated. Samples were equilibrated in 25-mL Pyrex centrifuge tubes (1:1.5 soil:solution, 5g:7.5 mL) for 17 h at 25 °C, centrifuged (10,000 x g, 15 min), and the supernatant filtered (Whatman 42 filter paper, Whatman, NJ). ^{14}C-labelled fluometuron remaining in solution after equilibration was counted for radioactivity (Tri-Carb 4000, Packard Instrument Co., Downers Grove, IL) after mixing with Eco-Lite scintillation cocktail (ICN, Costa Mesa, CA).

Agronomic Practices and Weed Counts

The Beasley site was conventionally tilled and irrigated. Weed management included initial burndown with glyphosate [N-(phosphonomethyl)glycine]. Following re-bedding of rows, fluometuron and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] were applied pre-emergence (1.7 and 1.1 kg ha^{-1}, respectively) in a 43-cm band at planting. In 1996 and 1997, weed counts were taken six weeks following fluometuron and metolachlor application and prior to post-emergence application of cyanazine and MSMA. Weeds were counted in one-meter strips within 15 cm of the cotton row, since the fluometuron was applied in a band along the top of the row. The weeds were categorized as controlled or not controlled (7) by fluometuron and metolachlor.

Surface Movement of Herbicide

Fluometuron herbicide was applied in a band on top of the row beds (Figure 2a). A study was conducted to evaluate herbicide movement from the band at the top of the row bed, into the row furrow, and down the slope (Figure 2b). In

1996, three rows were selected that sloped (approximately 1% slope) 50 to 80 m toward a drainage ditch. The rows were spaced 30 m apart. From each row, four sampling sites were designated (Figure 2b): top of the slope, end of the row at the bottom of the slope, turn-row (2 to 3 m wide) area between the row end and a grassy area, and grassy area between turn-row and ditch (3 to 4 m wide). Soil was sampled from the surface 0 to 2 cm depth in the furrow between row beds (Figure 2a). Soil was assessed at that shallow depth because the primary interest was in surface movement of fluometuron. Fluometuron leached below 2 cm would not likely be moved in subsequent runoff events. Samplings were taken before fluometuron application, just after fluometuron application, 11 days after application, and 34 days after application. Rain and / or irrigation events occurred just prior to the last two samplings. Soil samples were frozen until extraction and analysis as described previously.

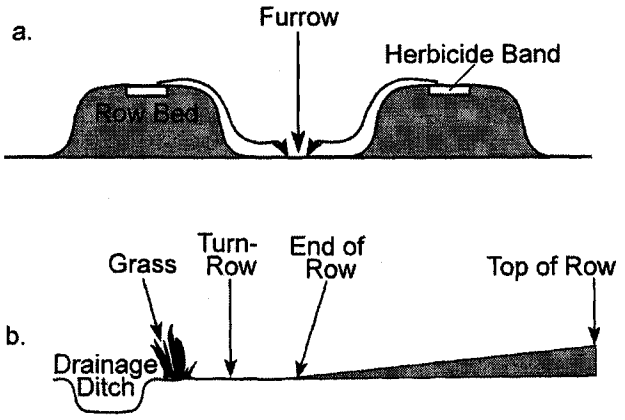

Figure2. Ilustrations of (a) row beds and herbicide band applied to the top of the row. Herbicide potentially could move from top of row bed into the furrow between row beds. (b) Soil samples were collected in the furrow, and sampling points include the top of the row, end of the row, turn-row area between the row end and grass, and grass strip.

Riparian Evaluations of Herbicide Degradation Potential

A large riparian forest adjoins Beasley Lake. This area is a wetland with a channel that runs through the middle, serving as a conduit for water draining from surrounding fields into the lake. Part of our objective was to assess the

capability of the riparian area to filter contaminants moving in runoff toward the lake. Soil samples were collected from the field and three zones along the riparian channel toward Beasley Lake: 0 to 25 m from dam at edge of field, 50 to 200 m, and 400 to 800 m (Figure 1). Three enzyme assays were conducted to estimate heterotrophic microbial activity and the potential for herbicide degradation. Hydrolytic enzyme activity (esterase, lipase and protease) assays were conducted using fluorescein diacetate (FDA) as substrate (15). Dehydrogenase activity was assayed using triphenyl tetrazolium chloride (TTC) as substrate (3.0% aqueous with 0.1% yeast extract as an exogenous carbon source) (16). Aryl acylamidase was assessed using 2-nitroacetanilide (2-NAA) as substrate (17). All assays were conducted with three substrate replicates and one no-substrate control for each sample. Activities per hour were calculated based upon extinction coefficients and are reported as nmole of product formed (fluorescein for FDA, triphenyl formazan for TTC, and 2-nitroaniline for 2-NAA) g^{-1} soil (oven dry weight) h^{-1}. The potential for aerobic fluometuron degradation was determined in a soil slurry assay (1:10 dilution of soil, fresh soil weight). One mL of the soil dilution was transferred to sterile screw cap tubes and 1.0 mL of fluometuron solution (20 $\mu g\ mL^{-1}$) was added (five replicate tubes per sample). Tubes were incubated on a shaking incubator (25°C, 75 rpm) for 28 days. The study was terminated by adding 2 mL methanol, shaking at 75 rpm for an additional 24 h, centrifugation (10 min. 10,000 x g) and filtered (0.2 µm). Concentrations of fluometuron and the metabolite DMFM were determined by HPLC as described previously.

Evaluations of Herbicide in Lake Water

Surface (0 to 20 cm deep) water samples were collected monthly from three locations within Beasley Lake. Water samples (300 mL) were centrifuged and filtered through Empore C18 (Varian, Walnut Creek, CA) discs. The discs were eluted in 20 mL ethyl acetate and then concentrated to 2 mL. The concentrated samples were analyzed with HPLC as described previously.

Statistical Analyses

Geostatistics were used to assess the spatial variability of soil characteristics, weed populations, and fluometuron sorption (GS+, Gamma Design Software, Plainwell, MI). Linear or spherical models were used to describe these soil characteristics. These models, together with experimental data, were used to estimate average values (18) for soil properties and weed densities in square 0.36 ha areas centered about each sampling grid node.

Effects of soil properties on weed populations were examined with regressions and cross-semivariograms (18, 19). For further details on geostatistical analyses, readers are referred to Gaston et al. (4).

Results and Discussion

Soil Characterization and Fluometuron Sorption

Soil characteristics for the 40-ha field dissipation area are shown in Table I. In both surface and subsurface, there was a wide range in values, reflecting the alluvial origins of the soils in this watershed. Soil clay tended to be higher, and OC and sand lower in the 15 to 25 cm depth.

Table I. Soil characteristics in the surface and subsurface soil in the Beasley Lake watershed.

Property	*Soil Depth*			
	0 to 5 cm		*15 to 25 cm*	
	Range	*Mean (Std. Dev.)*	*Range*	*Mean (Std. Dev.)*
% Clay	13 to 59	31.0 (10.7)	22 to 63	40.4 (9.9)
% Sand	1 to 49	17.5 (10.1)	1 to 39	11.2 (8.7)
% Organic C	0.51 to 2.53	1.67 (0.36)	0.07 to 0.96	0.47 (0.21)

Fluometuron sorption in the 0 to 5 cm depth ranged from 15 to 53 % of applied (mean 34.0 %; std. dev. 9.3), and in the 15 to 25 cm depth, sorption ranges were 18 to 58 % of applied (mean 35.0 %, std. dev. 9.1). Correlations were used to compare fluometuron sorption with other soil parameters, and for both 0 to 5 cm and 15 to 25 cm soil depths, the trends were the same (Table II). Organic C was positively correlated with organic matter. Sorption of substituted urea herbicides, such as fluometuron, in soil is believed to be due to a combination of mechanisms, primarily related to OC content. Nonionic

mechanisms described as hydrophobic bonding (20, 21) or van der Waals attractions (22) likely play a role. Mechanisms such as hydrogen bonding (23, 24, 25, 26) may be involved with sorption to polar sites in soil.

In the Beasley watershed soils, a positive correlation between fluometuron sorption and clay content also was obtained, while the sand fraction was negatively correlated with fluometuron sorption (Table II). However, the role of clay in the sorption of substituted ureas is not clear, and poor correlations of urea sorption and clay content have been observed in other studies (20, 21, 23, 27, 28, 29, 30). One distinction between those studies cited and the present study is that these soils are from the same locale, Beasley watershed, and share common characteristics, such as mineralogy. It has been shown that the extent of complex formation between substituted ureas and clay minerals, such as montmorillonite, can depend on the characteristics of the cations associated with them (23, 31, 32), and it is likely that the montmorillonitic fraction in the Beasely soils was similar. Although some of the correlation may result from co-correlation between clay and OC, the correlation of fluometuron sorption with clay content increased in the 15 to 25 cm depth, while the correlation with OC decreased. The lower correlation in the 15 to 25 cm depth was attributed to a 70% lower OC content, and the higher correlation with clay was likely due to a higher clay content in the subsurface.

Table II. Correlation (r) between soil characteristics and fluometuron sorption in surface and subsurface soil in the Beasley Lake watershed.

Property	*Soil Depth*	
	0-5 cm	*15-25 cm*
	---------- (r)* ----------	
Clay	0.65	0.72
Sand	-0.55	-0.55
Organic C	0.68	0.47

*Significant at 0.05 probability level.

Geostatistical models were used to describe semivariograms for the measured soil characteristics such as OC and texture (4) and for fluometuron sorption, which were then used to generate contour maps of the variables by

kriging (Figure 3). The contour plots illustrate the variability of these alluvial soils. The lighter areas in Figure 3 represent lower values of a corresponding characteristic. Similarities in the contour patterns can be observed and support the correlations shown in Table II, especially for clay and herbicide sorption. Areas of higher clay and OC tended to occur in depressions or at the bottoms of slopes, reflecting depositions of sediment from runoff over a number of years. The patterns observed here also reflect the alluvial origins of these soils. The ridges, or lower clay areas, are essentially old sand bars formed when the river meandered back and forth across this area.

Spatial variability of soil characteristics can be used to assess biological parameters for a defined area. One agronomic parameter that Gaston et al. (4) studied in relationship to soil properties was weed population. Figure 4 illustrates a positive relationship between weed population and organic matter and clay. As either soil organic matter or clay contents increases, so does the number of potential exchange sites for any herbicide that is applied to the soil. This implies that in areas with high clay or organic matter, it would be necessary to apply more herbicide to attain weed control comparable to areas with lower clay or organic matter. The weed data shown in Figure 4 consist of total weeds. When only the weed species controlled by fluometuron was considered, spatial relationships were less clear. However, weeds tended to reoccur in areas where clay and OC were relatively high, indicating a relationship between herbicide persistence and soil properties. However, relatively coarse textured areas were commonly weed-free for two years. These observations suggest that greater uniformity of weed control might be achieved by a variable rate of herbicide application. Also, adequate weed control might be achieved at a reduced rate of application in sandy, low OC areas.

Fluometuron Field Dissipation

Field dissipation of fluometuron was measured to evaluate relationships between soil characteristics and herbicide dissipation. Correlations between the half-life of fluometuron in the surface soil and several soil parameters are presented in Table III. There was a significant positive relationship between fluometuron dissipation and clay content, with a negative relationship for the coarser textured soil fractions. As a result of the significant correlations of herbicide dissipation with clay and sand, soils were categorized into two groups based on clay content. The values for each group were averaged over the course of the 28-day assessment period and are shown in Figure 5. More rapid herbicide dissipation was observed in soils with lower clay content, and this was attributed to several factors. There is the potential for some sequestration or protection from degradation when herbicide is sorbed (11). Coarser textured soils are more aerated, providing an environment conducive for oxidative

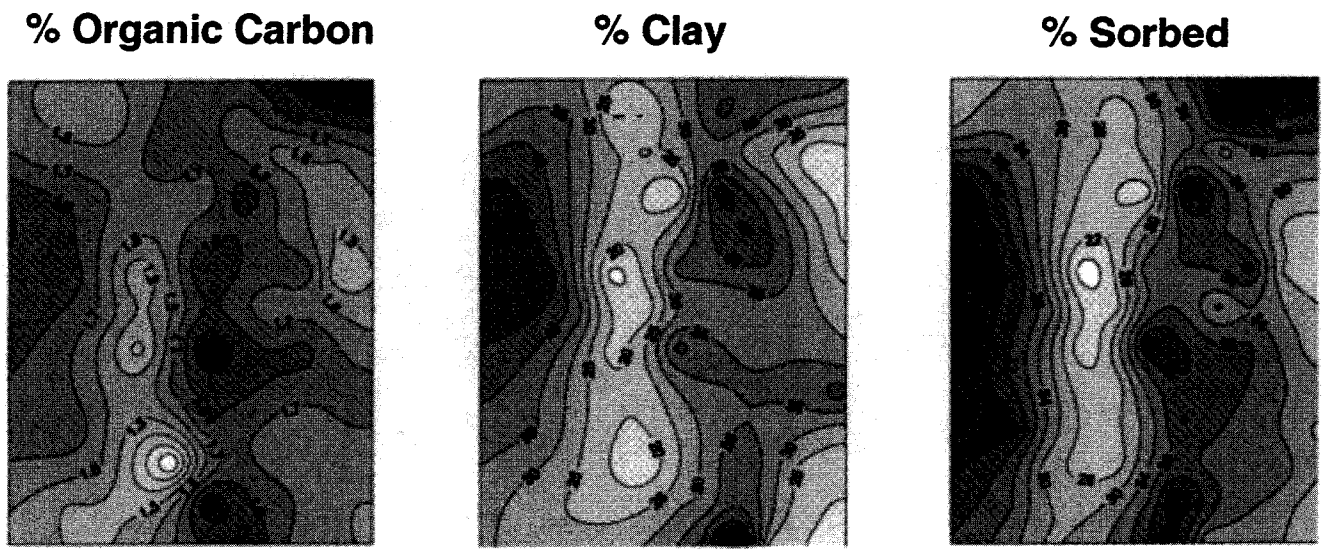

Figure 3. Soil contour plot of percent organic C, percent clay, and percent fluometuron sorption in a cotton production area,Beasley Lake watershed. The soil depth is 0 to 5 cm.

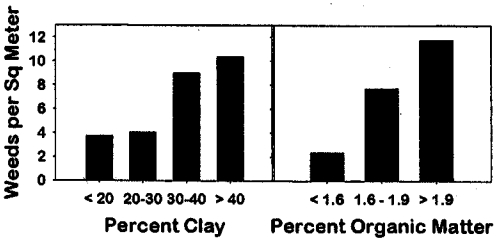

Figure 4. Effect of soil clay and organic matter content on control of weeds (adapted from Gaston et al., 2001).

processes such as *N*-dealkylation of fluometuron. Another consideration is that there is less fluometuron retention in the coarser textured soils, and the herbicide is more subject to movement away from the site of application by leaching or surface runoff.

No relationship was observed between fluometuron dissipation and OC (Table III). Several conflicting factors likely contributed to a lack of correlation between herbicide dissipation and OC content. Under optimum moisture conditions, higher OC levels in surface soils are often associated with enhanced microbial activity. High microbial activities can lead to co-metabolism of xenobiotics in soil. The potential, therefore, exists for a positive relationship between OC levels and herbicide dissipation. However, surface soils often are dry crusts, even during the traditionally wet Spring when the fluometuron was applied. The dry soil condition would severely reduce microbial activity and accompanying herbicide metabolism. Also, in soils with higher OC, there may have been some protection from degradation or lowered mobility because of enhanced herbicide sorption. Another consideration is that, while there was a wide range in OC levels for the surface soils in this watershed, the average OC level (Table I), is relatively low and may not be sufficient to enhance microbial activity to any significant degree.

Table III. Correlation (r) of surface soil properties with fluometuron dissipation (half-life) and average DMFM (μg g^{-1}) concentration.

Soil Property	*Fluometuron (half-life)*		*DMFM (average conc.)*	
	r	Prob. > [r]	R	Prob. > [r]
Clay	0.62	0.05	0.52	0.06
Sand	-0.46	0.10	-0.29	NS
Silt	-0.57	0.05	-0.61	0.05
OC	0.28	NS	0.23	NS

Note: NS = Not Significant

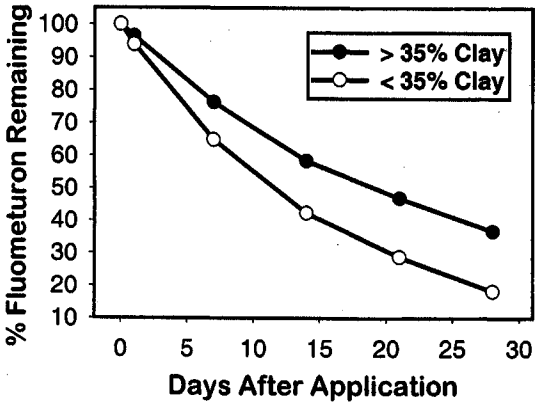

Figure 5. Effect of clay content on fluometuron dissipation from surface (0-5 cm) soil.

In the 5 to 15 cm soil depth, fluometuron was detected erratically in some plots, usually later than two weeks after application, and for only a short period of time (data not shown). No trends related to soil characteristics were observed in the 5 to 15 cm samples. Herbicide was not detected at depths below 15 cm. Herbicide sorption is often greater in surface than sub-surface soil (1, 10, 33, 34). In most of these studies, the increased sorption capacity of surface soils was primarily attributed to a greater mass of organic carbon (greater number of sorption sites) rather than to a stronger affinity or energy of sorption by organic components in the soils. Enhanced fluometuron sorption in the surface would reduce mobility to greater soil depths, and this may have been a factor in the low levels of fluometuron measured in soil at depths below 5 cm. The absence of fluometuron in soil , however, does not conclusively demonstrate that fluometuron did not leach. For example, Essington et al. (35) measured fluometuron in leachate collected at 90 cm soil depths, attributing movement primarily to preferential flow.

Demethylated fluometuron or DMFM is one of the primary metabolites of fluometuron measured in soil. For each sampling area, the DMFM concentration over the 28-day period was averaged and correlated with various soil characteristics (Table III). Similar to fluometuron, there was a positive correlation for clay and a negative relationship for silt, but no relationship was significant for sand or organic C.

The soils were grouped according to clay content and the average DMFM concentrations in soil (Figure 6). The pattern for DMFM in surface soil indicates that it does not accumulate, but the peaks coincide with the decline in fluometuron concentration, and then the DMFM dissipates. The soils with higher clay generally accumulated more DMFM than lower clay soils. While

DMFM sorption was not evaluated in this watershed, in another study (36), DMFM sorption was measured for soils of varying soil properties. Dundee silt loam and Tunica clay had similar organic carbon levels (1.7 and 1.5 %, respectively), but different clay contents (21 and 55 %, respectively). The Tunica clay is predominantly montmorillonitic and shows higher DMFM sorption ($K_{Freundlich}$ 3.7, N=0.76) than the Dundee silt loam ($K_{Freundlich}$ 3.0, N=0.77). As with fluometuron, some of the same arguments could be made that greater sorption in the higher clay soils reduced the mobility and enhanced protection from degradation.

Surface Movement of Fluometuron

Fluometuron concentrations in the soil surface (0 to 2 cm) at various sampling locations are presented in Figure 7 during the first month after application. Baseline (before herbicide application) fluometuron concentrations were negligible in all four sampling locations, providing an excellent reference point from which to evaluate subsequent changes. Fluometuron concentration was detected in all locations two days after application even though no measurable precipitation was recorded. This may have been due to overspray or drift. After the first rain and an irrigation with a total of 3 cm water, fluometuron at the top of the slope and end of slope increased. Precipitation fell (11 cm) prior to the last sampling. The most dramatic increase in fluometuron concentration was measured in the turn-row area. The turn-row was a convergence area for all runoff flowing down the row slope, not just for the rows that were evaluated, but for all rows. As such, the turn-row area was a mixing zone and the fluometuron measured likely was from several sources. During heavy rain, the water ponded in the turn-row until it either could seep through or flood over the grass area to the ditch. Soil depths greater than 2 cm were not evaluated in the turn-row to determine the extent to which fluometuron may have leached.

It is noteworthy that relatively little fluometuron was measured in the surface soil from the grass area, indicating the effectiveness of the grass strip as a physical barrier restricting sediment or water movement. Also, fluometuron may have moved by mass flow to the ditch during times of flooding, with little residence time in the grass area. Additionally, there were breaks in the grass strip and eroded areas that would have provided channels for excess water to drain from the turn-row area to the ditch while bypassing the grass area. Some infiltration of runoff may have occurred in the grass area, which could have lowered outflow concentrations of herbicide due to sorption to soil or vegetative material (37, 38). Also, enhanced degradation of herbicide can occur in grass areas if residence time is sufficient (39, 40).

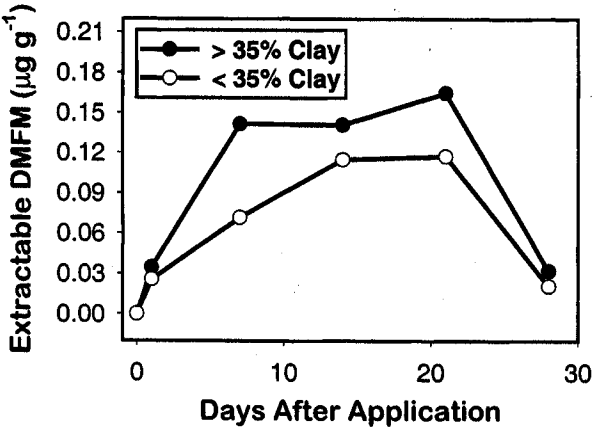

Figure 6. Effect of clay content on demethylated fluometuron (DMFM) dissipation from surface (0-5 cm) soil.

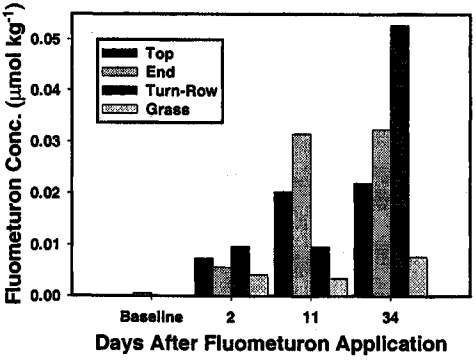

Figure 7. Surface movement of fluometuron in soil (0 to 2 cm) within a row furrow.

Riparian Area and Lake

Three enzyme activities, esterase, dehydrogenase and aryl acylamidase, were significantly greater in riparian zone soil compared to cropland soil (Table IV). Esterase, dehydrogenase, and aryl acylamidase activities were about 8 to 18, 3 to 12, and 1.5 to 3 fold-greater in riparian soil compared to the cultivated soil, respectively. The highest levels of all three enzymes were observed in the zone closest to the lake that had the highest soil moisture, OC, and clay contents. Cooper et al. (41) found similar conditions where the textural composition of

soil near the entry point into forested riparian areas was sandier, while soil further into the riparian zone was predominantly silt and clay. Soil enzymatic activity can be used either in a lower resolution application as an index of general soil microbial activity or may be used for a higher resolution application for understanding a specific process (42). FDA hydrolytic activity represents a wide range of hydrolytic activity (esterase, lipase and protease) activity and correlates with soil respiratory activity. Dehydrogenase activity actually measures electron transport system activity in that the substrate TTC is used as an alternative electron acceptor (43), under both aerobic and anaerobic conditions. Both FDA-hydrolysis and TTC-dehydrogenase thus described the generic spatial variation in microbial activity due to position along the riparian zone. Aryl acylamidase activity assesses hydrolytic cleavage of an amide bond and thus can be used to describe a process such as herbicide degradation, e.g., acylanilide and phenylurea herbicides.

Table IV. Soil enzyme activity and *in* vitro fluometuron degradation in soils collected along a transect of the Beasley Lake riparian zone.

Sampling Location	*FDA-esterase*	*TTC dehydro-genase*	*2-NAA aryl acylamidase*	*DMFM Formed*
	nmol formed g^{-1} $soil^{-1}$ h^{-1}			nmol g^{-1}
Cultivated Field	133 ± 44*	1.8 ± 0.8	28 ± 4	28 ± 5
Riparian Zone 1 (Dam to 25 m)	1507 ± 566	6.1 ± 0.8	42 ± 6	57 ± 17
Riparian Zone 2 (50 to 200 m)	1106 ± 93	6.4 ± 3.3	67 ± 22	62 ± 13
Riparian Zone 3 (400 to 800 m)	2361 ± 494	22.7 ± 14.7	88 ± 33	111 ± 27

*Mean ± standard deviation of three replicates

The potential for soils to degrade fluometuron in a soil slurry system was studied by monitoring both dissipation of the parent compound and accumulation of the metabolites. The DMFM metabolite accumulated in all soils with the greatest accumulation in soil suspensions from the riparian zones (Table IV). Patterns of fluometuron dissipation exhibited a similar trend as DMFM accumulation (data not shown). Studies by Entry and Emminham (44) indicated that atrazine and 2,4-D were more rapidly degraded in riparian zones under coniferous forests compared to grasslands. Higher microbial activity and

populations observed in Mississippi Delta riparian zones should facilitate rapid degradation of pesticides. Preservation and maintenance of forested riparian zones should be an important management practice to reduce non-point pollution of surface waters by agrochemicals.

There is concern that bodies of water, such as lakes, are the sink for agrochemicals such as pesticides and nutrients. Questions are raised as to the extent these chemicals are reaching the lakes and whether management practices are impeding movement of chemicals into the lakes. Table V shows the concentrations of fluometuron and DMFM in lake water during the period from May to October. This period coincides with the time just after fluometuron application and subsequent dissipation in the field. Allowing for a lag time in May, during which the fluometuron moved to the lake in sufficient quantity for detection, the occurrence of fluometuron in the lake mirrored what was observed in the field. There is a gradual buildup in fluometuron concentration in the lake during June through July, with a peak in July. Concentrations then decline to undetectable levels from September to October. DMFM followed a similar pattern, but at lower concentrations (Table V). No TFMA was observed in any samples from these studies, in contrast to other reports (6, 13). Concentrations and dynamics of appearance of fluometuron and DMFM are similar to those observed in Mississippi Delta streams (6). Vegetative filter strips and a large riparian zone may have entrapped and impeded fluometuron movement, thus delaying fluometuron appearance until over a month after application. DMFM generated in the field during fluometuron degradation is subject to movement from the field to the lake. DMFM is likely less mobile than fluometuron, based on its higher sorption K value relative to fluometuron (45). It is likely, therefore, that much of the DMFM measured in lake water is a result of *in situ* metabolism of fluometuron, e.g., algal *N*-dealkylation (46).

Table V. Fluometuron concentrations in Beasley Lake, 1997

Month	*Fluometuron*	*DMFM*
	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$
May	<0.1	<0.1
June	3.2 ± 1.9	0.8 ± 0.6
July	5.7 ± 3.4	2.0 ± 0.5
August	4.8 ± 2.2	1.8 ± 0.6
September	0.7 ± 0.6	0.7 ± 0.6
October	<0.1	<0.1

References

1. Locke, M.A. *J. Environ. Qual.* **1992,** *21*, 558-566.
2. Locke, M.A.; Gaston, L.A.; Zablotowicz, R.M. *J. Agric. Food Chem.* **1996,** *44*, 1128-1134.
3. Locke, M.A.; Gaston, L.A.; Zablotowicz, R.M. *J. Agric. Food Chem.* **1997,** *45*, 286-293.
4. Gaston, L.A., Locke, M.A.; Zablotowicz, R.M.; Reddy, K.N. *Soil Sci. Soc. Am. J.* **2001,** *65*, In press.
5. Novak, J.M.; Moorman, T.B.; Cambardella, C.A. *J. Environ. Qual.* **1997,** *26*, 1271-1277.
6. Coupe, R.H.; Thurman, E.M.; Zimmerman, L.R. *Environ. Sci. Technol.* **1998,** *32*, 3673-3680
7. Mississippi State University Extension Service. Weed control guidelines for Mississippi. Mississippi State University, Mississippi State, MS, 2001; Pub. 1532, 197 pp.
8. LaFleur, K.S.; Wojeck, G.A.; McCaskill, W.R. *J. Environ. Qual.* **1973,** *2*, 515-518.
9. Rogers, C.B.; Talbert, R.E.; Mattice, J.D.; Lavy, T.L.; Frans, R.E. *Weed Sci.* **1985,** *34*, 122-130.
10. Brown, B.A.; Hayes, R.M.; Tyler, D.D.; Mueller, T.C. *Weed Sci.* **1994,** *44*, 171-175.
11. Zablotowicz, R.M.; Locke, M.A.; Gaston, L.A.; Bryson, C.T. *Soil and Tillage Res.* **2000,** *57*, 61-68.
12. Bozarth, G.A.; Funderburk, H.H. *Weed Sci.* **1971,** *19*, 691-695.
13. Thurman, E.M.; Bastian, K.C.; Mollhagen, T. *Sci. Tot. Environ.* **2000,** *248*, 189-200.
14. Cooper, C.M.; Rebich, R.A.; Locke, M.A. In *Proc. 3rd Natl. Workshop on Constructed Wetlands Conference / BMPs for Nutrient Reduction and Coastal Water Protection*, USDA-CSREES, EPA, USDA-ARS, CTIC, and ASAE, 1999, pp. 33-34.
15. Schnürer, J.; Rosswall, T. *Appl. Environ. Microbiol.* **1982,** *43*, 1256-1261.
16. Casida, L.E., Jr. *Appl. Environ. Microbiol.* **1977**, 34, 630-636.
17. Zablotowicz, R.M.; Hoagland, R.E.; Wagner, S.C. *Soil Biol. Biochem.* **1998,** *30*, 679-686.
18. David, M. *Geostatistical ore reserve estimation*; Elsevier Scientific Publ. Co., New York, NY, 1977.
19. Yeats, S.R.; Warrick, A.W. *Soil Sci. Soc. Am. J.* **1987,** *51*, 23-30.
20. Carringer, R.D.; Weber, J.B.; Monaco, T.J. *J. Agric. Food Chem.* **1975**, *23*, 568-572.
21. Kozak, J.; Weber, J.B. *Weed Sci.* **1983**, *31*, 368-372.
22. Hance, R.J. *Weed Res.* **1969**, *9*, 108-113.

23. Bailey, G.W.; White, J.L.; Rothberg, T. *Soil Sci. Soc. Am. Proc.* **1968**, *32*, 222-234.
24. LaFleur, K.S. *Soil Sci.* **1973**, *116*, 376-382.
25. Bouchard, D.C.; Lavy, T.L.; Marx, D.B. *Weed Sci.* **1982**, *30*, 629-632.
26. Bouchard, D.C.; Wood, A.L. *Toxicol. Indust. Health* **1988**, *4*, 341-349.
27. Hance, R.J. *Weed Res.* **1965**, *5*, 108-114.
28. Savage, K.E.; Wauchope, R.D. *Weed Sci.* **1974**, *22*, 106-110.
29. Grover, R. *Can. J. Soil Sci.* **1975**, *55*, 127-135.
30. Peck, D.E.; Corwin, D.L.; Farmer, W.J. *J. Environ. Qual.* **1980**, *9*, 101-106.
31. Hance, R.J. *Weed Res.* **1971**, *11*, 106-110.
32. Khan, S.U. *Can. J. Soil Sci.* **1974**, *54*, 235-237.
33. Locke, M.A.; Zablotowicz, R.M.; Gaston, L.A. In *Conservation farming: A focus on water quality*; Kingery, W.L; Buehring, N. Eds.; MAFES Special Bull. 88-7, 1995, pp. 55-58.
34. Reddy, K.N.; Locke, M.A.; Wagner, S.C.; Zablotowicz, R.M.; Gaston, L.A.; Smeda, R.J. *J. Agric. Food Chem.* **1995**, *43*, 2752-2757.
35. Essington, M.E.; Tyler, D.D.; Wilson, G.V. *Soil Sci.* **1995**, *160*, 405-414.
36. Locke, M.A.; Zablotowicz, R.M. *Weed Sci. Soc. Am. Abstr.* **2000**, *40*, 88.
37. Arora, K.; Mickelson, S.K.; Baker, J.L.; Tierney, D.P.; Peters, C.J. *Trans. Am. Soc. Agric. Eng.* **1996**, *39*, 2155-2162.
38. Misra, A.K.; Baker, J.L.; Mickelson, S.K.; Shang, H. *Trans. Am. Soc. Agric. Eng.* **1996**, *39*, 2105-2111.
39. Benoit, P.; Barriuso, E.; Vidon, P.; Real, B. *J. Environ. Qual.* **1999**, *28*, 121-129.
40. Staddon, W.J.; Locke, M.A.; Zablotowicz, R.M. *Am. Soc. Agron. Abstr.* **1998**, *90*, 31.
41. Cooper, J.R.; Gilliam, J.W.; Daniels, R.B.; Robarge, W.P. *J. Environ. Qual.* **1987**, *51*, 416-420.
42. Sinsabaugh, R.L. *Biol. Fert. Soils.* **1994**, *17*, 69-74.
43. Trevors, J.T. *CRC Critical Rev. Microbiol.* **1983**, *11*, 83-100.
44. Entry, J.A.; Emmingham, W.H. *Can. J. Soil Sci.* **1996**, *76*, 101-106.
45. Zablotowicz, R.M.; Locke, M.A.; Knight, S.S. In *Proc. Miss. Water Resources Researcg Conf.*; Ballweber, J.A. Ed.; Miss. Water Resources Res. Instit., 2000, pp. 38-42.
46. Locke, M.A.; Zablotowicz, R.M. *Am. Soc. Agron. Abstr.* **2000**, *40*, 88.

Reprinted from ACS Symposium Series 842
Terrestrial Field Dissipation Studies
Purpose, Design, and Interpretation
Ellen L. Arthur, Aldos C. Barefoot, Val E. Clay, Editors
Published 2003 by the American Chemical Society