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Fluometuron Adsorption to Soil Influenced by Best Management Practices (BMPs)

Established Filter Strip and Riparian Zones

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A study was established to determine soil properties and fluometuron adsorption in a Dundee silt loam collected from a cropped watershed and adjacent filter strip (0-2 cm depth); and a Dowling overwash phase of a riparian zone. Established (greater than 5 years) grass filter strip sampling points included a mixing zone (1 m prior to the filter strip edge, but not in cropped area), edge of filter strip, and locations at 1 m and 2 m into the filter strip. Sampling points in the riparian zone were: entrance and 10 m, 25 m, 50 m, 100 m, 200 m, 400 m, 600 m, and 800 m from the riparian entrance. Percent organic matter (OM), percent clay and cation exchange capacity (CEC) were higher with increased distance down slope from the established filter strip mixing zone to 2 m into the strip and ranged from 0.4% to 2.4%, 18% to 23%, and 12 to 18 cmol kg⁻¹, respectively. In the riparian zone, OM, clay, and CEC ranged from 2.3% to 4.5%, 22% to 40%, and 18 to 32 cmol kg⁻¹, respectively, with increasing

respectively, with increasing distance down slope from the drainage channel entrance, to 400-800 m from the entrance. Fluometuron adsorption to soil collected from locations at 1 m and 2 m from the established grass filter strip edge and within the riparian areas was higher than soil collected from the established filter strip mixing zone, strip edge, and adjacent cropped soil. Values of K_F were positively correlated with OM, clay and CEC ($r \geq 89$). Based on adsorptive soil properties, the use of filter strips and riparian zones as a BMP can improve surface water quality.

Introduction

The USEPA has stated that agricultural stresses, largely from excess nutrients, sediment, and pesticides, affect 58% of impaired lake acres, 55% of impaired stream miles, and 21% of impaired estuarine systems (1). Due to the humid sub-tropical climate in Mississippi, both weed and insect pressures have a high impact on farm production compared to other areas of the nation. Similarly, increased microbial activity promotes oxidation of organic matter, requiring the consistent use of synthetic fertilizer for nutrient replenishment. As a consequence, the intensity of agrichemical use in crop production is exceptionally high, particularly in cotton. Spring rainfall amount and intensity are also high, and a primary object for crop producers is to expeditiously move water off the field through trenched water furrows. Since many agricultural contaminants move off-site with water, the potential for significant contaminant flux through the ecosystem exists.

Currently, the Mississippi Department of Environmental Quality (MDEQ) is tasked with establishing total maximum daily loads (TMDLs) of nonpoint-source pollutants for bodies of water, and is responsible for administering pollution abatement programs to assure water quality improvement for impaired watersheds. Therefore, management systems evaluation area (MSEA) projects provide an excellent opportunity to educate the public with scientific information concerning cropped watersheds as a nonpoint contaminant source. MSEA projects are part of a program titled Agriculture Systems for Environmental Quality (ASEQ). They were included in the 1989 Initiative on Water Quality to investigate water quality contamination from pesticides and fertilizers used in field crop production. In 1994, the Mississippi Delta MSEA (MDMSEA) project was initiated to identify, implement, and evaluate BMPs for use in the Delta. A BMP is the physical application of plant, land, and water management

knowledge, in order to protect soil and water resources (2). Many mitigative practices are designed to lower the kinetic energy of moving water and thereby reduce the off-site transport of nonpoint-source contaminants such as pesticides, nutrients, and eroded sediment. Once effective BMPs have been developed, states may incorporate them into nonpoint-source pollution abatement programs.

MDMSEA research is being conducted by several local, state and federal agencies at three watersheds located in Sunflower and Leflore counties in Mississippi. Each location has a watershed that drains into an oxbow lake. These lakes were once a part of natural meandering channels or floodplains of the Sunflower or Yazoo Rivers. However, a change in the course of river flow has left these lakes isolated from their adjacent river channels. The cropped area surrounding the oxbow lake creates a closed watershed system, hence an ideal environment to study the physicochemical processes in runoff influenced by various BMPs. Some BMPs for improving and preserving water quality include: ultra low selective agrochemical applications, conservation tillage, grass filter strips, slotted board risers, and riparian zone management. This report will focus on the use of grass filter strips and a riparian zone as BMPs for surface water quality improvement.

Farmers generally cultivate land to the edge of ditches and roads, leaving no vegetation to interact with agrichemicals in runoff. Edge-of-field grass filter strips are designed to remove sediment, organic matter, and other pollutants from runoff by filtration, deposition, infiltration, sorption, decomposition, and volatilization, thereby improving water quality. Grass filter strips have been shown to reduce sediment and herbicides in runoff by least 50% in small plot research (3, 4, 5). In larger scale research conducted on a 0.41 ha watershed, filters strips retained 58, 73, and 69% of atrazine, metolachlor, and cyanazine, respectively, and sediment retention ranged from 40 to 100% (6). Soil loss from a 1.6 ha watershed with a 2.4% convex slope was reduced by as much as 46% through the use of filter strips (7). Depending on sediment retention, filter strips should effectively retain herbicide molecules that are strongly adsorbed to sediment in runoff. The strips may also reduce water loss, thus off-site losses of fluometuron suspended in the water phase would be minimized.

Historically, riparian zones and wetlands in the Mississippi Delta were viewed as undesirable swamps to be drained, and their benefits in water quality improvement went unnoticed. These zones are transitional between ecotones of land and water, and may serve as a BMP for water quality improvement (8). Riparian zones can remove sediment and other pollutants in runoff exiting adjacent croplands. Studies have shown that a riparian zone can retain 70 to 90% of total nitrogen inputs and that most NO_3^- removal occurs within 20 m of the forest/field boundary (9).

Fluometuron was chosen as our compound of study because it is commonly used in Mississippi cotton (*Gossypium hirsutum* L.) production and because detectable levels have been reported in surface water (10, 11). Fluometuron is an effective herbicide for annual grass and broadleaf weed control in cotton. Fluometuron was labeled for use in 1965 (12) and is one of several compounds that belong to the herbicide group known as the phenylureas or substituted ureas. Fluometuron is considered to be a nonionic molecule that does not ionize over a wide pH range (13). Fluometuron is also considered to be moderately water soluble, with reported solubility of 90 mg L⁻¹ at 20 to 25 C (14).

After application, the environmental fate of a herbicide depends on compound retention, transportation, transformation, and interactions of these processes (15). Potential environmental sinks in the soil-plant-atmosphere relationship include: sorption and desorption to the soil colloidal fraction, runoff movement in the dissolved or sorbed state, plant uptake, volatility, photolysis, and hydrodynamic transport as soluble constituents of the aqueous phase (convection, transpiration, or evaporation) (14). Herbicide retention primarily refers to adsorption, which is defined as the accumulation of a pesticide or other organic molecule at either the soil-water or the soil-air interface, resulting in the accumulation of molecular layers on the surface of soil particles (15). Adsorption is an important reversible process that is generally measured by herbicide disappearance from solution. When a herbicide molecule is adsorbed, it can move into the interior matrix of the colloidal fraction (clay minerals and humus) or plant biomass and become tightly bound (16). The influence of BMPs may change soil constituents, hence altering the physicochemical dynamics of compound retention, transportation, and transformation. Therefore, research was conducted to determine soil properties and fluometuron adsorption in soil from an established (> 5 yr) grass filter strip, riparian zone, and adjacent cropped watershed epipedon at Beasley Lake in Sunflower County, MS.

Materials and Methods

Soil Characterization

Research was conducted on a Dundee silt loam (fine silty, mixed, thermic, Aeric Ochraqualf) collected from a cropped area; adjacent established tall fescue (*Festuca arundinacea* Schreb.) filter strip (0-2 cm depth); and a Dowling overwash phase (fine, montmorillonitic, thermic, Vertic Epiaquept) of a riparian zone (17). These areas surround Beasley Lake in Sunflower County, MS, in the Mississippi River alluvial floodplain. In some areas, runoff from the cropped area

used for cotton production moves through an established tall fescue filter strip and a riparian zone before entering the lake. In other areas, runoff will pass through a filter strip and drainage channel before entering the riparian zone (Figure 1). Runoff in the drainage channel will be directed and released into the riparian zone and move in a slough through approximately 600 m of living hardwood trees. The distribution of vegetation changes at 400 and 600 m to a saturated region of mainly dead trees, with a thick understory of shrubs and phreatophytic (water-loving) plants prior to being discharged into an oxbow lake. Soil in the riparian zone will typically become saturated after a runoff event. The length of time saturated conditions persist depends on antecedent soil moisture, the amount of runoff water received, and other environmental conditions.

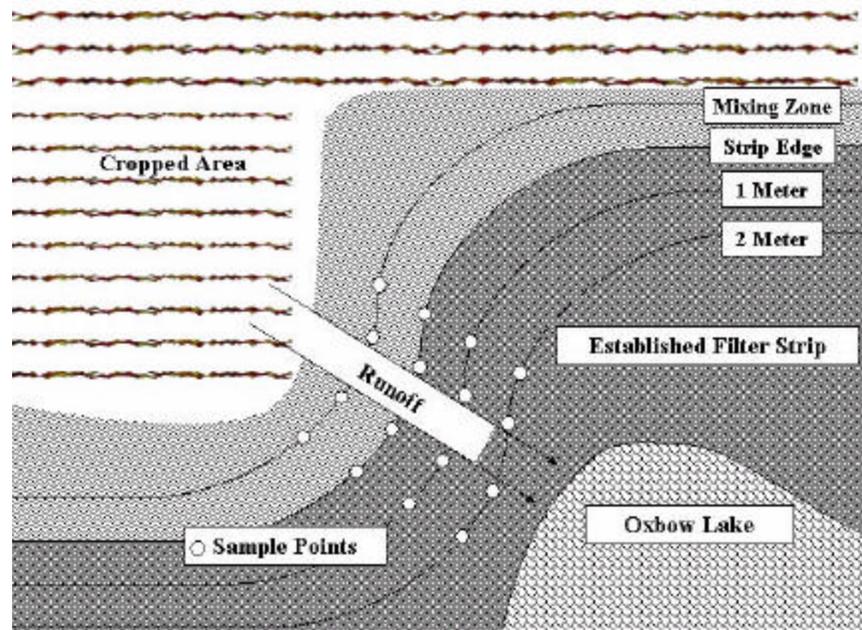


Figure 1. Diagram of established (greater than 5 years) tall fescue (*Festuca arundinacea* Schreb.) filter strip sampling points located at Beasley Lake in Sunflower County, MS.

All soil samples for this experiment were collected in the spring of 1996 prior to field preparation and agriculture chemical applications. The established filter

strip was sampled at four points along a transect in the mixing zone (1 m prior to the filter strip edge, but not in the crop area), the front edge of the filter strip, and at 1 and 2 m from the edge into the filter strip, resulting in sixteen sampling points for each grass filter strip. At each point, ten samples taken to a depth of 2 cm were combined to make a single composite sample. Sampling points in the riparian zone were: entrance and 10 m, 25 m, 50 m, 100 m, 200 m, 400 m, 600 m, and 800 m from the riparian entrance (Figure 2). Ten samples

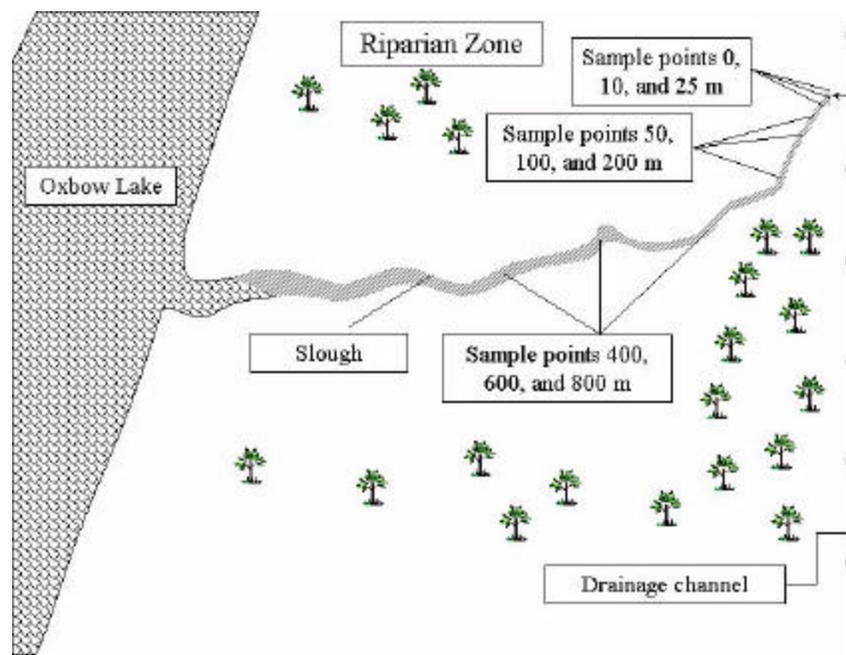


Figure 2. Diagram of riparian zone sampling points at Beasley Lake in Sunflower County, MS.

were collected to a depth of 2 cm at each sampling point. These samples were combined based on soil characteristics, resulting in composite samples for 0-25 m (riparian entrance), and 50-200 m and 400-800 m from the riparian entrance.

All soils were air-dried, screened through a 2-mm sieve, and stored at room temperature until analysis. Samples were analyzed for organic matter (OM) content by a colorimetric procedure (18), pH using a 1:2 soil to water suspension (19), and cation exchange capacity (CEC) by extraction and summation of

exchangeable acids and bases (20). Particle size analyses were conducted using the hydrometer method (21).

Fluometuron Adsorption

A batch equilibration method used by several researchers (22, 23, 24, 25) was employed to study fluometuron adsorption to soil. Soil (5 g) was transferred to 50-ml graduated polypropylene centrifuge tubes (Corning Incorporated, Pulteney St, Corning, NY 14831). Technical grade fluometuron (96.8% chemical purity)(Syngenta, 410 Swing Rd., Greensboro, NC 27409) was dissolved in 0.01 M CaCl₂ to achieve solution concentrations of 0.85, 4.7, 17.7, and 34.9 $\mu\text{mol L}^{-1}$. The highest concentration was equivalent to 15.7 times the recommended field rate of 2.2 kg ai ha⁻¹ uniformly incorporated to a 15-cm soil depth. Fluometuron solutions contained 166.5 Bq ml⁻¹ uniformly ring-labeled ¹⁴C-fluometuron (specific activity 17.3 Bq g⁻¹, 99% radiochemical purity) (Novartis, 410 Swing Rd., Greensboro, NC 27409). Ten ml of each of these four solutions were added to the soil; samples were shaken for 15 h at room temperature to allow the soil-herbicide system to reach equilibrium. After equilibration, samples were centrifuged (400 x g for 20 min) and a 1-ml aliquot of supernatant was transferred to 15 ml of water-accepting scintillation cocktail (Scintiverse, Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785). The ¹⁴C radioactivity was counted for each sample using liquid scintillation spectrometry (Model LS 6000IC, Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, CA 92634-3100) with internal quench correction standards. Fluometuron adsorption to soil was determined by a change in the amount of herbicide in solution, and blank samples were used to adjust for background.

Adsorption isotherm models were developed using the Freundlich equation (26) computed as $[Q] = K_F[C]^{1/n}$. Where [Q] = amount adsorbed (mg g^{-1}), K_F = coefficient (ml g^{-1}), [C] = equilibrium herbicide concentration (mg ml^{-1}), and 1/n = dimensionless coefficient. Freundlich coefficients were determined by the regression of log [Q] against log [C]. The K_F and 1/n coefficients are interpreted as indices of adsorption capacity and adsorption intensity, respectively (27, 28). Data were subjected to analysis of variance, and mean values of K_F and 1/n were separated between soils using Fisher's protected Least Significant Difference (LSD) analysis at a probability level of $\alpha = 0.05$. Pearson correlation coefficients were used to relate effects of soil properties to fluometuron adsorption across soils.

Results and Discussion

Soil Properties

Soil samples collected from all areas of the established filter strip, riparian zone, and cropped area were compared to determine the difference in soil properties. Sand content was at least 38% in entrance areas of the established filter strip (mixing zone) and riparian zone (0-25m), with only 5% sand content just prior to entrance into the lake (Table 1).

Table I. Selected Chemical and Physical Properties of Cropped, Filter Strip, and Riparian Soils

<i>Sample Point</i>	<i>pH</i> ^a	<i>CEC</i> ^b	<i>OM</i> ^c	<i>Sand</i> ^d	<i>Silt</i> ^d	<i>Clay</i> ^d
		cmol kg ⁻¹		%		
Crop	4.7	11.7	0.7	28	59	13
Established-strip mix	5.9	12.2	0.4	46	36	18
Established-strip edge	6.0	14.4	0.9	40	39	21
Established-strip 1 m	6.3	18.2	2.1	21	58	22
Established-strip 2 m	6.0	18.1	2.4	31	46	23
Riparian 0-25 m	6.8	18.4	2.3	38	40	22
Riparian 50-200 m	6.4	23.3	3.1	7	62	26
Riparian 400-800 m	5.8	31.7	4.5	5	55	40
<i>LSD (α = 0.05)</i>	<i>0.3</i>	<i>2.7</i>	<i>0.6</i>	<i>7</i>	<i>6</i>	<i>4</i>

^a Soil pH determined using 1:2 soil to water suspension. ^b CEC was determined by extraction and summation of exchangeable acids and bases. ^c Soil OM was determined by a colorimetric procedure. ^d Particle size analyses were performed using a hydrometer method.

Clay content was 13% in the cropped area, which was lower than any other area sampled. The clay content ranged from 18 to 26% in soil from all areas of the filter strip and areas within 0 to 200m of the riparian zone entrance. Clay content was highest in the 400 to 800m riparian area, which was the area of the riparian zone nearest to the lake. This suggests that runoff water kinetic energy decreased as it moved through the grass filter strip and riparian zone, causing coarser fractions to settle out of suspension, and finer sediment to remain suspended before being deposited as distance increased through these areas. Gilliam et al. (29) reported similar results where coarse sediment was deposited

close to the field and sediment layers consisting of clay-sized materials developed with distance.

Soil collected 50-200 m and 400-800 m from the riparian entrance contained at least 3% OM and had a CEC of at least 23 cmol kg⁻¹, which was higher compared to soil from all other areas (Table 1). The OM content and CEC ranged from 2.1 to 2.4% and 18.1 to 18.4 cmol kg⁻¹, respectively, in soil collected from the entrance of the riparian area and interior areas (1 and 2 m from strip edge) of the established filter strip, which was lower compared to soil from other riparian areas. However, OM content was less than 1 % and CEC was lower than 14.5 cmol kg⁻¹ in soil collected from exterior areas (mixing zone and strip edge) of the established filter strip and the cropped area.

The partial decomposition of fescue grass in the established filter strip interior areas likely contributed to higher OM (24). The higher OM content in soil from riparian areas was due to well-decomposed forest litter. Also, slow drainage of surface and subsurface water contributed to saturated conditions in the riparian areas, which can reduce OM decomposition (30). McLatchey and Reddy reported a threefold increase in OM decomposition with a change from anaerobic to aerobic conditions (31). The higher CEC in these areas results from the combination of higher OM and clay content. Cation exchange capacity was correlated to OM ($r = 0.61$) and clay ($r = 0.76$), which emphasizes the importance of these two soil factors on the CEC (data not shown).

Fluometuron Adsorption

Freundlich constants, K_F and $1/n$, ranged from 0.81 to 4.58 mL g⁻¹ and 0.90 to 1.01, respectively, among all soils (Table II). Gaston and Locke reported similar parameter values of 1.45 mL g⁻¹ for K_F , and 0.90 for $1/n$ for fluometuron adsorption to a Dundee silty clay loam collected from Mississippi (32). Others reported values of 0.90 for K_F and 1.08 for $1/n$ with a Bosket very fine sandy loam (33). In general, values of $1/n$ have been reported from 0.70 to 1.20 in adsorption experiments using 50 various pesticides (34).

In the established filter strip, K_F values ranged from 0.81 to 1.21 with soil from the strip exterior (mixing zone and strip edge) and 2.35 to 2.51 with soil from the strip interior (1 and 2 m from strip edge) (Table II). Adsorption to soil from the established filter strip exterior was less than to cropped area soil, based on values of K_F . Adsorption to soil from the established filter strip interior was greater than to cropped area soil and at least 1.5 times higher than adsorption to soil from strip exterior areas. Fluometuron adsorption isotherms illustrate fluometuron retention in established filter strip and cropped soils (Figure 3).

Lower fluometuron adsorption to established strip exterior areas and cropped area was probably due to lower organic matter content in the mixing

zone, strip edge, and cropped soil samples compared to the strip interior soil samples (Table I). Results from other research emphasize a strong correlation of

Table II. Freundlich Coefficients Determined from Batch Adsorption Techniques with Soils Collected from a Cropped Area, Established Filter Strip, and Riparian Zone.

Sample Point	Freundlich Coefficients	
	K_F	$1/n$
	mL g ⁻¹	
Crop	1.48	0.92
Established-strip mix	0.81	1.01
Established-strip edge	1.21	1.00
Established-strip 1 m	2.51	0.98
Established-strip 2 m	2.35	0.95
Riparian 0-25 m	2.60	0.93
Riparian 50-200 m	3.01	0.90
Riparian 400-800 m	4.58	0.93
<i>LSD (a = 0.05)</i>	<i>0.26</i>	<i>0.04</i>

fluometuron adsorption with soil organic matter (35, 36, 37, 33). In addition, a similar experiment conducted by Benoit et al. illustrated that adsorption of isoproturon, a phenylurea herbicide, to surface soil (0-2 cm) collected from a perennial ryegrass (*Lolium perenne* L.) filter strip was almost three times higher than to cropped area soil (24). They attributed higher adsorption to the high density of partially decomposed plant residues.

Values of K_F for riparian zone soil ranged from 2.60 to 4.58 with an increase in distance from channel entrance (0 to 25 m) to the area prior to the lake (400 to 800 m) (Table II). Fluometuron adsorption to soil collected from 50-200 m and 400-800 m from the riparian entrance was greater than to all other soils in the experiment. Adsorption of fluometuron to soil collected 0-25 m from the riparian entrance was no different than to soil collected from the established filter strip at land 2 m from strip edge. Isotherms illustrate fluometuron adsorption to soil from riparian forest and cropped areas (Figure 4).

In general, the adsorption of fluometuron to soils evaluated in this experiment followed the order: filter strip mixing zone < filter strip edge < cropped area < filter strip 2 m = filter strip 1 m = riparian entrance < riparian 50-200 m < riparian 400-800 m (Table II).

There was a strong relationship between fluometuron adsorption and soil OM, clay content, and CEC across all soil samples, with correlation coefficients of 0.98, 0.89, and 0.97, respectively (Table III).

As mentioned above, it is well documented that fluometuron adsorption is highly correlated to OM content. The positive correlation to clay content is consistent with some research (38), while others have reported a very low

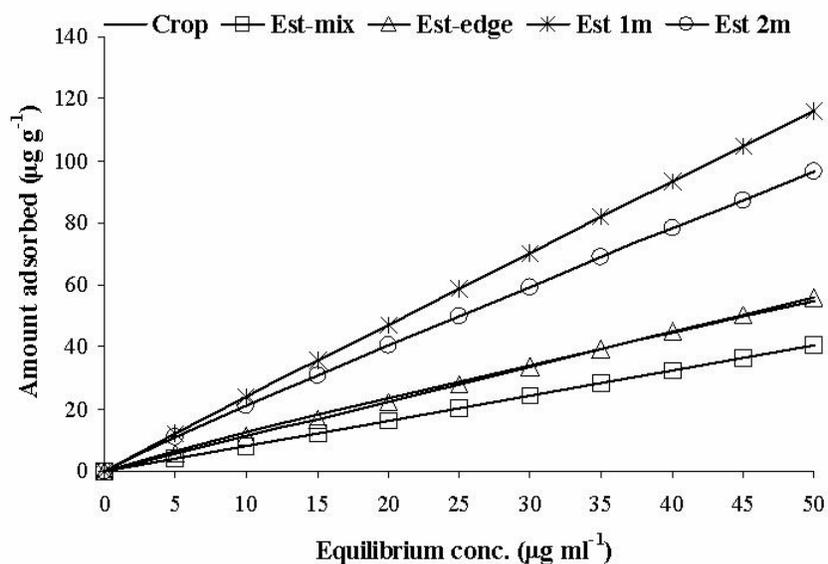


Figure 3. Adsorption isotherms that describe fluometuron adsorption to soil influenced by an established (greater than 5 years) tall fescue (*Festuca arundinacea* Schreb.) filter strip located at Beasley Lake in Sunflower County, MS. Strip sampling points include a mixing zone (1 m prior to edge), strip edge, 1 m into strip, and 2 m into strip.

correlation ($r = 0.09$ to 0.13) between adsorption and clay content of eight Czechoslovakian soils involving five phenylurea herbicides (36). Weber et al. reported that fluometuron adsorption was higher when a montmorillonite, a 2:1 expanding clay was added to soil media compared to a kaolinite, a 1:1 nonexpanding clay (39). Brown et al. reported a significant correlation ($r = 0.82$) between CEC and fluometuron adsorption (35).

Organic matter content and CEC were highest in soil collected from the riparian zone. This was due to the accumulation of well-decomposed forest litter,

which can increase herbicide adsorption and prolong herbicide residence time (22). Adsorption was likely higher with increasing distance into the forest due to increased clay content and an increase in anaerobic conditions, which enhances organic residue preservation (30). As soil becomes saturated, gas exchange between soil and air is reduced, microbial populations change, and pH changes, which affects enzymatic activity and organic matter decomposition (31). Spatial differences in texture were due to coarse particle deposition near the forest entrance followed by fine particle deposition as runoff moved downslope (Figure 2). The OM content and fluometuron adsorption in established strip interior soil

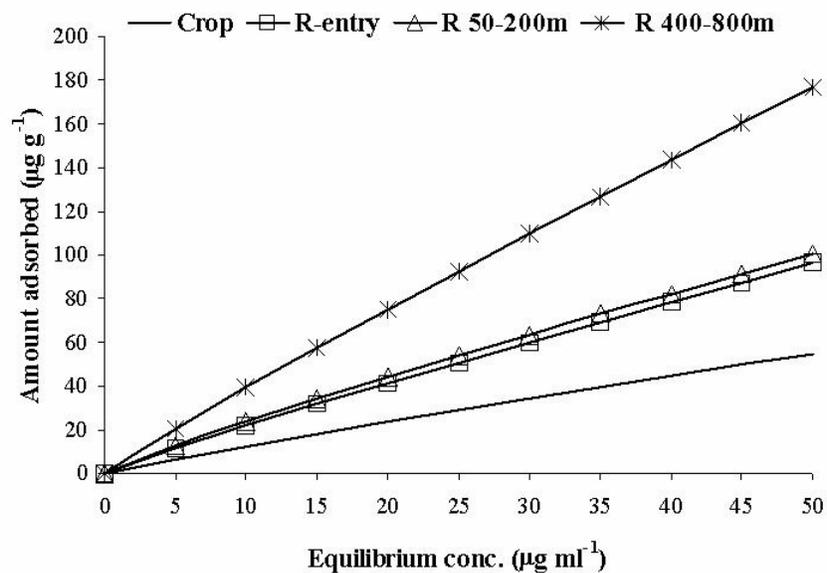


Figure 4. Adsorption isotherms that describe fluometuron adsorption to soil influenced by a riparian zone located at Beasley Lake in Sunflower County, MS. Sampling points include 0-25 m (entrance), 50-200 m from entrance, and 400-800 m from entrance.

(1 and 2 m from strip edge) was greater than strip exterior (mixing zone and strip edge), which was probably due to the presence of partially decomposed grass residue. This resulted in an adsorptive capacity for the established strip interior that was similar to the riparian zone entrance (0-25 m).

In conclusion, filter strip establishment and riparian zone management should promote soil properties such as OM and consequent CEC to enhance adsorption of fluometuron to soil in these areas. Therefore, adoption of filter strips and riparian zones as a BMP can improve surface water quality based on adsorptive soil properties and allow the continued use of valuable herbicides in the Mississippi Delta.

Table III. Correlation Coefficients for Various Soil Properties with Fluometuron Adsorption for Soil Samples from a Cropped Area, Filter Strips, and Riparian Zone at Beasley Lake in Sunflower Co., MS

<i>Soil Properties</i> ^a	<i>Pearson Correlation Coefficients</i>
	<i>Across Soil Samples</i>
PH	0.25
CEC	0.97
Sand	-0.84
Silt	0.51
Clay	0.89
OM	0.98

^a Abbreviations: CEC, cation exchange capacity; OM, organic matter.

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