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Transport of atrazine through soil columns with or without switchgrass roots

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Abstract

Fate and transport of atrazine in the presence of plant roots in soils is not adequately described in literature. Our objectives were to evaluate the effects of switchgrass (*Panicum virgatum* L.) roots on the transport of bromide and atrazine under constant pore water velocity. Two agricultural soil types, Emporia (fine loamy, siliceous, thermic Typic Hapludult) and Cullen (clayey, mixed, thermic Typic Hapludult) were used. The soils were taken from the A horizon in an area that has no history of pesticide application. Eight replicated columns (four for Emporia and four for Cullen) were used. Four columns, two of each soil type, were planted with warm season switchgrass and four other columns, two of each soil type, were left fallow. When the plants passed the tillering stage, the aboveground biomass was hand clipped from each column. A 505.6 mg Br/column tracer and 5.30 mg atrazine/column (3.0 kg /ha) were mixed with 100 g soil and uniformly applied on the surface of each column and left for 24 h to permit adsorption of atrazine onto switchgrass roots and soil. Leaching patterns differed between columns with and without switchgrass roots. The deterministic two-site/two region nonequilibrium model provided an excellent fit to all bromide and atrazine effluent curves. Switchgrass likely favored the creation of macropores that contributes to accelerated transport through the unsaturated zone, thus potentially increasing groundwater pollution. The breakthrough curves for both soils were similar; however, the early breakthrough and tailing of atrazine indicated the presence of preferential flow. Early breakthrough and long tails in the effluent curve were observed for bromide and atrazine in the presence of switchgrass roots indicating a nonequilibrium behavior. It appears that roots have not decomposed sufficiently to provide additional surface area or humus to affect binding and breakdown of atrazine.

Key words: Cullen, Emporia**,** mobile, modeling, immobile, rain simulators, atrazine, switchgrass, breakthrough, transport.

Introduction

Farmers in North America who are involved actively in row crop production use pesticides to optimize crop production and to sustain productivity. One commonly used herbicide for corn (*Zea mays* L.) production is atrazine [2-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-trazine-2,4-diamine]. This herbicide, used to control most small-seeded annual weeds and grasses, is detected frequently in surface and ground water [23]. The concerns are due to the health hazards associated with the entry of these chemicals into the food chain of animals and humans [6, 14]. The mobility of agriculturally related chemicals in the vadose zone has been quantified in recent years [1, 3, 5, 28].

Many farmers have adopted conservation tillage practices as important methods of crop production in that conventional tillage (CT) practices have been associated with excessive soil erosion, nutrient loss by runoff, and relatively high-energy costs. Conservation tillage systems allow crop residues to be left on the soil surface to conserve soil water and reduce soil erosion. One type of conservation tillage with relatively minimum soil disturbance is the no-till (NT) system. Under the NT crop production system, macropores develop as a result of channeling by plant roots, earthworms or soil shrinkage cracks. Herbicides are usually applied under NT practices to control weeds or winter covers. When sufficient rainfall occurs, infiltration under NT conditions is often higher than under CT. This action increases the potential for shallow ground water loading due to movement through preferential paths in the soil profile [10, 21, 25, 28]. Tillage practices at various locations have shown different results based on local climate, soil water holding capacity, soil topography and drainage characteristics [27]. Xue *et al.* [30] observed longer tailing and earlier breakthrough of alachlor {2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide} in NT soil columns than in CT soil columns under saturated conditions. Thomas and Phillips [31] observed greater leaching of NO_3^- in NT than in CT.

The path in which solute is transported in soil is important when assessing potential shallow ground water loading of pesticides. Work done by Bruseau *et al.* [2] separated nonequilibrium transport processes into two general classes: physical nonequilibrium and chemical sorption-related nonequilibrium. Preferential flow can result in both physical and hydraulic non-equilibrium, which affects sorbing or nonsorbing solutes. Chemical nonequilibrium and intrasorbent diffusion give rise to sorption-related nonequilibrium that involves only sorbing solutes.

Sorption of herbicides onto root mass and soil organic matter has practical implications to the movement and distribution of herbicides. Herbicide binding in a soil can be weak or strong depending on the amount of organic matter present and the degree of decomposition of plant residue within the soil. The degree of adsorption varies with the herbicide characteristics, root mass density, clay content and amount of organic C in a soil. The presence of roots may increase adsorption and prolong herbicide residence times in the upper layers of a soil, and hence reduce herbicide leaching [15]. The overall effect may be a reduction of herbicide contamination of groundwater. Herbicides adsorbed on plant root surfaces also are more susceptible to degradation by microorganisms further reducing the leaching losses and potential risk of groundwater contamination.

While herbicide adsorption to plant roots may retard herbicide transport, plant roots, on the other hand, create macropores that may facilitate transport through the soil profile. The use of switchgrass as a vegetated filter strip (VFS) is increasingly becoming acceptable in the farming community as a conservation practice to control erosion. As a component of best management practices, switchgrass vegetation is used routinely to filter nutrients, sediment, organics, pathogens and pesticides from agricultural runoff before they reach a water system [4]. Switchgrass has a fibrous root system close to the soil surface that facilitates the filtration process. The use of switchgrass in VFS on end rows of croplands to minimize sediment and pesticide transport by runoff has been well documented [9]. However, further investigation is necessary to determine the effects of switchgrass roots on herbicide transport in the soil profile. The objectives of this study were: (1) to evaluate the effect of switchgrass roots on atrazine transport, and (2) to model and compare the transport of atrazine and bromide in two major agricultural soils during constant water flow.

Materials and Methods

Experimental setup: Transport of atrazine in two soil types with or without switchgrass roots was determined using disturbed soil columns (Fig. 1). Both soils are important agricultural soils in Virginia. These soils are deep and well drained. The Cullen soil was formed from weathered residuum of the Piedmont Uplands and the Emporia soil was formed from stratified fluvial and marine sediments of the coastal plain. The Cullen soil was sampled from an agricultural farmland, whereas the Emporia soil was collected from an area planted to a loblolly pine (*Pinus taeda* L.). Soil samples were taken from the A horizon for the Cullen (0-25 cm) and Emporia (0-20 cm) soils. The soil samples were air-dried and passed through a 2-mm sieve prior to selected laboratory chemical and physical analysis, i.e., determined were particle size distribution by the pipette method [20], pH in 0.01 M $CaCl_2$ [16], organic carbon (OC) content by the Walkley-Black procedure [17], cation exchange capacity (CEC) as determined by A & L Laboratories (Richmond, VA) and rainfall-runoff erosivity factor (R-factor) (Table 1).

Figure 1. Experimental setup of soil columns and rainfall simulators.

Table 1. Selected properties of Cullen and Emporia soils.

Soil property	Cullen	Emporia
Sand (g kg^{-1})	350	610
Silt (g kg^{-1})	340	330
Clay (g kg^{-1})	310	60
CEC (cmol kg^{-1})	6.0	1.2
pH	5.7	4.3
OC (g kg^{-1})	13.0	6.3
R-factor	5.99	2.96
Texture class	Clay loam	Sandy loam

Polyvinyl chloride (PVC) columns (15 cm diameter, 45 cm long) were cut length-wise into two halves. Ridges of silicone sealant were laid 5-cm apart along the interior surface of each section to prevent bypassing leakage along the soil-PVC interface. The two halves were then joined together with silicone sealant, and columns were reinforced using duct tape and two circular rings around each column. Eight columns were assembled in similar manner with each column having a 15-cm diameter PVC end plate. Each end plate had a 0.5 cm diameter hole in the center to allow for drainage. The inner side of the end plate was covered with glass fiber cheesecloth to filter sediment movement and a plastic tube attached to the end plate to collect solution. Four columns were packed with the Cullen soil to a bulk density (ρ) of 1.36 g cm^{-3} and four columns with Emporia soil to 1.53 g cm^{-3} (Table 2). All columns were packed to soil length of 40 cm. The dry weights of the repacked columns were prerecorded before planting.

Table 2. Miscible displacement experimental conditions.

Soil	Treatment	Column #	ρ g cm^{-3}	Q cm min^{-1}	V cm min^{-1}	θ_m cm^3 cm^{-3}	PV cm^3
Cullen	No roots	1	1.36	0.0272	0.0508	0.526	4321.2
		2	1.36	0.0260	0.0485	0.526	4321.2
	With roots	1	1.36	0.0027	0.0050	0.526	4321.2
		2	1.36	0.0018	0.0034	0.526	4321.2
Emporia	No roots	1	1.53	0.0413	0.0801	0.515	4721.1
		2	1.53	0.0337	0.0654	0.515	4721.1
	With roots	1	1.53	0.0040	0.0078	0.515	4721.1
		2	1.53	0.0070	0.0136	0.515	4721.1

All PVC columns were saturated with distilled water from the bottom, and the weight of each column was recorded. Four columns (two from each soil) were planted with switchgrass. Seeds were planted about 2-cm deep in the columns placed in tanks with water sub-irrigation. Fertilization with 100-mL of Peters 20N:20P:20K (20 g L^{-1}) was done weekly. Seedlings at the three–leaf stage were thinned to eight evenly spaced plants per column and allowed to grow through the summer in outdoors ambient conditions. Eight months after planting, the dry foliage was cut at soil level, and the columns were brought into the greenhouse. A 100-g sample of soil was removed from the surface of each column and mixed with 5.3 mg of atrazine in 10 ml of 0.88 M KBr solution (equivalent to 3.0 kg ha^{-1} of atrazine). All columns were saturated from the bottom with 0.005 M of $CaCl_2$ solution, allowed to drain for 24 h, and weights were recorded. The atrazine and bromide treated samples (100 g) were then replaced on the surface of the respective column. The columns were then set under a rainfall simulator (Fig. 1). The rainfall simulator consisted of an airtight clear acrylic reservoir (15 cm diameter) piercing the bottom end, and an adjustable bubbling tube (20 cm long) to control the pressure head [18]. The bubbling tube was closed with a rubber stopper to prevent unnecessary loss of water. By adjusting the height of the bubbling tube, a water flux was adjusted to simulate rainfall at 1 cm hr^{-1}.

This rate was selected to mimic a worse case scenario rain event in Virginia. Leachate from the bottom of each column was collected in increments to yield approximately five pore volumes (PV). Columns were allowed to drain for 24 h before they were split open and soil sectioned into 0-5, 5-10, 10-20 and 20-35 cm depth increments. Leachates and soil samples were stored at 4°C until analysis.

Column leachate samples were thawed at 23±2°C and then vacuum filtered through glass filters (0.7 µm pore size). Bromide concentrations were determined using a bromide specific ion electrode calibrated with KBr standards. Kits (Quantix Pesticide Immunoassay Kits, Idetek, Inc., Sunnyvale, CA) were used for the immunoassay analysis of atrazine in leachate samples and soil extracts. Briefly, a 200-µL sample was added to the appropriate microcups. A 50-µL enzyme conjugate solution was immediately pipetted into each of the microcups, and the whole microwell module was shaken on an orbital plate shaker at 3000 rpm for 60 min. The microcups were then washed five times with a wash solution. A 200-µL substrate solution was added to each microcup and mixed on the orbital shaker for 10 min. At the end of the incubation period, 50-µL of stop solution was added to each microcup, mixed for 10 min. and the absorbance read at 650 nm. Standard curves were fitted with four concentrations from 0 to 1 mg L^{-1}. Atrazine concentrations were calculated from the standards.

Atrazine was extracted from soil samples from each depth of the columns. Twenty grams of soil (oven dry basis) were placed in 200-ml Erlenmeyer flasks with 75 ml of methanol: water (3:1 by volume) solution and shaken for 30 min at 1500 rpm. Soil slurries were vacuum filtered through glass filters (0.7 µm pore size) and the filtrate was analyzed for atrazine as described above. In addition, soil samples of 25 g (oven dry basis) from each soil type were spiked with atrazine (1 mg kg^{-1}) and extracted following the above procedures to determine extraction efficiency. The extraction efficiency reported for each soil type is the average of three samples.

Modeling solute transport: The experimental data (bromide and atrazine) were analyzed using the physical two-region nonequilibrium model [19, 24, 26]. The physical nature of each soil column was separated into two regions: a mobile region and an immobile region. It was assumed by van Genuchten [24] that convective-dispersive transport of solute is restricted to the mobile phase and that the immobile phase is diffusion limited. The equations governing solute transport for the two-region model are:

$$(\theta_m + f\rho K_d)\partial C_m/\partial t + [\theta_{im} + (1 - f)\rho K_d]\partial C_{im}/\partial t = \theta_m D_m \partial C_m/\partial z^2 - q\,\partial C_m/\partial z \quad (1)$$

$$[\theta_{im} + (1 - f)\rho K_d]\,\partial C_{im}/\partial t = \alpha(C_m - C_{im}) \quad (2)$$

where the subscripts m and im denote the mobile and immobile regions, respectively, $\theta_m + \theta_{im} = \theta_v$, f is the fraction of sorption sites that equilibrate with the mobile regions; C is the solution-phase solute concentration (mg L^{-1}); D is the dispersion coefficient (cm^2 min^{-1}); α is the mass-transfer coefficient between the mobile and immobile water regions (min^{-1}); t is time (h); q is the flux (cm min^{-1}); and z is distance from solute origin (cm). The initial and boundary conditions used were:

$$\begin{array}{lll} C_m = 0 & t = 0, 0 \le z < L & (3) \\ C_{im} = 0 & t = 0, L_i \le z < L & (4) \\ C_{in} = C_0 & t = 0, 0 < z < L & (5) \\ vC_m - D\partial C_m/\partial z = 0 & z = 0 & (6) \\ \partial C_m/\partial z = 0 & z = L, t > 0 & (7) \end{array}$$

where L is column length. The dimensionless parameters associated with the model are:

$$\beta = (\theta_m + \rho K_d)/(\theta_v + \rho K_d) \quad (8)$$

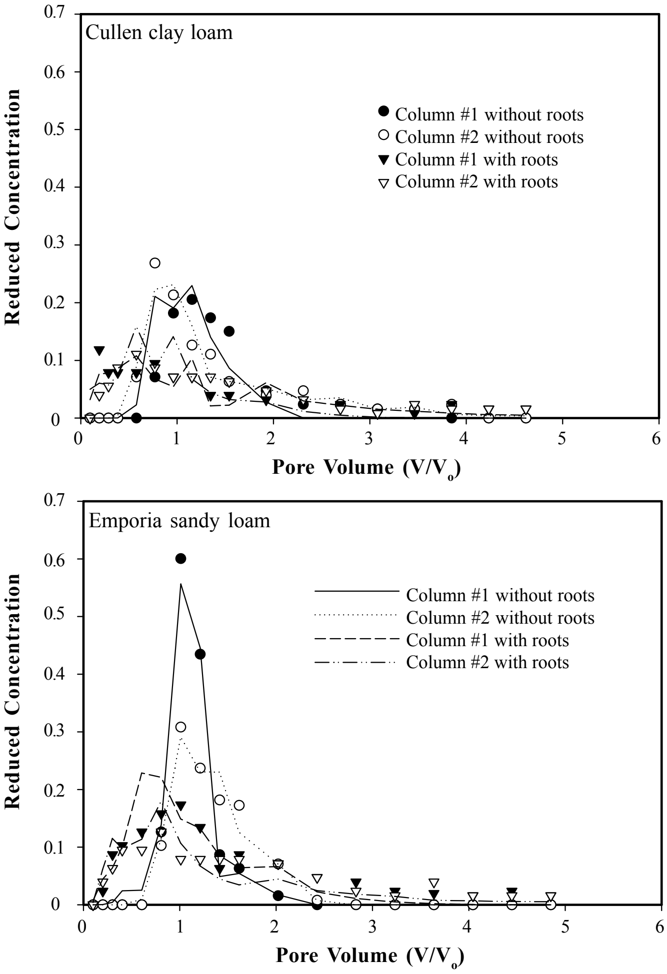
where β is the fraction of mobile water content and K_d is distribution coefficient (cm^3 kg^{-1}). Values of D, β and α for Br$^-$ and β and α for atrazine in each soil column were computed using the program CXTFIT [19] that uses a nonlinear least-square inversion technique. This program can be used to optimize parameters for several theoretical one-dimensional solute transport models. The root mean square error (rmse) for each parameter and the coefficient of determination (r^2) were used to evaluate the predicted breakthrough curves [22, 29].

Results and Discussion

The movement of atrazine was described by the physical non-equilibrium two-region model shown in Equations 1 to 8. The model fitted the experimental atrazine data well (Table 3) and provided root mean square error (rmse) values ranging from 0.0019 to 0.0026 and high r^2 values (0.89 to 0.99). Good fit was found generally between observed and predicted values using the two-site, two-region, non-equilibrium model for all columns for bromide and atrazine breakthrough curves (BTCs) (Figs 2 and 3). The results indicate substantially different leaching patterns for columns with or without switchgrass roots. The variability in model parameter values under similar experimental conditions suggests that the fit between the measures and modeled data is not unique.

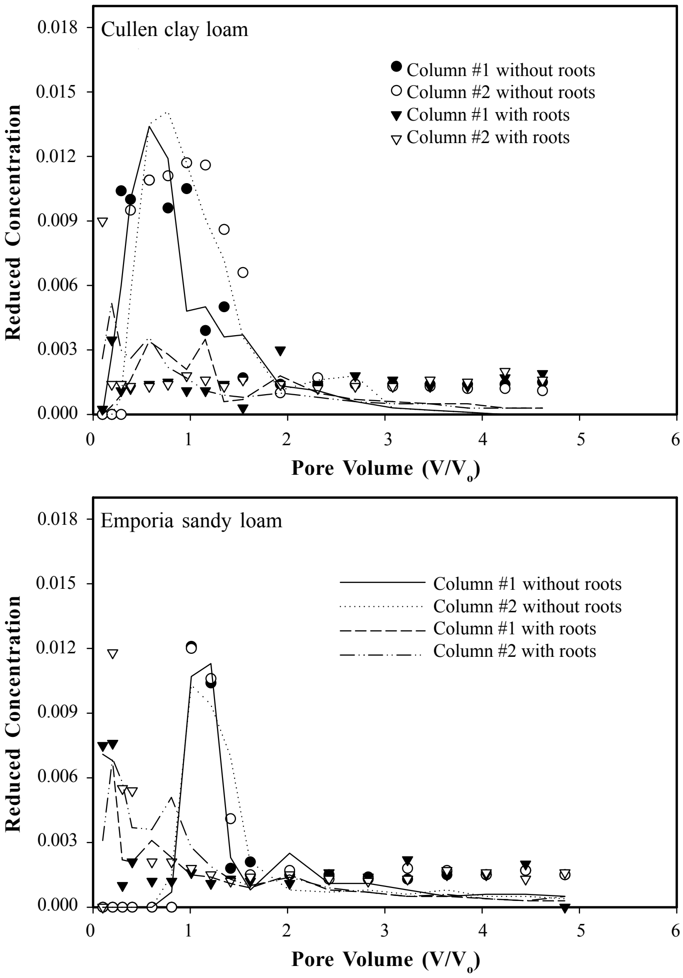
Table 3. Estimated β, α, θ_m and D_m obtained by fitting the two-region model to the experimental breakthrough curves.

			--------------------------------- Bromide				-------------------------------------		------------------- Atrazine		-------------------	
Soil	Treatment	Column #	β	α	θ_m	D_m	rmse	r^2	β	α	rmse	r^2
Cullen	No roots	1	0.936	1.2 x 10^{-3}	0.501	4.58 x 10^{-2}	0.0972	0.95	0.1404	4.14 x 10^{-5}	0.0026	0.99
		2	0.706	1.5 x 10^{-4}	0.378	1.06 x 10^{-1}	0.0148	0.99	0.1311	2.85 x 10^{-5}	0.0023	0.99
		Avg.	0.821	6.8 x 10^{-4}	0.450	7.59 x 10^{-2}	--	--	0.1358	3.50 x 10^{-5}	--	--
	With roots	1	0.125	8.3 x 10^{-5}	0.191	1.25 x 10^{-1}	0.0168	0.99	0.9815	6.75 x 10^{-12}	0.0029	0.89
		2	1.0 x 10^{-4}	1.0 x 10^{-4}	5.4 x 10^{-5}	1.00 x 10^{-7}	0.1095	0.88	0.9891	4.53 x 10^{-12}	0.0034	0.84
		Avg.	0.0626	8.2 x 10^{-5}	0.096	6.30 x10^{-2}	--	--	0.9853	5.64 x 10^{-12}	--	--
Emporia	No roots	1	1.0 x 10^{-4}	2.9 x 10^{-2}	5.2 x 10^{-5}	2.80 x 10^{-3}	0.1862	0.92	0.4265	4.90 x 10^{-4}	0.0019	0.99
		2	0.404	8.7 x 10^{-3}	0.208	1.19 x 10^{-5}	0.0143	0.99	0.3264	2.60 x 10^{-4}	0.0023	0.98
		Avg.	0.202	1.9 x 10^{-2}	0.104	1.03 x 10^{-3}	--	--	0.3764	3.75 x 10^{-4}	--	--
	With roots	1	0.864	1.0 x 10^{-2}	0.445	6.95 x 10^{-2}	0.1152	0.94	0.8051	1.00 x 10-^{11}	0.0027	0.91
		2	0.813	1.1 x 10^{-2}	0.419	5.91 x 10^{-1}	0.5339	0.80	0.7015	1.70 x 10^{-11}	0.0026	0.96
		Avg.	0.838	1.1 x 10^{-2}	0.432	3.30 x 10^{-1}	--	--	0.7533	8.50 x 10^{-12}	--	--



Co=Initial concentration, C= Concentration in effluent, V= Volume effluent Vo= Total volume

Figure 2. Bromide breakthrough curves for Cullen and Emporia soils with and without switchgrass roots. Lines indicate model fitted data.



Co=Initial concentration, C= Concentration in effluent, V= Volume effluent Vo= Total volume

Figure 3. Atrazine breakthrough curves for Cullen and Emporia soils with and without switchgrass roots. Lines indicate model fitted data.

It is shown from simulation of the mobile-immobile model that matrix diffusion is an important process for controlling solute transport. Values of α ranged from 8.2×10^{-5} to 1.9×10^{-2} min^{-1} for bromide and 8.5×10^{-12} to 4.9×10^{-4} min^{-1} for atrazine; indicating matrix diffusion ($\alpha > 0$). Study conducted by Helmke *et al.* [7] to experimentally determine effective diffusion parameters in the matrix of fractured till showed independent estimates of α for three tracers using the radial method resulted in values that were one to two orders of magnitude less than those estimated by fitting the mobile-immobile model to BTCs. Values of á in this study should be considered fairly accurate, though they were determined by the inverse method which has been shown to produce nonunique and/or insensitive estimates of α [8, 19]. Atrazine and bromide breakthrough curves for the columns with switchgrass were shifted to the left and exhibited asymmetry and tailing compared to the columns without switchgrass roots. Average D_m value for the Emporia columns with roots were relatively higher than those without roots, suggesting a wide distribution of mobile pore water velocity ($v_m=q/\theta_m$) and preferential flow [11, 12, 21]. A study conducted by Johnson [13] on saturated atrazine more influenced by displacement of water in finer pores, thereby causing dispersion of Br. Although the Cullen soil is a finer texture soil, a similar trend was observed in the average D_m values as the Emporia soil but with relatively lower mobile phase dispersion in the columns with roots.

For the columns with roots, average peak atrazine concentration was reached after 0.1 pore volume (PV) for Cullen and 0.14 PV for Emporia. Arrival of solute concentrations before 1 PV had passed through each column suggests macropores and the assumption of no dispersion. Peak concentrations were higher in leachates for columns without switchgrass roots after 1.0 PV for both soils. The distribution pattern of atrazine and bromide remained transport in conventionally tilled and no-till soil columns showed an average D_m value for no-till 6 times higher than the average D_m value for the conventional till soil columns. The Emporia soil is much sandier (Table 1) and thus less influenced by macropore flow and similar for columns with or without switchgrass roots after a total of 2.0 PV. However, the concentration of atrazine and bromide in the leachate decreased progressively with increasing time. More than 90% of the bromide was recovered in the leachate and no bromide was detected in the soil column at the end of displacement. The presence of roots within the columns also caused tailing of atrazine and bromide in the leachate. No bromide or atrazine was detected in the first four leachates for columns without switchgrass roots. These results fit the classical convective-dispersive equation described by Van Genuchten [24] for a noninteracting solute under steady-state water flow conditions through homogeneous soil without preferential flow. Attempts were made to reach steady-state conditions for this study; however, near steady-state conditions was established. Flow through the columns was by gravity; therefore periodic occurred through the rainfall simulation was in process. The total atrazine that leached through the columns with switchgrass roots was 53 and 18% lower than through those columns without switchgrass roots for the Cullen and Emporia soils, respectively. Switchgrass had a considerable effect on the amount of atrazine leached through the columns, i.e., more asymmetry and lower peak concentrations occurred in the presence of switchgrass roots. While roots of grasses in general may create macropores for water transport, reactive solute transport may be retarded in such soil environment.

Average resident atrazine concentration in all columns remained relatively constant with depth (Table 4). However, average resident atrazine concentration in the Emporia soil was much higher than that in the Cullen soil irrespective of the root presence (Table 4). Higher resident atrazine concentration in the Emporia soil columns could also be due to ponding of water in the bottom of the columns. During ponding, atrazine would have a greater chance to adsorb to the soil, resulting in the higher concentration observed (Table 4). The total atrazine recovered from Cullen soil columns with and without switchgrass was 1.59 and 1.31 mg, respectively. The total atrazine detected from the Emporia soil with switchgrass was 2.5 mg, whereas from the column without roots was 2.2 mg. The amount applied to each column was 5.3 mg, and thus the total detected from each soil type was less than 50% of that applied. The reported concentrations were not adjusted for extraction efficiency, which was 60% for the Cullen soil and 70% for the Emporia soil. This underestimated the total amount detected. In addition, there was some loss of atrazine while the leachate was collected and extracted from the soil. Another possible explanation for the fairly small recovery of atrazine from both soils is degradation of the parent compound.

Table 4. Total amount of atrazine retained in Cullen and Emporia soils with or without switchgrass roots after leaching.

Soil depth (cm)	Resident atrazine concentration (μg kg^{-1})			
	Cullen clay loam		Emporia sandy loam	
	No roots	With roots	No roots	With roots
0-5	96.6	189.8	192.4	222.1
5-10	109.1	139.9	155.4	182.1
10-20	113.7	84.9	148.8	229.1
20-40	99.3	89.3	176.3	195.2

Conclusions

Switchgrass favors the creation of preferential flow and, hence, contributes to accelerate the transport of the front through the unsaturated zone, thus potentially increasing groundwater pollution. It appears that roots have not decomposed sufficiently to provide additional surface area or humus to affect binding and breakdown of atrazine. Leaching patterns varied between columns with and without switchgrass roots. Early breakthrough and long tails in the effluent curve were observed for bromide and atrazine in the presence of switchgrass roots indicating the presence of nonequilibrium behavior. The deterministic two-site/two region nonequilibrium model provided a good fit of bromide and atrazine BTCs; however, the fit was not unique to the system under study due to variability in model parameter values under similar experimental conditions. The breakthrough curves for both soils were similar; however, the early breakthrough and tailing of atrazine indicated the presence of nonequilibrium sorption. These data show the effect of switchgrass roots on the fate and transport of atrazine after eight months of establishment. However, switchgrass is perennial and can remain in filter strips for many years. With older switchgrass stands, the greater amounts of decayed roots could influence the fate and transport of atrazine.

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