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TRANSPORT AND FATE OF ATRAZINE IN MIDWESTERN RIPARIAN BUFFER STRIPS[1]

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ABSTRACT: The fate of pesticides entering the Riparian Buffer Strips (RBS) has not been well documented. This study compared the transport and fate of atrazine in soil of three-, five-, and nine-year-old switchgrass (*Panicum virgatum* L.) RBS to that in adjacent soils cropped to a corn-soybean rotation or a grass-alfalfa pasture. Undisturbed soil columns were collected from the RBS and cropped areas within the Bear Creek watershed, near Roland, Iowa. Atrazine and bromide breakthrough curves obtained using intact soil columns under saturated conditions were described by a two-region, mobile-immobile transport model. Preferential flow of bromide and atrazine was evident in five- and nine-year-old RBS soil, but there was little difference in transport characteristics between these two RBS soils and the adjacent cropped soils. There was a trend towards an increase in dispersion coefficients between the five- and nine-year-old RBS sites, which suggests an increased degree of preferential flow with increasing RBS age. Despite similar texture and organic C contents, atrazine sorption was significantly greater in RBS soil than the adjacent cropped soil. Cropped soil degraded atrazine faster than the RBS soil. The rapid degradation of atrazine in the corn-soybean soil adjacent to the five-year-old RBS (atrazine half-life of 19 days) appeared to be due to a larger population of atrazine-degrading microorganisms. Atrazine-degrading microorganisms in the corn-soybean soil were 50,940 cells g^{-1} soil compared with 2,970 cells g^{-1} soil in 5-year-old RBS soil which resulted in 60 percent mineralization of [^{14}C-UL-atrazine] in the corn-soybean soil.
(KEY TERMS: modeling; water quality; atrazine; transport; leaching; buffer strips.)

INTRODUCTION

Pesticides have been detected in surface water and ground water of many states (Hallberg, 1989; Thurman *et al.*, 1992; Kolpin *et al.*, 1995; Baker and Richards, 2000). Riparian buffer strips (RBS) are one of the best management practices proposed for reducing transport of pesticides to surface water (Fawcett, 1998). These are strips of native or introduced grasses planted between a pesticide-treated field and adjacent streams or ponds. The combination of parallel strips of dense grasses with shrubs and trees is termed a multi-species riparian buffer strip (Schultz *et al.*, 1995). RBS remove pesticides from runoff water through several mechanisms. Pesticides adsorbed to soil particles are trapped in RBS as runoff water slows and sediments are deposited (Patty *et al.*, 1997). However, herbicides that are primarily carried in the aqueous phase of runoff, such as atrazine, are retained in grass strips through infiltration and adsorption (Hall *et al.*, 1983; Arora *et al.*, 1996; Misra *et al.*, 1996).

The fact that herbicide retention in RBS is linked to the infiltration process raises interesting questions about RBS performance. Losses of herbicides with surface runoff are greatest immediately after application and often occur in response to large precipitation events (Leonard, 1990). Runoff begins when rainfall exceeds the saturated conductivity of the soil surface, which suggests that RBS soils will need to drain more rapidly than adjacent crop lands in order to have the available pore space to infiltrate runoff from contributing crop lands. The dense perrenial grasses planted in RBS modify the soil due to the effects of a perennial root system on soil macropore development and soil structure (Carter *et al.*, 1994). While a well developed macropore network increases infiltration, macropore induced preferential flow facilitates chemical mobility and increases the potential for contamination of shallow ground water. RBS could be analogous to no-till systems in the sense that the soils have received little disturbance and leaching of

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pesticides could be rapid due to macropore transport (Isensee *et al.*, 1990). Lowrance *et al.* (1997) showed that infiltration of herbicides into an RBS corresponded to localized increases in herbicide concentrations in ground water at a site in the southeast USA.

The transport and fate of pesticides in RBS have not received much attention, despite the fact that RBS are located very close to both surface water and shallow ground water. Benoit *et al.* (1999) reported high levels of sorption and rapid degradation of isoproturon in soil from a perrenial ryegrass (*Lolium perenne*) buffer strip. Mersie *et al.* (1999a) used small boxes of soil and simulated runoff to assess the effect of switchgrass buffers, which increased herbicide retention over bare soil. In a companion study, switchgrass plants increased the leaching of atrazine, compared to unplanted soil (Mersie *et al.*, 1999b). In this study we compared the movement and fate of atrazine in soil from the switchgrass component of a RBS to that in nearby cropped soils. More specifically, we compared the steady-state, saturated flow transport of atrazine and bromide through intact soil columns from the RBS and cropped soils. This approach has been used in the past to measure hydraulic properties of soils and to make inferences about mechanisms of pesticide transport in soil. These experiments were complemented by laboratory studies on atrazine adsorption and degradation. Atrazine was chosen for study because of its common use as a herbicide and widespread detection in surface and ground water (Thurman *et al.*, 1992; Kolpin *et al.*, 1995; Ma and Selim, 1996; Baker and Richards, 2000).

MATERIALS AND METHODS

The study areas are switchgrass components of multi-species riparian buffer strip along Bear Creek, located approximately 2.4 km north of the town of Roland in Story County, Iowa (Simpkins and Schultz, 1993). The RBS is designed as grass-shrub-tree planting with the grass band adjacent to the crop land. The Bear Creek watershed is situated within the Des Moines lobe landscape, the depositional remnant of the late Wisconsin glaciation in Iowa (Schultz *et al.*, 1995). About 87 percent of the watershed is cropped to a corn-soybean rotation. The study sites are located on the Risdal and Strum farms, located in the southern half of the Bear Creek channel system. The three- and nine-year-old switchgrass buffer strips (ages in 1998) are located adjacent to each other and are next to a long-term alfalfa-grass pasture. The five-year-old switchgrass buffer strip (age in 1998) is adjacent to a corn-soybean rotation on the Strum farm. This site is located upstream from the Risdal farm and also is part of a multi-species RBS. Each grass-shrub-tree buffer is approximately 20 m wide. The soils adjacent to Bear Creek at these two sites are mapped as Clarion (fine loamy, mixed, mesic Typic Haploaquoll) and Coland soils (fine loamy, mixed, mesic Cumulic Haploaquoll) (DeWitt, 1984), but the switchgrass stands are planted on soils that transition between the Coland and Clarion series.

Atrazine and Bromide Transport Experiments

In May 1998, undisturbed soil columns were collected from the three- and five-year-old switchgrass buffer strips and from the adjacent cropped areas (three replications each). Corn was at the two- to three-leaf stage at the time of sampling. At each site, the individual columns were separated by 5 to 10 m within the RBS and by about 10 m from the columns in the cropped area. Undisturbed soil columns (three replications each) were collected in September 1998 from the nine-year-old switchgrass buffer strip and its adjacent cropped area.

Soil columns were obtained using a Giddings soil probe to gently push steel cylinders (20 cm in diameter and approximately 36 cm long) downward until the soil was within 10 cm from the top of the column. Plant shoots and residue were cleared from the soil surface prior to obtaining the soil columns. The soil columns in the steel cylinders were excavated by hand. The bottom of the soil column was visually inspected for signs of disturbance. Based on the length of soil entering the tube, we determined that compaction ranged from zero to five percent. All columns were kept in the greenhouse and watered as needed until they were used in the leaching experiment. To prevent preferential flow along the column sidewalls, silicone sealant was added around the edge of the column before starting the transport experiment.

Procedures for the transport experiments were similar to those used by Singh and Kanwar (1991). The soil columns were saturated from the bottom with 5 mM calcium sulfate ($CaSO_4$) solution for 24 to 36 hours. After saturation, the soil columns were placed in metal funnels filled with sand and a steady-state flow of 5 mM calcium sulfate solution was applied to the soil columns using a Mariotte bottle arrangement to maintain a constant head on the column surface. After steady-state flow conditions were reached, the 5 mM calcium sulfate was replaced with a 9.7-L of water containing 1.0 mg L^{-1} atrazine and 400 mg L^{-1} potassium bromide (KBr) also using the

Mariotte bottle arrangement. The 9.7-L volume of atrazine-bromide solution is equivalent to approximately 1 cm of runoff entering the RBS from a hypothetical adjacent corn crop, assuming a crop area to RBS area ratio of 30 to one. After infiltration of the atrazine and bromide solution, two pore volumes of 5 mM $CaSO_4$ solution were applied to leach out the atrazine and bromide retained in the soil columns. Leachate samples were captured in glass bottles and stored at 4°C. Atrazine in water was determined by HPLC by direct injection of filtered water samples with a minimum detectable concentration of 0.02 mg L^{-1} (Struthers *et al.,* 1998). Bromide concentration was determined using an automated flow analysis (Lachat Instruments, Milwaukee, Wisconsin) procedure with bromide detected at one to 60 mg L^{-1} (American Public Health Assoc., 1998).

At seven and 14 days after the initial leaching experiment, columns were leached again with 11 L of water (without atrazine) to simulate additional rainfall and runoff events. Each application of water simulated 4 cm of rainfall (1.3 L) combined with 1 cm of runoff (9.70 L) entering the RBS, for a total volume of 11 L. Iowa Rainfall Intensity-Duration-Frequency Curves predict that a storm delivering 4 cm of rainfall would occur every 2.1 years. All of the leachate from each event was collected as a single sample and analyzed by HPLC for the atrazine concentration. One week after the second leaching event, the columns were dried, weighed, and sectioned into 7.5-cm depth increments. Residual atrazine was extracted with methanol and analyzed by GC for the concentration of atrazine.

Atrazine and bromide breakthrough curves (BTCs) were constructed by plotting the relative pore volume (volume eluted/pore volume) against the relative atrazine or bromide concentration (C/C_0), with C_0 being the solute concentration entering the column and C is the measured concentration of atrazine or bromide in the leachate. Soil porosity for all columns were estimated by using measured bulk-density (derived from column length and weight) and particle density (2.65 g cm^{-3}). Bromide and BTCs were fit to a two-region, mobile-immobile solute transport equation (van Genuchten and Wierenga, 1976; van Genuchten and Wagenet, 1989) using a computer program, VisualBTC (M. Helmke, unpublished work). This program is computationally equivalent to CXTFIT and produces optimized estimates of the dispersion coefficient (D), mobile porosity (θ_m), a mass transfer parameter (α), and sorption coefficient (K_d) using nonlinear least-squares regression procedures. The parameter (α) is first-order rate coefficient for solute transfer between the mobile and immobile flow regions. We assumed that there was no sorption of bromide to the soil, therefore the partition coefficient (K_d) was set to zero for modeling of bromide BTC. The D and θ_m determined for individual columns from bromide BTC were used as constants during the modeling of atrazine BTC for the same corresponding columns. Atrazine degradation was assumed to be negligible and f (fraction of sorption sites available to atrazine; see van Genuchten and Wagenet, 1989) was assumed to be one.

Data were analyzed by means of analysis of variance (ANOVA) (SAS Institute, Inc. 1985) using different aged vegetation types (crop or RBS) as main treatments. Significant differences between means were determined by Fisher's protected least-significant-difference test.

Fate of Atrazine in RBS and Cropped Area Soils

Soil samples collected concurrently from the same three-, five-, and nine-year-old switchgrass RBS and adjacent cropped areas were used to determine soil properties and to assess atrazine sorption and degradation. The area within 5 m from where each soil column was collected was subsampled three times using a soil probe with a 3-cm diameter to depths of 0-15 cm and 15-30 cm. The three subsamples from each depth increment were composited in the field and stored at 4°C until use. Detailed procedures for measurement of soil properties are reported by Cambardella *et al.* (1994). Briefly, soil was passed through a 2-mm sieve and roots, stones, and residues were removed and moisture content was determined gravimetrically. Soil textures and water contents at -50 kPa water potential at each depth were analyzed by Midwest Laboratories, Inc. (Omaha, Nebraska). Organic carbon and total nitrogen were determined by using dry combustion methods using a Carlo-Erba NA 1500 NCS elemental analyzer. Soil pH was measured in 0.01 M $CaCl_2$ (2:1) soil slurry. Soil microbial biomass carbon was measured using the fumigation-extraction method with automated analysis of soluble carbon in the extracts.

Atrazine degradation in soil was measured by mixing 50 g of soil with an atrazine solution to provide a final concentration of 1000 µg kg^{-1} soil. Water potential was adjusted to -50 kPa and samples were incubated at 25°C in closed 0.95 L glass jars. Triplicate samples were extracted at 0, 7, 14, 28, 59, 71, 91, 112, and 133 days and analyzed for atrazine concentration by gas chromatography (GC) using procedures previously described by Moorman *et al.* (1999). Atrazine degradation over time was described by least-squares regression using the first order kinetic model; $C = C_i e^{-kt}$ or to a modified model $C = C_i e^{-kt} + Y_a$. In the regression, C is the mean of the measured atrazine concentrations (μg kg^{-1} soil); C_i is the initial atrazine concentration (μg kg^{-1} soil); k is the first-order degradation rate constant (day^{-1}); t is time (days); and Y_a is the residual concentration of atrazine (μg kg^{-1} soil) that is treated as an asymptotic limit in the regression. This concentration probably represents atrazine that is not bioavailable and degrades very slowly over time. The mean concentrations at sampling times (t) were weighted with inverse of the squared variance, which compensates for the nonconstant error structure and improves estimates of the model parameters.

Mineralization of uniformly ring-labeled [^{14}C]atrazine was investigated by using soil from the top 15 cm and the 15-30 cm depth of three-, five-, and nine-year-old switchgrass RBS and their adjacent cropped areas using previously described methods (Struthers *et al.*, 1998). Atrazine (99 percent purity) was purchased from Chem Service, West Chester, Pennsylvania. The [^{14}C-UL-ring]atrazine (98 percent purity) was purchased from Sigma Chemical Co., St. Louis, Missouri. The mineralization studies were conducted concurrently with the degradation experiment with an initial atrazine concentration of 1.0 mg kg^{-1} soil. At the end of the mineralization study (day 133), residual [^{14}C]atrazine and metabolites was extracted twice with a methanol/water (4:1, v/v) solution, concentrated by evaporation and measured by HPLC. Bound ^{14}C residues were determined by combustion, base trapping of $^{14}CO_2$, and liquid scintillation spectroscopy. The most-probable-number (MPN) technique was used with [^{14}C-UL-ring]-atrazine as a substrate to determine the populations of atrazine-degrading microorganisms in soil samples (Jayachandran *et al.*, 1998).

Adsorption of atrazine to surface and subsurface soil from switchgrass RBS and cropped area was determined by conducting batch equilibrium experiments using methods of Jayachandran *et al.* (1998). Equilibration solutions contained [^{14}C-UL-ring] atrazine at concentrations of 0.05, 1.0, 5.0, 10, and 20 μg mL^{-1} in 10 mM $CaCl_2$ with radioactivity at 41.1 Bq mL^{-1}. Adsorption isotherms were fit to the Freundlich model by non-linear least squares regression.

RESULTS AND DISCUSSION

The sandy loam soil textures were similar at all RBS and cropped sites, which suggests that the different aged switchgrass stands were established on similar soil (Table 1). Soil pH ranged from 5.2 to 6.7 with the lowest pH in the nine-year-old RBS soil and the adjacent alfalfa pasture soil. Organic carbon, as expected, decreases with depth, but there were no statistically significant trends in organic C with increased age of the switchgrass. However, the corn-soybean soil contains an average of 35.7 Mg C ha^{-1} to a depth of 30 cm compared to 70.9 Mg C ha^{-1} in the adjacent five-year-old switchgrass. There were no differences in organic C content or bulk density between the alfalfa-grass pasture and the three- and nine-

TABLE 1. Physical and Chemical Properties of Soils Collected From Switchgrass RBS and Adjacent Cropped Areas.

Vegetation	Sand (percent)	Silt (percent)	Clay (percent)	Organic C (percent)	Total N (percent)	pH	Bulk Density (g cm^{-3})	Microbial Biomass C (mg kg^{-1})
0 to 15 cm Depth								
Switchgrass, Three-Year	70	22	8	2.82 ± 0.66	0.25 ± 0.05	6.49	1.21	758 ± 359
Alfalfa Pasture	70	20	10	2.33 ± 0.69	0.20 ± 0.06	6.36	1.28	855 ± 28
Switchgrass, Five-Year	76	14	10	2.36 ± 1.10	0.21 ± 0.09	6.35	1.31	408 ± 174
Corn-Soybean	76	14	10	0.71 ± 0.24	0.07 ± 0.02	6.26	1.54	230 ± 7
Switchgrass, Nine-Year	66	22	12	2.19 ± 0.33	0.19 ± 0.02	5.24	1.21	343 ± 45
Alfalfa Pasture	64	24	12	2.46 ± 1.15	0.21 ± 0.10	5.29	1.24	486 ± 29
15 to 30 cm Depth								
Switchgrass, Three-Year	71	15	14	1.30 ± 0.16	0.11 ± 0.02	6.58	1.63	341 ± 63
Alfalfa Pasture	70	18	12	1.86 ± 0.59	0.17 ± 0.05	6.69	1.66	370 ± 48
Switchgrass, Five-Year	80	10	10	0.95 ± 0.42	0.09 ± 0.04	6.19	1.72	198 ± 152
Corn-Soybean	74	16	10	0.78 ± 0.23	0.07 ± 0.02	6.18	1.65	72 ± 3
Switchgrass, Nine-Year	62	24	14	1.24 ± 0.21	0.11 ± 0.02	5.29	1.28	322 ± 107
Alfalfa Pasture	66	20	14	2.04 ± 0.85	0.18 ± 0.08	5.31	1.27	206 ± 12

year-old switchgrass. Microbial biomass C follows total soil organic C and accounts for 1.6 to 3.7 percent of the total soil C in the 0 to 15 cm increment.

Transport of Bromide and Atrazine

The shape of BTC can provide information about water flow in soil and the behavior of solutes within the soil. Undisturbed soil columns from five- and nine-year-old RBS and adjacent cropped areas were used as experimental units for comparing atrazine transport in RBS and cropped area soil. Columns from the three-year-old switchgrass stands transmitted very little water, which prevented us from producing BTC. We resampled the three-year-old switchgrass stands, but these columns also behaved the same way. We have not determined the reasons for the very slow flow observed in these columns, but prior to establishment of the RBS, the land was a heavily used pasture and we believe that the results from the three-year-old switchgrass stand are likely due to some localized, pre-establishment condition. Representative bromide and atrazine for BTC are shown in Figure 1. Early breakthrough of bromide is evident in all columns with the relative concentration (C/C_0) of bromide in the leachate reaching 0.5 well before one pore volume. Atrazine transport is retarded relative to bromide due to adsorption to soil. In two of the three columns from the nine-year-old switchgrass ,atrazine breakthrough was very rapid with the relative concentration exceeding 0.5 prior to one pore volume of drainage. In the columns from the five-year-old switchgrass, atrazine breakthrough was less rapid, with atrazine C/C_0 reaching approximately 0.5 at one pore volume of drainage in two columns and atrazine C/C_0 reaching a maximum of only 0.25 in the third column. In the corn-soybean field adjacent to the five-year-old switchgrass RBS, the maximum C/C_0 of atrazine was reached only after two or more pore volumes of water had leached through the columns.

Preferential flow through macropores, fractures or other channels has been documented as a mechanism for the rapid leaching of atrazine and other pesticides (Zins *et al.*, 1991; Flury *et al.*, 1995). We have applied the two-region mobile-immobile solute transport model developed previously by van Genuchten and others to our study of atrazine and bromide leaching (van Genuchten and Wierenga, 1976; van Genuchten and Wagenet, 1989). Other researchers have applied the mobile-immobile transport model to solute transport with preferential flow (Seyfried and Rao, 1987; Singh and Kanwar, 1992; Li and Ghodrati, 1994). The coefficients of determination (r^2) ranged from 0.90 to 0.99 and indicated a good fit of the data to the model. BTC constructed using the standard, one-compartment form of the convective dispersion equation resulted in significantly lower r^2 values and visibly poorer fit to the experimental data (data not shown).

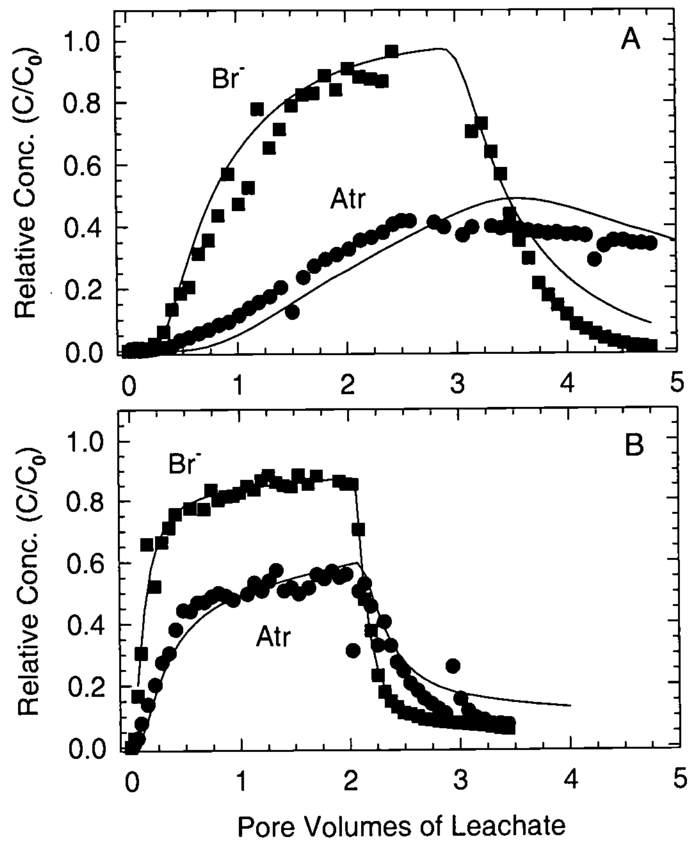

Figure 1. BTC for Atrazine (circles) and Bromide (squares) in Corn-Soybean Soil (A) or Five-Year-Old Switchgrass Riparian Buffer Soil (B). Solid lines indicate concentrations predicted by the mobile-immobile water transport model (see results for Replication 2 in Tables 2 and 3).

Mobile porosity is the fraction of total porosity that contributes to solute transport and immobile pore water fractions increase with increasing macropore flow (van Genuchten and Wierenga, 1976; Li and Ghodrati, 1994). Our analyses of bromide BTCs show that the immobile pore water fraction in the five-year-old RBS soil columns (Table 2) is significantly larger ($P < 0.05$) than that in corn-soybean soil columns, indicating greater macropore flow in five-year-old soil than corn-soybean soil. Mean values of D for the five-year-old RBS soil are larger than D of the corn-soybean soil (Table 2), but the values are not significantly different. Hydrodynamic dispersion (D) is a consequence of widely ranged pore-water velocities and can also indicate preferential flow through

TABLE 2. Parameters Describing Water Movement and Bromide BTC in Saturated Soil Columns Taken From Switchgrass and Other Vegetation.

Vegetation	Replication	Pore Water Velocity[a] (cm hr^{-1})	Solution Flux (cm hr^{-1})	D (x 10^{-6}) (m^2 s^{-1})	θ_{im}[b] (% θ_t)	α (x 10^{-5})[c] (s^{-1})	Initial Breakthrough (pore volume)
Switchgrass, Five-Year	1	13.8	5.90	8.63	47	0.18	0.03
	2	9.1	4.18	4.86	80	0.87	0.17
	3	1.5	0.58	0.59	72	96.0	0.03
	Mean	8.1 ± 6.2	3.56 ± 2.70	4.70 ± 4.02	66 ± 18*	32.40 ± 55.1	0.08 ± 0.08
Corn-Soybean	1	3.7	1.48	0.31	20	0.0084	0.03
	2	10.3	3.67	0.73	38	2.93	0.14
	3	8.2	3.53	1.51	28	0.11	0.25
	Mean	7.4 ± 3.3	2.92 ± 1.22	0.86 ± 0.61	29 ± 9	1.02 ± 1.66	0.14 ± 0.11
Switchgrass, Nine-Year	1	3.1	1.69	2.02	49	0.03	0.07
	2	11.7	6.44	58.0	43	3.73	0.17
	3	34.4	17.86	33.8	79	2.04	0.01
	Mean	16.4 ± 16.2	8.68 ± 8.32	31.05 ± 28.11	57 ± 19	1.93 ± 1.85	0.08 ± 0.08
Alfalfa Pasture	1	0.6	0.32	0.08	56	0.05	0.02
	2	6.7	3.35	2.95	73	1.06	0.04
	3	14.6	7.88	3.9.9	67	0.31	0.03
	Mean	7.3 ± 7.0	3.85 ± 3.82	14.0 ± 22.2	65 ± 9	0.48 ± 0.53	0.03 ± 0.01

[a]Average pore water velocity which is the solution flux/total porosity. Solution flux is the specific discharge of water per unit area per unit time.
[b]Immobile porosity. θ_t is total porosity. *Indicates significant difference from adjacent cropped soil ($P \leq 0.05$).
[c]First order rate coefficient for diffusion between mobile and immobile water.

macropores (Singh and Kanwar, 1992). The annual tillage in the corn-soybean system probably destroys some macropores. Both average solution flux and average pore water velocity of five-year-old RBS are slightly greater in comparison with corn-soybean soil columns, suggesting that the macropore network in the five-year-old RBS soil transmits more water in comparison with the cropped soil.

In general, nine-year-old RBS soil columns have the same degree of preferential flow as those from the adjacent grass-alfalfa pasture, as indicated by similar amounts of immobile pore water and the same magnitude of dispersion (Table 2). Zins *et al.* (1991) found that alfalfa roots caused some preferential flow of water and atrazine through soil columns. Meek *et al.* (1992) reported that alfalfa roots could increase the infiltration rate by reforming macropore channels that were destroyed by tillage. Therefore, the preferential flow in this alfalfa pasture soil probably resulted from alfalfa root channels acting as macropores.

The BTC for atrazine show the effects of retardation to varying extents (Figure 1). The maximum relative atrazine concentrations (C/C_0) are less than those for bromide and there is extreme tailing in some BTC, such as for the corn-soybean soil shown in Figure 1B. During the modeling of atrazine BTC we used the dispersion coefficients (D) and mobile water fraction (θ_m) values obtained from bromide BTC for the same columns. The dispersion coefficient (D) includes both hydraulic dispersion and molecular diffusion components, but the hydraulic dispersion component is usually far larger, thus the difference in diffusion coefficients between atrazine and bromide is negligible. The use of D and θ_m from the bromide BTC reduces the number of unconstrained parameters estimated by the model, and should provide better estimates of α and K_d for atrazine (Table 3). In addition we assumed that sorption occurs only in the immobile phase. Retardation factors (R) were estimated by the model with $R = 1 + K_d\rho/\theta$, where ρ is bulk density (kg m^{-3}), K_d is the sorption coefficient (m^3 kg^{-1}), and θ is volumetric water content (cm^3 cm^{-3}). The retardation factor is an important index of atrazine retention and R values show a trend towards lower values for the nine-year-old switchgrass and adjacent grass-alfalfa pasture compared to the five-year-old switchgrass and adjacent corn soybean soil. The parameter a is a first-order rate coefficient that governs movement of solute between the mobile and immobile transport regions. Values of α for atrazine BTC are generally similar for the different vegetation types. Larger values of α would tend to increase the

TABLE 3. Parameters Describing Atrazine BTC in Soil Columns From Switchgrass Buffers and Adjacent Crops.

Vegetation	Replication	$\alpha(x10^{-5})^a$ (s^{-1})	$K_d{}^b$ $(L\ kg^{-1})$	R^c	Initial Breakthrough (pore volume)
Switchgrass, Five-Year	1	3.81	0.36	2.24	0.10
	2	4.11	0.82	3.54	0.43
	3	1.87	2.32	10.62	0.03
	Mean	3.26 ± 1.22	1.16 ± 1.03	5.47 ± 4.51	0.19 ± 0.21
Corn-Soybean	1	2.43	1.79	8.07	0.03
	2	3.64	0.73	4.46	0.45
	3	1.91	0.59	3.05	0.45
	Mean	2.66 ± 0.89	1.04 ± 0.66	5.20± 2.59	0.31 ± 0.24
Switchgrass, Nine-Year	1	44.80	2.26	5.92	0.09
	2	2.40	0.43	2.03	0.24
	3	2.80	0.40	1.99	0.04
	Mean	16.70 ± 2.43	1.03 ± 1.06	3.31 ± 2.26	0.12 ± 0.10
Alfalfa Pasture	1	0.29	0.73	2.65	0.24
	2	0.72	0.33	1.89	0.04
	3	0.13	1.26	3.82	0.03
	Mean	0.34 ± 0.35	0.77 ± 0.45	2.79 ± 0.97	0.10 ± 0.12

[a]First order rate coefficient for exchange of atrazine between mobile and immobile water.
[b]Sorption coefficient (K_d) estimated from atrazine breakthrough curves and transformed from $m^3\ kg^{-1}$ to $L\ kg^{-1}$.
[c]Retardation factor defined as $R = 1 + K_d\rho/\theta$, where ρ is bulk density ($kg\ m^{-3}$), K_d is the sorption coefficient and θ is total porosity ($cm^3\ cm^{-3}$).

exchange of atrazine between mobile and immobile water, such as the water inside aggregates, which would tend to delay atrazine leaching by shifting the BTC towards the right.

There is evidence of preferential transport of atrazine in the RBS soils. For instance, two of the three soil columns (see Figure 1A) from the five-year RBS have atrazine C/C_0 values that reach approximately 0.5 after one pore volume of leaching, which is faster than would be expected from a solute that is adsorbed to the soil. In the third column (Replication 3) there is relatively little water flux (Table 2) and relatively little atrazine is transported. Similarly, atrazine is preferentially transported in two of the three columns from nine-year-old switchgrass RBS with C/C_0 reaching 0.8 at one pore volume (data not shown). Likewise, similar results were obtained in the pasture soil adjacent to the nine-year-old RBS.

There is substantial variability in the the parameters describing water flow and the BTC of bromide and atrazine (Tables 2 and 3), with pore water velocity, solution flux, and D varying by an order of magnitude within soil from a particular RBS or cropped soil, with the exception of the tilled soil cropped to the corn-soybean rotation. Variability of these parameters in the corn-soybean soil is still large, but generally less than for the other soils. The physical disruption caused by tillage may also act to reduce variability within the corn-soybean soil. The variability within the five-year and nine-year RBS suggests that infiltration of water and solutes of the the RBS in the field will occur discontinuously and that some areas will be far more effective in infiltration than other areas. Large variations in soil hydrologic properties have been reported previously (Wilson and Luxmoore, 1988; Logsdon and Jaynes, 1996).

Atrazine Retention in Soil

Atrazine distribution in soil after two simulated rainfall events is presented in Figure 2. The columns were leached with water to determine if atrazine retained in the soil columns could be released. This was done one week and two weeks after the transport experiment was completed by applying a total volume of 11-L of water (without atrazine). The five-year-old RBS soil retained greater average amount of atrazine in the upper part of the soil (0-7.5 cm soil depth) than in the 15-30 cm depths. On the other hand, soil from a corn-soybean field adjacent to 5-year-old RBS retained more atrazine in the 22.5 to 30 cm depth than in the 0 to 22.5 cm depth. The nine-year-old RBS soil also retained more atrazine in the soil surface (0-7.5 cm) than in the deeper part. Soil from the alfalfa pasture has a lower concentrations of atrazine compared to the nine-year-old RBS.

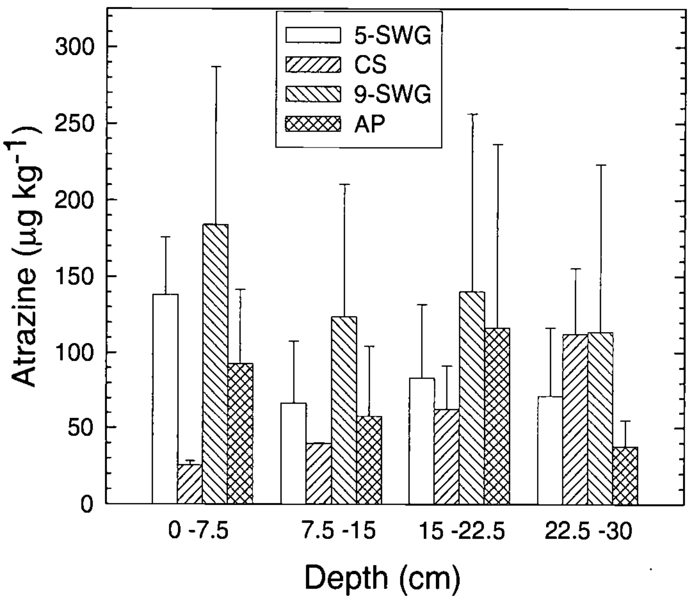

Figure 2. Atrazine Distribution in Soil Columns After Leaching Experiments. SWG indicates the five- or nine-year-old switchgrass soils, CS indicates the corn-soybean soil, and AP indicates the alfalfa pasture.

Less atrazine was found in the leachate from RBS soil columns than in leachate from cropped soil columns. Approximately 5 percent of applied atrazine is detected in the leachates from five- and nine-year-old RBS soil columns after two rainfall events (Table 4). About 10 percent of applied atrazine was detected in the leachate from the corn-soybean and grass-alfalfa soils. The retention and leaching of atrazine reflect the combined effects of adsorption and degradation over a short time period.

TABLE 4. Effect of Vegetation on Atrazine Retention in Soil Columns During a Transport Experiment and Subsequent Leaching of Atrazine in Response to Simulated Rainfall.

Vegetation	Retention[a] (percent)	Atrazine Leached[b] (percent)
Switchgrass, Five-Year	55 ± 20	5 ± 3
Corn-Soybean	66± 18	9 ± 4
Switchgrass, Nine-Year	36 ± 27	5 ± 3
Alfalfa Pasture	39 ± 17	11 ± 6

[a]Percent of atrazine applied in saturated flow leaching experiment.
[b]Atrazine leached in two pulses seven and 14 days after the saturated flow leaching experiment expressed as percent of atrazine applied.

Adsorption of Atrazine

Atrazine sorption in soils is generally controlled by organic C contents, clay type and quantity and soil pH (Koskinen and Clay, 1997). The similar origins, pH and textures of the soils used in these experiments suggest that differences in pH, clay type or clay content are not contributing to differences in atrazine adsorption. The conversion of cultivated crop land to a RBS should increase soil C content. The effect of the RBS on soil C is most visible in the contrast between the five-year-old switchgrass and the adjacent corn and soybean field, where the RBS has a three-fold greater C content than the cropped soil (Table 1). This effect is mitigated by the similar C contents in these two soils at the 15 to 30 cm depth. The Freundlich isotherm described atrazine sorption over a range of concentrations with regression r^2 values of 0.95 or greater for all isotherms (Figure 3). All isotherms show some evidence of nonlinearity, but 1/n values are fairly similar for all soils. The five-year switchgrass RBS has a significantly greater adsorption K_f than the cropped surface soil (Table 5), which is consistent with the relative organic C contents of these two soils. Atrazine sorption K_f values for the three-year and nine-year switchgrass soils are also greater than their adjacent soils, which are both part of the alfalfa-grass pasture. The absence of tillage in the pasture soil has probably lessened the effect of conversion to an RBS, because organic C contents are not statistically different between the pasture and the RBS. Thus, the increase in atrazine sorption by the switchgrass RBS soils may reflect the qualitative nature of organic C deposited in the surface soil by the switchgrass. Future increases in C content of the RBS soil will increase atrazine sorption, which will further increase the retention of atrazine. The decrease in K_f values with depth is due to the lower organic carbon contents of the deeper soil. This is in accord with previous reports (Seybold *et al.*, 1994; Jenks *et al.*, 1998).

The K_d values obtained from the atrazine BTC modeling (Table 3) are lower than the K_f values from the batch experiment (Table 5). These results are consistent with other investigations where the K_d from column experiments was lower than sorption coefficients from batch experiments (Gonzalez and Ukrainczyk, 1999). The lower K_d values from column experiments likely result from incomplete equilibration during transport compared to batch experiments. The mean K_d obtained from the column experiments show fewer differences between the different soils than the batch equilibration measurements. The large column to column variation makes the trends due to RBS establishment less clear.

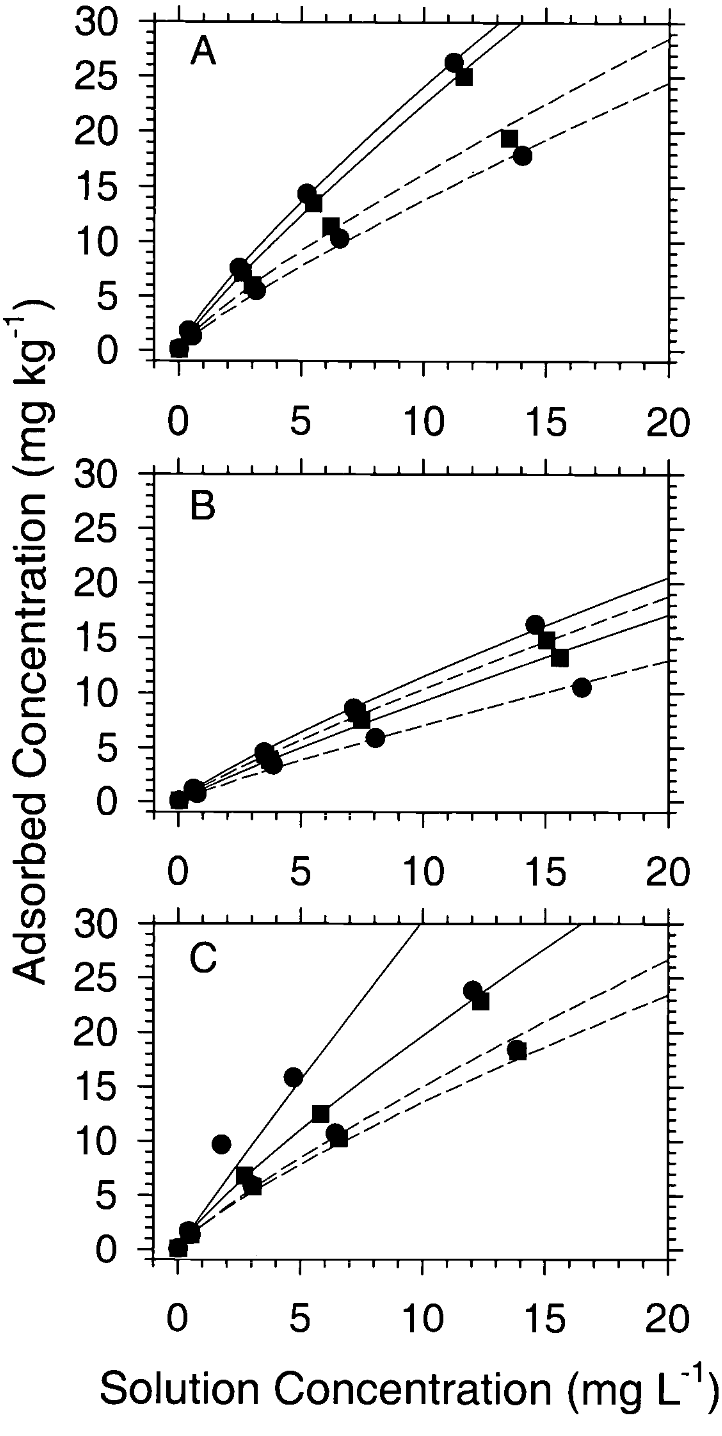

Figure 3. Adsorption Isotherms for Atrazine in Soil From the the 0 to 15 cm (solid lines) and 15 to 30 cm (dashed lines) Depths. (A) Three-year-old switchgrass (circles) and pasture (squares); (B) five-year-old switchgrass (circles) and corn-soybean rotation (squares); C) nine-year-old switchgrass (circles) and pasture (squares). Symbols represent means of measurements and solid lines are the isotherms fit by least-squares regression.

TABLE 5. Freundlich Isotherm Parameters (K_f and 1/n) for Atrazine Adsorption to Soil From Switchgrass RBS and Adjacent Cropped Lands.

Vegetation	0 to 15 cm K_f[a] (L kg^{-1})	0 to 15 cm 1/n	15 to 30 cm K_f* (L kg^{-1})	15 to 30 cm 1/n
Switchgrass, Three-Year	3.64*	0.82	2.05	0.83
Alfalfa Pasture	3.10	0.86	2.45	0.82
Switchgrass, Five-Year	1.66*	0.84	0.93	0.88
Corn/Soybean	1.19	0.89	1.43	0.86
Switchgrass, Nine-Year	3.32*	0.96	2.22	0.83
Alfalfa pasture	2.85	0.84	2.20	0.79

[a]Mean of three replications. *Significant difference between switchgrass RBS soil and adjacent cropped soil ($P \leq 0.05$).

Atrazine Degradation

We conducted two laboratory identical experiments to assess atrazine degradation and fate. Dissipation of atrazine measured by extraction and GC was accompanied by a parallel experiment using [^{14}C]atrazine. First-order kinetics described atrazine degradation in all soils but two, where the extra term (Y_a) was used. The r^2 for nonlinear regressions used to estimate degradation rate constants (k) and half-lives were greater than 0.90, except for the three-year-old switchgrass (15 to 30 cm) data, where the r^2 was 0.77.

Atrazine was degraded more quickly in the soil from the corn-soybean rotation than the soil from the adjacent five-year-old switchgrass RBS, or the nine-year-old RBS, or the alfalfa pasture (Table 6). Sixty percent of the applied [^{14}C]atrazine was also mineralized to $^{14}CO_2$ in surface soil of the corn-soybean rotation, compared to only 12 percent mineralized in the adjacent five-year-old switchgrass soil and less than 4 percent in the other soils. Similar trends were observed in the soil from the 15 to 30 cm depth. The shorter half-life of atrazine in the corn-soybean soil was accompanied by less extractable ^{14}C (atrazine and metabolites) and less bound ^{14}C-residues. Recovery of ^{14}C from individual soil samples ranged from 58 to 79 percent, with an average recovery of 77 percent, which would suggest that concentrations of atrazine and metabolites in this experiment are slightly underestimated.

The greater atrazine degradation and mineralization rates in the corn-soybean soil are due to a larger population of atrazine-degrading microorganisms in that soil (Table 6). The total atrazine mineralized was correlated with the population of atrazine degraders (r^2 = 0.72). Several studies show that frequent exposure to atrazine increases the rate of degradation

TABLE 6. Degradation Half-Life and Distribution of [^{14}C] Atrazine in Soils From Switchgrass or Crops After 133 Days Incubation Under Constant Temperature and Moisture Conditions.

Vegetation	Half-Life (d)[a] k ± s.e. (d^{-1})	Ya[b] (μg kg^{-1})	$^{14}CO_2$[c]	Extractable ^{14}C (% of applied)	Bound ^{14}C (% of applied)	Atrazine-Degraders[d] (cells/g soil)
			0 to 15 cm Depth			
Switchgrass, Three-Year	52 0.0134 ± 0.0012	NE	1	46	32	6649 ± 4958
Alfalfa Pasture	28 0.0252 ± 0.0049	95	4	40	35	2926 ± 2716
Switchgrass, Five-Year	28* 0.0244 ± 0.0022	NE	12*	31	28	2972 ± 3198*
Corn/Soybean	19 0.0373 ± 0.0045	NE	60	3	8	50940 ± 35836
Switchgrass, Nine-Year	39 0.0176 ± 0.0008	NE	2	34	36	310 ± 161
Alfalfa Pasture	27 0.0254 ± 0.0052	117	3	30	36	1125 ± 1654
			15 to 30 cm Depth			
Switchgrass, Three-Year	121 0.0057 ± 0.0013	NE	2	59	17	546 ± 678
Alfalfa Pasture	85 0.0081 ± 0.0010	NE	2	50	22	102 ± 35
Switchgrass, Five-Year	26 0.0269 ± 0.0015	NE	10*	39	25	771 ± 812*
Corn-Soybean	14 0.0490 ± 0.0058	NE	49	6	10	11331 ± 1642
Switchgrass, Nine-Year	47 0.0148 ± 0.0019	NE	3	35	30	1141 ± 1330
Alfalfa Pasture	61 0.0114 ± 0.0005	NE	2	29	27	370 ± 389

[a]k is the mean degradation rate coefficient and standard error of the estimate. *Significantly different ($P \leq 0.05$) from adjacent cropped soil.
[b]Y_a is an estimate of residual atrazine using a modified first-order kinetic model. NE indicates Y_a was not estimated.
[c]Cumulative $^{14}CO_2$ evolved during 133 days as a percent of applied ^{14}C.
[d]Residual ^{14}C remaining in soil after solvent extraction after 133 days.

(Ostrofsky *et al.*, 1997; Jayachandran *et al.*, 1998; Barriuso and Houot, 1996). We suggest that the more frequent exposure of the microorganisms in the corn-soybean soil to atrazine sustains the larger population of atrazine degraders, while the infrequent exposure to atrazine in the switchgrass soil results in a decline in atrazine-degrader populations. This is support by the distribution of total microbial biomass which is greater in the switchgrass RBS than in the corn-soybean soil (Table 1). Our results are perhaps different from those of Mersie *et al.* (1999a), who reported faster atrazine degradation in soil planted to switchgrass compared to unvegetated soil, although the differences in experimental methods make direct comparison of these studies difficult.

CONCLUSIONS

Riparian Buffer Strips (RBS) receive atrazine in runoff water from adjacent agricultural areas. RBS remove atrazine from the runoff through infiltration and sorption. Perrenial grass establishment may change the ability of the soil to inflitrate water and atrazine and to retain atrazine that does infiltrate. Two-thirds of the five- and nine-year-old RBS soil columns showed evidence of preferential flow of atrazine and bromide. These qualitative observations are support by BTC modeling which shows that the five-year-old switchgrass soil has significantly greater fraction of immobile porosity than the adjacent corn and soybean soil, even though the five-year-old switchgrass soil has a slightly greater solution flux than the corn-soybean soil. There was little difference between the switchgrass RBS and the grass-alfalfa pasture, which would be consistent with the absence of tillage in both managements. Preferential flow channels are likely to increase the capacity of RBS to infiltrate runoff water, thus increasing the efficiency of the RBS in removal of atrazine. In contrast to these results are the results obtained with the three-year-old switchgrass soil, which transmitted very little water. The fact that one-third of the soil columns from the switchgrass RBS did not show preferential transport and transmitted water slowly suggests that infiltration of water will be patchy.

Degradation of atrazine is slower under switchgrass RBS compared to the adjacent cropped soil, which with preferential flow would increase the potential leaching of atrazine to ground water. This is apparently offset by the greater capacity of the switchgrass soils to adsorb atrazine. Despite the trend towards increased preferential flow in in the five- and nine-year-old RBS soils relative to the corn-soybean soil, there is little evidence to suggest that atrazine leaching in RBS soils represents a greater hazard than leaching in cropped soils. The similar masses of residual atrazine retained after the leaching experiments and the lower amounts of atrazine released in leachate support this conclusion.

Our experiments provide information on changes in soil induced by the establishment of switchgrass riparian buffers. We show evidence of changes in soil hydrology, herbicide adsorption and degradation. Our results show that the net result of these changes is fairly modest, but the switchgrass buffers used were all under ten years of age. This suggests that buffer establishment will result in only modest improvements in pesticide retention over the short-term. Changes in the soil system may continue to develop over time, with corresponding increases in pesticide retention. The high degree of variability within the five- and nine-year-old switchgrass RBS and the non-transmissive three-year-old RBS indicate that there are likely to be areas where buffer retention of pesticides is likely to be limited.

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