

HERBICIDE TRANSPORT IN A RESTORED RIPARIAN FOREST BUFFER SYSTEM

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ABSTRACT. Little is known about the effects of restored riparian forest buffers on transport of herbicides. The effect of a restored riparian forest buffer system (RFBS) on transport of two herbicides, atrazine and alachlor, was studied during 1993–1994. Herbicides were applied above a restored 3-zone riparian buffer system in April of 1993 and 1994. Bromide was applied as a tracer with the April 1993 herbicide application. The buffer system was managed based on USDA recommendations and averaged 38 m in width. The system included a grass buffer strip immediately adjacent to the application area (zone 3), an area of planted pines downslope from the grass buffer (zone 2), and a narrow area of planted hardwoods containing the stream channel system (zone 1). Most of the herbicide transport in surface runoff occurred before June 30 with about 250 mm of cumulative rainfall after herbicide application. During this period of higher herbicide transport, atrazine and alachlor concentrations averaging $12.7 \mu\text{g L}^{-1}$ and $1.3 \mu\text{g L}^{-1}$, respectively, at the field edge were reduced to $0.66 \mu\text{g L}^{-1}$ and $0.06 \mu\text{g L}^{-1}$, respectively, as runoff neared the stream. The effect of dilution versus other concentration reduction factors (infiltration, adsorption) was estimated for surface runoff using the bromide concentration data. Concentration reduction was greatest per meter of flow length in the grass buffer adjacent to the field. There was only minor transport of herbicides through the buffer system in shallow groundwater. Average herbicide concentrations were at or below detection limits in groundwater near the stream for the entire study period. The restored riparian forest buffer had similar effects on herbicide transport as a mature buffer.

Keywords. Riparian, Buffer, Forest, Herbicide, Transport, Atrazine, Alachlor, Groundwater, Runoff.

Although the literature on riparian forest buffers establishes their effectiveness as nutrient and sediment filters under a range of environmental and hydrologic conditions, very little is known about their effectiveness for control of pesticide transport. Paterson and Schnoor (1992) found that atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and alachlor [2-chloro-2,6-diethyl-N-(methoxymethyl)-acetanilide] degraded more rapidly in a riparian zone soil under hybrid poplars (*Populus sp.*) than in soils where herbicides were applied to row crops. Paterson and Schnoor did not address the transport of herbicides into and through the riparian ecosystems but examined the fate of the herbicides when applied directly in streamside areas. Wu et al. (1983) and Correll et al. (1978) examined transport of atrazine and alachlor in surface runoff from row crop fields to estuarine waters in the Rhode River Watershed of the Chesapeake Bay. Streams in the watershed were bordered by naturally

occurring riparian forest ecosystems. They found that most herbicide transport was in the aqueous phase of surface runoff and that most transport occurred in a few runoff events after application. Linear regression of herbicide loading rates with percentage of land in agriculture for the watersheds did not give a direct relationship. They hypothesized that this might be due to the effects of riparian forests on surface runoff.

Herbicide removal in grass buffer strips has received more study. Asmussen et al. (1977) found that about 70% of 2,4-D in runoff was retained in a 24.4 m grass waterway. Rohde et al. (1980) found that 86% to 96% of trifluralin could be retained in vegetated buffer strips. Hall et al. (1983) found that edge-of-field losses could be reduced by over 90% by an oat strip used as a field edge buffer. Recently, Arora et al. (1996) reported that retention of atrazine in a bromegrass strip (*Bromus inermis* Leysser) ranged from 11% to 100% in natural rainfall runoff events. The variability in the retention was due to variability among events in amount of infiltration. Infiltration was the key process for retention by the grass buffer for atrazine and the other two herbicides studied (metolachlor and cyanazine). In a related study, Misra et al. (1996) found higher percent retention of herbicides at higher inflow concentrations. At a nominal concentration of $100 \mu\text{g L}^{-1}$, 29% of the inflow atrazine was retained. At a concentration of $1000 \mu\text{g L}^{-1}$, 49% of atrazine was retained. Lowrance et al. (1997) found that a mature riparian forest buffer was effective in limiting atrazine and alachlor movement to streams in the southeastern coastal plain. This article reports on a companion study in which we examined atrazine, alachlor, and bromide (as a tracer) movement through a restored, rather than mature, riparian forest buffer.

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The purpose of this study was to determine the effects of a restored riparian buffer system on surface and subsurface transport of two common use herbicides: atrazine and alachlor. The study was designed to: (1) compare herbicide transport in grass and forest zones of a riparian buffer system, (2) examine interactions of surface runoff and shallow groundwater in herbicide transport, (3) determine the importance of dilution of surface-borne chemicals versus other processes (primarily infiltration and adsorption) in the riparian zone, and (4) compare performance of a restored riparian buffer system to a nearby mature riparian buffer system previously reported (Lowrance et al., 1997).

MATERIALS AND METHODS

STUDY SITE

The study was done at the Dairy Wetland research site on the Animal Science Research Farm that is part of the University of Georgia Coastal Plain Experiment Station near Tifton, Georgia. The site is located in the Tifton-Vidalia Upland portion of the Gulf-Atlantic Coastal Plain in the headwaters of the Suwannee River basin (fig. 1). The climate of the Tifton-Vidalia Upland is humid subtropical, providing abundant rainfall and a long growing season. Average monthly temperatures range from 11°C in January to 27°C in July and August with a 47-year mean annual temperature of 19.2°C (Batten, 1980). The average frost-free season is 253 days. Precipitation follows a definite seasonal pattern with generally low rainfall from September through November and an increase in precipitation in December through early May. Rainfall typically decreases again in May and early June. Summer thunderstorms and tropical depressions cause July and August to be wetter months on average.

Because of both a plinthic soil horizon and the presence of a geologic formation (Hawthorn Formation) which limits deep recharge to the regional aquifer system, most of the

excess precipitation in the Tifton-Vidalia Upland moves either laterally in shallow saturated and unsaturated flow or moves in surface runoff during storm events. The general hydrology of the Tifton-Vidalia Upland is reflected at the Animal Science Farm and makes this region and the particular site ideal for the study of surface runoff and shallow subsurface transport of agricultural pollutants into riparian ecosystems.

A 3-zone riparian buffer system, as prescribed by USDA Forest Service specifications (Welsch, 1991), was established at this site in 1991. The Dairy Wetland is approximately 1 ha in size and is located on an intermittent first-order stream in which both zones 1 and 2 of the riparian forest were logged in 1985 and replaced with a wet pasture. A farm pond was then constructed downslope from the wetland. The riparian forest was re-established in February 1991 by planting hardwoods in zone 1 and slash pine in zone 2. On the east side of the Dairy Wetland, zone 3 is an 8 m wide strip of common Bermudagrass (*Cynodon dactylon* L. Pers.) and Bahia grass (*Paspalum notatum* Flugge). Zone 2 is a 20 m wide band of slash pine (*Pinus elliottii* Engelm.). Zone 1 is a 10 m wide band of trees with mostly hardwoods including swamp black gum (*Nyssasylvatica* var. *biflora* Marsh.), green ash (*Fraxinus pennsylvanica* L.), and yellow poplar (*Liriodendron tulipifera* L.). The entire 3-zone buffer averages 38 m in width (fig. 2).

The soil at the Dairy Wetland is an Alapaha loamy sand (fine-loamy, siliceous, acid, thermic Typic Fluvaquents). The soil of the adjacent upland area is a Tifton loamy sand (fine-loamy, siliceous, thermic, Plinthic Kandudult) (Calhoun, 1983).

Herbicide was applied on a 10 m × 100 m (0.1 ha) strip upslope of zone 3 (fig. 2). The application strip upslope of zone 3 was harrowed in December 1992 and was to be harrowed again before herbicide application. Unusually wet conditions during the early months of 1993, in addition to increasingly wet conditions at the Dairy Wetland, made any type of tillage operation impossible even as late as mid-April. Because it appeared that soil conditions in the application strip would not improve appreciably before mid-May, the decision was made to apply the herbicide directly onto the grass. In preparation, the application strip was closely mowed and thoroughly raked.

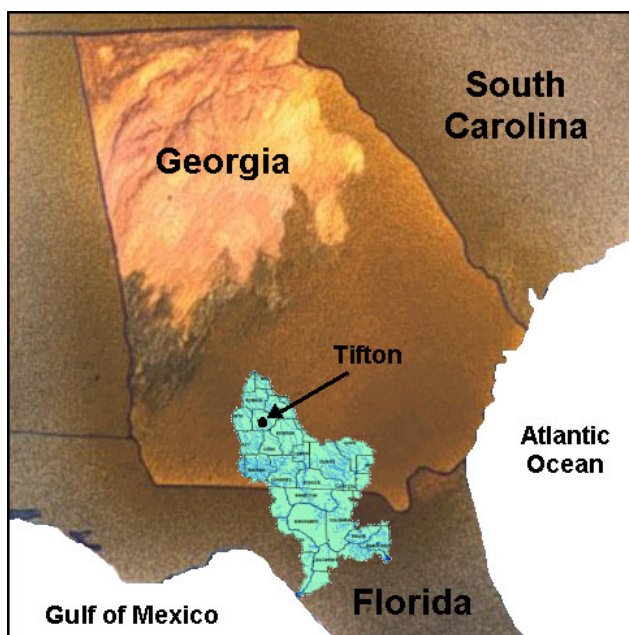


Figure 1. The location of the Dairy Wetland research site near Tifton. The site is located within the Suwannee River Basin of the southeastern coastal plain of the United States.

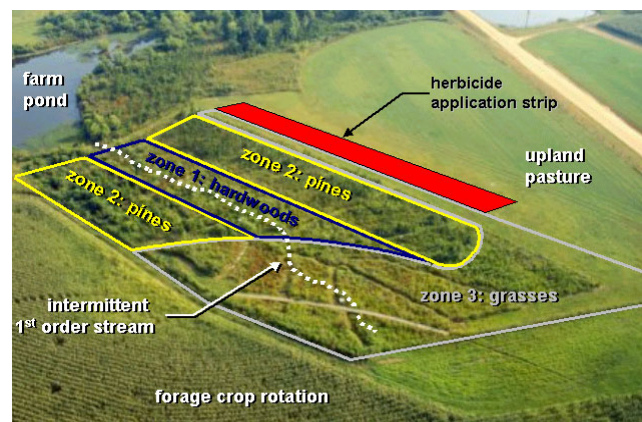


Figure 2. Aerial photo of the Dairy Wetland research site showing how the 3-zone riparian buffer system was implemented during restoration of the wetland area.

Herbicides were applied on April 14, 1993, and April 21, 1994, at application rates of 17.10 kg ha⁻¹ active ingredient atrazine and 20.5 kg ha⁻¹ active ingredient alachlor. The herbicides were applied with a dilute tank mix to ensure that the herbicide came into contact with the soil despite the vegetative material. Following herbicide application in 1993, potassium bromide (KBr), a conservative tracer, was applied at a rate of 150 kg ha⁻¹. KBr was not applied in 1994.

INSTRUMENTATION

The Dairy Wetland research site was originally developed to examine the fate and transport of nutrients moving downslope in surface runoff or shallow groundwater flow from an upland forage production field receiving liquid dairy manure (Vellidis et al., 1994) applied from a center-pivot irrigation system. Instrumentation for the herbicide study was installed beginning in January 1993.

Monitoring Well Network

A network of 75 monitoring wells was established on the east slope of the Dairy Wetland. The network consisted of 36 shallow and 39 deep wells. Shallow wells were screened from 0.1 to 0.6 m below the soil surface, while deep wells were screened from 0.6 to 2.0 m below the soil surface. Wells were assembled from threaded PVC pipe and screened with 0.25 mm well screen. The wells were installed using the same methods as at the companion study site (Lowrance et al., 1997). Six well transects were installed with each transect containing 12 wells — a shallow and deep well pair at each of 6 positions. The transect positions, in meters from the edge of the application strip, were: 0 m (the upslope edge of the zone 3 grass buffer), 8 m (the upslope edge of the zone 2 managed forest buffer — pines), 13 m, 18 m, 28 m (upslope edge of the zone 1 forest buffer — hardwoods), and 38 m (near the stream channel) (fig. 3). Three wells were installed along a road adjacent to the research site to monitor for any chemical movement from adjacent fields.

The 75 wells were installed in two phases. In 1993, pairs of shallow and deep wells were installed at the 0, 8, 13, and 18 m positions. Only deep wells were installed at the 28 and 38 m positions. Twelve additional shallow wells were installed at the 28 and 38 m positions between February and March 1994.

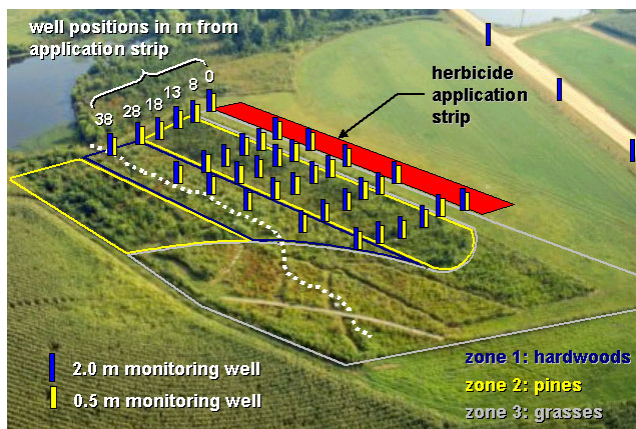


Figure 3. Aerial photo of the Dairy Wetland research site showing the location of the 75 wells and the boundaries of the 3 zones.

Well water samples were taken bi-weekly. Before each well sampling, the depth of water below the ground surface was measured manually, and at least one well volume was removed and discarded. Well samples were collected into chemically clean (liquinox wash, tapwater rinse, acid wash with 10% HCl, distilled deionized water rinse, acetone rinse) glass bottles with Teflon-lined caps, stored in coolers in the field, and transported to a refrigerator (4°C) at the lab within 2 h of collection.

Surface Runoff Collector Network

Three transects of four 0.3 m wide Low-Impact Flow Event (LIFE) samplers (Sheridan et al., 1996) were installed to sample surface runoff. In each transect, the collectors were installed at the upslope edge of zones 1, 2, and 3 and at the mid-point of zone 2 (fig. 4). Two transects had instruments that retained 10% of the collected sample. The third transect had instruments that retained 1% of the collected sample. This design ensures that a measurable volume can be collected over a wide range of runoff events. The 10% collection is made by splitting the flow into 10 pathways at the back of the collector and collecting flow from one pathway. The 1% sample is collected by connecting two 10% samples in series. The sample receptacle is large enough to contain runoff from approximately a 10-year return interval event in the 1% samplers. The receptacle is made from a 1 m long piece of 0.1 m diameter PVC pipe with capped openings at each end. PVC joints were welded using heated PVC to avoid possible interferences of solvents in PVC cement with the herbicide analysis. The samplers were positioned so as not to interfere with surface runoff collection at the next zonal interface. The three samplers at the upslope end of zone 3 are designated position 1, and the upslope end of zone 2 is position 2. The middle of zone 2 is position 3, and the upslope end of zone 1 is position 4 (fig. 4). Having two types of samplers (10% and 1%) allows both large and small runoff events to be sampled and runoff volumes obtained. Samples from all collectors that had volumes greater than 100 ml were used for each surface runoff event.

Surface runoff sample volumes were measured and subsamples collected for herbicide analysis on the workday following each runoff event. Multiple events in a day were not collected separately. Samples were collected by pumping

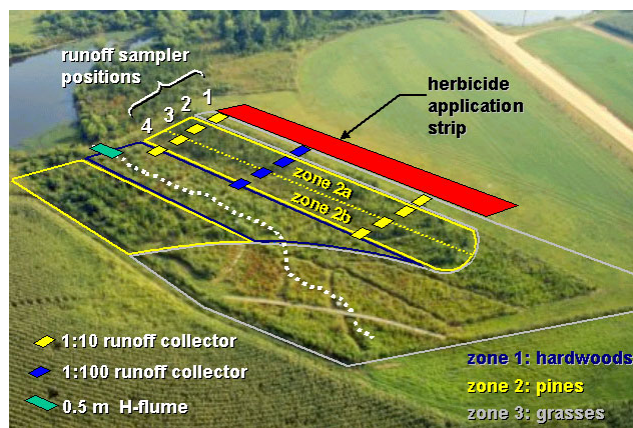


Figure 4. Aerial photo of the Dairy Wetland research site showing the location of the 9 surface runoff collectors and the boundaries of the 3 zones. Zone 2 was subdivided into zones 2a and 2b for surface runoff data analysis purposes.

the receptacles with a peristaltic pump while agitating the sample by mixing with the inlet line of the pump. Samples were collected into chemically clean glass bottles fitted with Teflon-lined caps. Surface runoff samples were stored in coolers in the field and transported to lab refrigerators (4°C) within 2 h of collection.

SAMPLE HANDLING, PREPARATION, AND ANALYSIS

All groundwater and surface runoff samples were screened for herbicide content using the magnetic-particle based enzyme-linked immunosorbent assay (ELISA) techniques developed by Ohmicron Corp. (Newtown, Pa.). Manufacturer-determined detection limits for atrazine and alachlor using this method are 0.05 $\mu\text{g L}^{-1}$, although the effective detection limit for alachlor may be higher (approximately 0.09 $\mu\text{g L}^{-1}$; Marti, 1992). Groundwater samples testing positive for either atrazine or alachlor and that were above the gas chromatography (GC) lower detection limits (0.16 $\mu\text{g L}^{-1}$ for atrazine and 0.10 $\mu\text{g L}^{-1}$ for alachlor) were confirmed by GC analysis.

Surface runoff samples, including sediment and water, were prepared for GC analysis by liquid/liquid extraction. This allowed recovery of sediment-associated atrazine and alachlor. A known mass of bulk water sample (approximately 500 mL) was extracted with 100 mL of dichloromethane using a separatory funnel. Funnels were shaken vigorously for 1 min. and then allowed to settle for 10 min. The bottom dichloromethane layer was drained through a glass-fiber filter and the extraction procedure was repeated. The total volume of dichloromethane (approximately 200 mL) was poured into a 500 mL round-bottom flask and evaporated to dryness using a rotary evaporator. Following evaporation, 5 mL of HPLC-grade methanol was added to each cooled flask and swirled thoroughly around the sides to dissolve the atrazine and alachlor. The methanol was filtered through a syringe filter (0.45 μm) and stored in cleaned glass vials. Extracted samples were stored at -10°C until analysis.

All well samples testing above GC detection limits and a random sampling of those below detection limits were prepared for GC analysis using conditioned cyclohexyl solid phase extraction columns (J.T. Baker, Phillipsburg, N.J.). A measured volume of the well sample (generally 200 mL, less if field sample volume was <200 mL) was drawn through the extraction column under vacuum. The extraction column was allowed to dry under vacuum followed by elution with 2.00 mL of HPLC-grade methanol. Extracted samples were stored at -10°C until analysis.

Freshly prepared laboratory standards were extracted by the appropriate technique and run periodically with groundwater and surface runoff samples. For well samples, these standards were prepared at 0, 0.5, 1, and 10 $\mu\text{g L}^{-1}$ of both atrazine and alachlor. For runoff samples, the standards were prepared at 0, 0.41, 1.65, and 13.20 $\mu\text{g L}^{-1}$ for atrazine and 0, 1.14, 4.56, and 36.54 $\mu\text{g L}^{-1}$ for alachlor. Standard additions were also prepared by adding herbicide standards to groundwater samples that had tested below detection limits by ELISA techniques. The standard additions were prepared to a concentration of 10 $\mu\text{g L}^{-1}$ for both atrazine and alachlor. Extracted standards and standard additions were used to check recovery and analysis and were generally within 10% of expected values. These values were not used to correct analytical results of samples. Samples that were above the high standard were diluted and reanalyzed.

Gas chromatograph analysis of extracted samples was done using a Varian model 3400 GC with a model 8100 autosampler, model 1075 split/splitless injector, and a thermionic specific detector (Varian Instruments, Sugarland, Texas). The column used was a J&W Scientific DB5 (Folsom, Cal.), 30 m length \times 0.25 mm ID with a 0.25 μm film thickness. The column was operated at 80°C for 1 minute, ramped up 15°C/min to 225°C and held for 4 minutes, and ramped up 25°C/min to 275°C and held for 4 minutes. The injector was operated at 225°C and the detector at 325°C.

Although the herbicide analysis was not confirmed by other means, there were high correlations between the ELISA and GC data for atrazine. The correlation coefficient (r) for the GC values versus the ELISA values was 0.97 with a significance level of 0.01. Although the Ohmicron ELISA method is cross-reactive with other triazine herbicides, there had been no other triazine herbicides applied in the three years prior to the start of this study (personal communication, University of Georgia Field Research Service). For alachlor, ELISA and GC methods were poorly correlated. The GC method does not detect a major soil metabolite of alachlor (ethanesulfonic acid), which is detected by the ELISA method offered by Ohmicron Corp. (written communication, Dr. J. X. Dautlick, Ohmicron Corp., 6 April 1993; Macomber et al., 1992). Consequently, sample-by-sample comparison between Ohmicron's alachlor assay and GC results showed that some samples were positive by immunoassay but were not confirmed by GC. Correlations between GC and ELISA for alachlor were not significant; therefore, all data analyses for alachlor are based on GC analysis only. Data analyses for atrazine are based on GC data where available, with ELISA data substituted for a small number of samples (<100 total) where GC data were missing.

DATA ANALYSIS

Herbicide concentration data were tested for normal distribution using the univariate procedure in the Statistical Analysis System (SAS, 1989). The concentration data were not normally distributed; therefore, typical analysis of variance was not used. Instead, the NPAR1WAY procedure of SAS with the Kruskal-Wallis test was used. NPAR1WAY is a nonparametric procedure that tests whether the distribution of a variable has the same location parameter across different groups. The Kruskal-Wallis procedure tests the null hypothesis that the groups are not different from each other by testing whether the rank sums are significantly different based on a chi-square distribution (Sokal and Rohlf, 1981). The nonparametric tests were done on data grouped by position (distance from field) and zone for both surface runoff and well samples. The means shown were not subjected to a parametric analysis of variance test; therefore, means separation tests were not used.

Surface Runoff

Surface runoff data were also grouped based on time after herbicide application. Because the primary objective of this study was to examine the effects of riparian buffer systems on herbicide transport from field edge to stream, the times of year when higher loadings or concentrations of herbicides were leaving the field edge were of particular importance. Surface runoff data were analyzed for significant differences in two sub-groupings of the entire data set: the after-applica-

tion time periods when significant edge-of-field transport occurred after herbicide application, and the between-application time periods when very little edge-of-field transport occurred. The after-application time period was defined based on either 250 mm of cumulative rainfall or through June 30, whichever came first (fig 5).

The surface runoff data were used to calculate loads for herbicides entering at the upslope edge of zones 3, 2, and 1 (figs. 2 and 4). Loads ($\mu\text{g m}^{-1}$ of interface) were calculated as the mass of herbicide moving into the sampler if the sampler width was 1 m. Loadings were also calculated for the mid-point of zone 2. During wet times of the year, when the stream channel system was expanded, the loads and runoff volumes entering zone 1 were essentially the same as stream inputs.

During a few selected storm events, the relative effects of actual herbicide removal processes and dilution on concentration changes in surface runoff within a zone (primarily adsorption and infiltration) were estimated. Dilution factors for the zones were calculated from the fractional changes in bromide concentrations as the water passed through the buffer zones. These estimates were made by assuming that the rainfall within a zone had zero bromide and herbicide concentration and that the concentration change of bromide was due to dilution. Herbicide removal could be due to either biochemical processes in the litter/soil layer or to infiltration. Runoff volumes and herbicide loads were estimated by assuming that the mean volumes and concentrations in surface runoff collectors were representative of the entire length of interface between zones. Dilution factors were calculated for zone 3, for the upper part of zone 2 (zone 2a, between sampler positions 2 and 3), and for the lower part of zone 2 (zone 2b, between sampler positions 3 and 4).

Shallow Groundwater

Concentrations in wells at the first four positions (0, 8, 13, 18 m) for the entire period of record and concentrations in wells at the final two positions (28 and 38 m) from March 1994 to October 1994 were computed as weighted averages of the wells screened at the two depths (0.1 to 0.6 m and 0.6 to 2.0 m). Weighting was based on depth of water in the well. From March 1993 to Feb 1994, concentrations at the final two positions (28 and 38 m) reflect data only from the deep wells.

RESULTS AND DISCUSSION

SURFACE RUNOFF MOVEMENT OF HERBICIDES AND BROMIDE

Herbicide concentrations and loads in surface runoff were reduced significantly during transit through the restored riparian buffer system (table 1). Pooling all data together for the entire study showed that average field edge concentrations were reduced by about an order of magnitude for atrazine and by a factor of about eight for alachlor. Bromide concentrations were reduced by about a factor of six. Relative load reductions compared to concentration reductions were greater for atrazine and slightly less for alachlor (table 1). When grouped by positions, there were significant differences at least at the 0.05 level for both concentrations and loads for both herbicides and for bromide.

Movement of the two herbicides in surface runoff took place primarily in events within a short period after application. Rainfall data for the entire period of record is shown in figure 6. Most of the herbicide movement from the field occurred by June 30, or with the first 250 mm of rainfall that occurred after application. During the after-application periods, edge-of-field concentrations of atrazine averaging

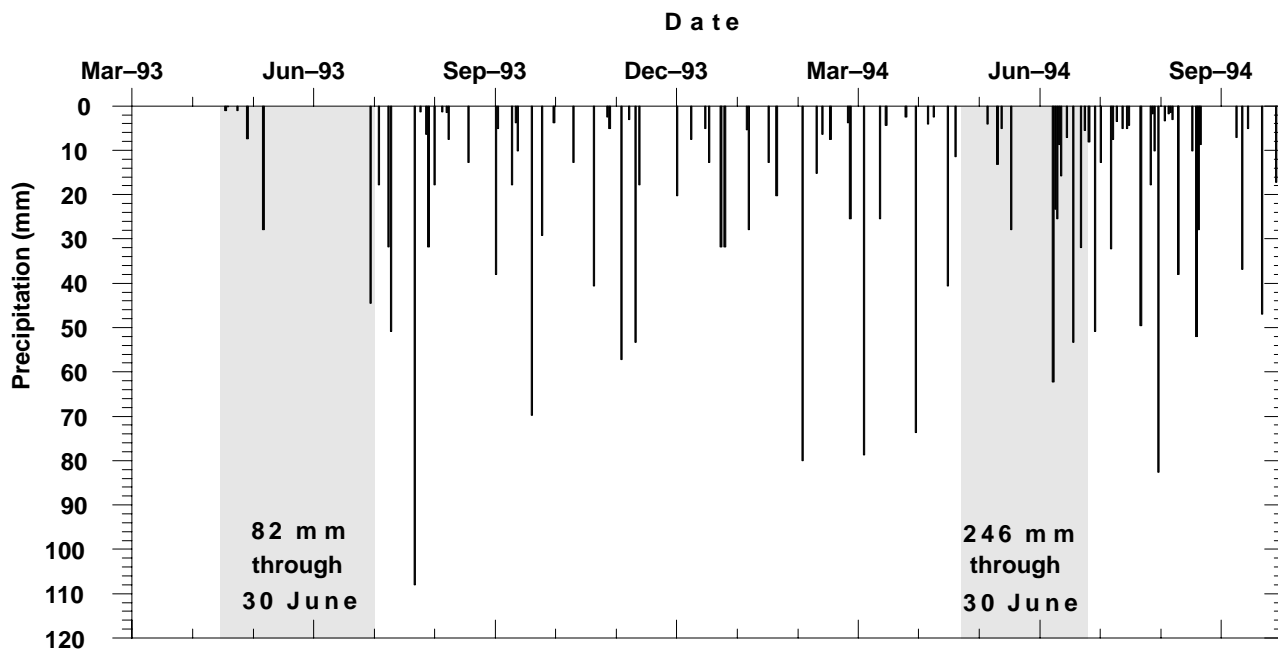


Figure 5. Precipitation at the Dairy Wetland. Shaded areas are the after-application time periods; unshaded areas are the between-application time periods. The after-application time period is based on 250 mm of cumulative rainfall or through June 30, whichever came first. Rainfall during each after-application period is given within the shaded areas. The between-application time period was from the end of the after-application period to the next herbicide application the following spring.

Table 1. Surface runoff atrazine and alachlor concentrations and loads and bromide concentrations for entire record period (1993–1994).

Position	Atrazine			Alachlor			Bromide						
	Concentration ($\mu\text{g L}^{-1}$)		n	Load ($\mu\text{g m}^{-1}$)		Concentration ($\mu\text{g L}^{-1}$)		n	Load ($\mu\text{g m}^{-1}$)		Concentration ($\mu\text{g L}^{-1}$)		
	mean	std. error		mean	std. error	mean	std. error		mean	std. error	mean	std. error	n
1. Field edge	2.2 ^[a]	0.51	174	1346 ^[a]	403	0.16 ^[a]	0.05	115	89 ^[a]	35	2.84 ^[a]	0.50	167
2. Upslope edge of zone 2	0.40	0.10	111	62	16	0.02	0.01	81	3.4	1.7	0.98	0.07	118
3. Middle of zone 2	0.21	0.05	121	122	71	0.03	0.02	85	5.9	3.6	0.56	0.03	143
4. Upslope edge of zone 1	0.27	0.06	129	62	14	0.02	0.01	92	14	8.9	0.45	0.02	156

^[a] Groups (positions) are significantly different at (at least) the 0.01 level based on the Kruskal–Wallis test.

Table 2. Surface runoff atrazine concentration and load for the after application and between application time periods.^[a]

Position	Atrazine – After Application			Atrazine – Between Applications						
	Concentration ($\mu\text{g L}^{-1}$)		n	Load ($\mu\text{g m}^{-1}$)		Concentration ($\mu\text{g L}^{-1}$)		Load ($\mu\text{g m}^{-1}$)		
	mean	std. error		mean	std. error	mean	std. error	n	mean	std. error
1. Field edge	12.7 ^[b]	4.17	18	5195 ^[b]	3377	1.02 ^[b]	0.13	156	897 ^[b]	205
2. Upslope edge of zone 2	1.35	0.81	11	195	136	0.29	0.06	100	47	9.7
3. Middle of zone 2	0.25	0.09	17	22	8.4	0.21	0.05	104	138	83
4. Upslope edge of zone 1	0.66	0.26	21	130	51	0.19	0.05	108	48	12

^[a] After application time period includes all samples following chemical application in March and continuing through June 30 or through 250 mm of cumulative rainfall, whichever came first. Between application time period includes samples beginning in July or after 250 mm of cumulative rainfall and continuing through the runoff event immediately before the next year's application of chemical (March). Mean followed by standard error of mean.

^[b] Groups (positions) are significantly different at (at least) the 0.01 level based on the Kruskal–Wallis test.

Table 3. Surface runoff alachlor concentration and load for the after application and between application time periods.^[a]

Position	Alachlor – After Application			Alachlor – Between Applications						
	Concentration ($\mu\text{g L}^{-1}$)		n	Load ($\mu\text{g m}^{-1}$)		Concentration ($\mu\text{g L}^{-1}$)		Load ($\mu\text{g m}^{-1}$)		
	mean	std. error		mean	std. error	mean	std. error	n	mean	std. error
1. Field edge	1.32 ^[b]	0.34	9	189 ^[b]	124	0.07 ^[b]	0.03	106	13 ^[b]	4
2. Upslope edge of zone 2	0.05	0.05	8	2.7	2.7	0.02	0.01	73	0.8	0.5
3. Middle of zone 2	0.04	0.03	9	1.3	1.1	0.03	0.02	76	1.8	1.2
4. Upslope edge of zone 1	0.06	0.04	13	15	13	0.01	0.01	79	2.4	2.3

^[a] After application time period includes all samples following chemical application in March and continuing through June 30 or through 250 mm of cumulative rainfall, whichever came first. Between application time period includes samples beginning in July or after 250 mm of cumulative rainfall and continuing through the runoff event immediately before the next year's application of chemical (March). Gas chromatograph data only.

^[b] Groups (positions) are significantly different at (at least) the 0.01 level based on the Kruskal–Wallis test.

Table 4. Atrazine concentration changes, dilution factors, and estimated concentration changes due to dilution and other factors for six storm events.

Date	Zone ^[a]	Atrazine Concentration Change ($\mu\text{g L}^{-1}$)	Dilution Factor ^[b]	Dilution Concentration Change ($\mu\text{g L}^{-1}$)	Net Concentration Change	
					($\mu\text{g L}^{-1}$) ^[c]	(% m^{-1}) ^[d]
20 Jul 1993	3	1.70	0.60	1.02	0.68	5.00
20 Jul 1993	2a	0.81	0.23	0.19	0.62	5.10
20 Jul 1993	2b	0.85	0.60	0.51	0.34	4.00
22 Sep 1993	3	1.57	0.67	1.05	0.52	4.14
22 Sep 1993	2a	0.26	0.18	0.05	0.21	5.38
22 Sep 1993	2b	BD ^[e]	0.06	—	—	—
16 May 1994	3	27.62	0.52	14.4	13.2	5.97
16 May 1994	2a	4.21	0.47	1.98	2.23	3.53
16 May 1994	2b	0.13	−0.06	−0.01	0.14	7.18
16 Jun 1994	3	15.75	0.30	4.72	11.03	8.75
16 Jun 1994	2a	1.65	0.46	0.76	0.89	3.60
16 Jun 1994	2b	−0.80	0.46	−0.37	0.43	−3.58

^[a] Zone 2a is from position 2 to position 3 (upper part of zone 2); zone 2b is from position 3 to position 4 (lower part of zone 2).

^[b] From bromide concentration change data.

^[c] Net concentration change (NCC) is the concentration change not due to the dilution factor.

^[d] NCC (% m^{-1}) is based on flow length of 8 m (zone 3) and 15 m each for zones 2a and 2b.

^[e] BD = below detection limit in both samples above and below the zone.

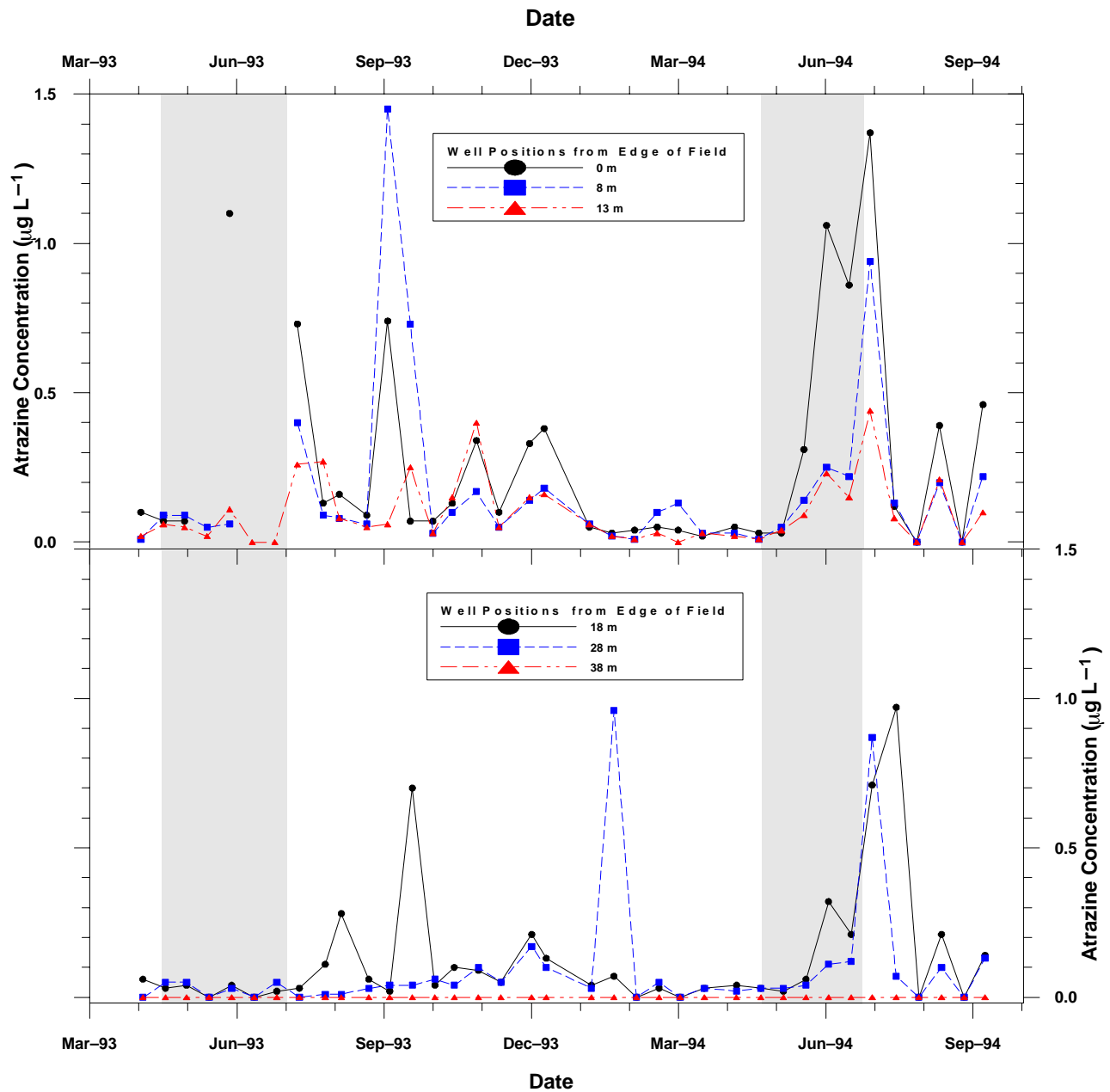


Figure 6. Atrazine concentrations in wells at positions 1–3 (top) and positions 4–6 (bottom). Shaded areas are the after-application time periods; unshaded areas are the between-application time periods. The after-application time period is based on 250 mm of cumulative rainfall or through June 30, whichever came first. The between-application time period was from the end of the after-application period to the next herbicide application the following spring.

12.7 $\mu\text{g L}^{-1}$ were reduced to 0.66 $\mu\text{g L}^{-1}$ as water entered zone 1 near the stream (table 2). Alachlor concentration in the after-application period was reduced from 1.3 $\mu\text{g L}^{-1}$ at field edge to 0.06 $\mu\text{g L}^{-1}$ near the stream (table 3). Load reductions were generally comparable to the concentration reductions. Concentration and load reductions for alachlor were minor during the between-application period. Atrazine concentration and load reductions during the between-application period were higher than for alachlor on a percent basis but were minor in terms of actual concentrations or loads because of the low edge-of-field loading (tables 2 and 3).

Dilution factors (fractional change in bromide concentrations) of surface runoff by rainfall and net infiltration were calculated for zone 3 and zones 2a (upper) and 2b (lower) for

two rainfall events in both years of the study (table 4). The four storms ranged from 22 mm to 98 mm of rainfall. These rainfall events are typical for the region. Sheridan (unpublished) showed that rainfall events ranging from 12.7 mm produced runoff at Station Z, a 0.34 ha field near the study site. Rainfall events greater than 98 mm occurred about every two years. Dilution factors were 0.52, 0.34, and 0.26, respectively, in zones 3, 2a, and 2b. Dilution concentration changes were then used to calculate the percent concentration change for dilution and concentration changes due to removal for the six runoff events. Data are presented for atrazine in table 4. The dilution factor for each zone or sub-zone was applied to concentration changes between each surface runoff collector to determine the dilution

concentration change. Net concentration change (NCC) is the total concentration change minus the dilution concentration change. The NCC was further calculated as % of original concentration and the % of the original concentration per meter of flow length. Zone 2b showed a slight increase in bromide concentration for one event, giving a negative dilution concentration change. Net concentration changes and net concentration changes/meter of flow length were greater in zone 3, the grass strip. Results were similar for alachlor. The average NCC (%) per meter of flow length for zones 3, 2a, and 2b were 5.96, 4.40, and 2.53 % m⁻¹, respectively. The NCC per meter of flow length was significantly different among the zones at the 0.005 level based on the Kruskal–Wallis test.

HERBICIDES IN SHALLOW GROUNDWATER

Herbicide concentrations at well positions 0, 8, 13, 18, 28, and 38 m from the application area are shown in figures 6 and 7. Atrazine concentrations in shallow groundwater were consistently at or below detection limits for the analytical procedures for the first two months after application for all positions relative to the application area (fig. 6). Concentrations of atrazine reaching the 38 m position (near the stream) were below detection limits for the entire study. Mean concentrations for the study were highest at the 0 m and 18 m well distances. In both years, the high concentrations in the 18 m wells occurred after runoff events that contained elevated concentrations. Thus, it is possible that surface runoff caused infiltration of atrazine-enriched water at the

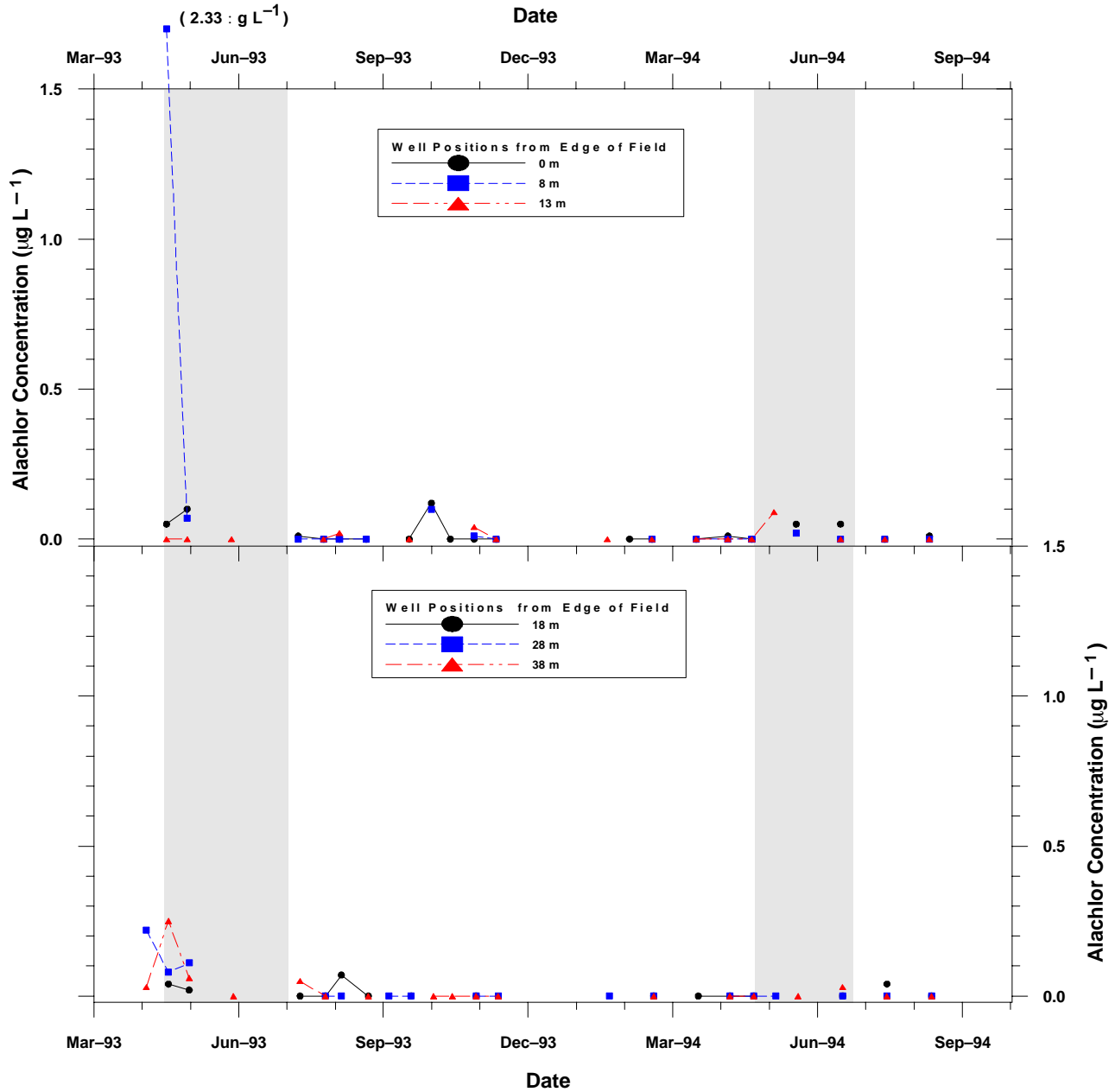


Figure 7. Alachlor concentrations in wells at positions 1–3 (top) and positions 4–6 (bottom). Shaded areas are the after-application time periods; unshaded areas are the between-application time periods. The after-application time period is based on 250 mm of cumulative rainfall or through June 30, whichever came first. The between-application time period was from the end of the after-application period to the next herbicide application the following spring.

18 m wells. There appears to be a more general elevation of atrazine in all wells except the 38 m distance in 1994. Except for one sample date shortly after application at the 8 m position, alachlor concentrations were typically at or below detection limits for most positions and sampling dates in the study (fig. 7). There were no significant differences for atrazine or alachlor concentrations by distance from the application area.

IMPORTANCE OF THE TIMING OF RUNOFF EVENTS

The importance of runoff events soon after herbicide application has been reported in other studies of herbicide transport (Rohde et al., 1981; Arora et al., 1996; Lowrance et al., 1997). Thus, the condition of the riparian buffer system when these high surface runoff concentrations occur is critical to control of the herbicide in runoff. Available soil moisture storage and infiltration, vegetation condition, and dilution all affect the buffer system capacity. Arora et al. (1996) found that with 9% infiltration of surface runoff, atrazine, metolachlor, and cyanazine retentions were 13%, 22%, and 15%, respectively. Percent retention of the herbicide increased with increased infiltration, to a high of 100% retention with 100% infiltration (Arora et al., 1996). Although vegetation condition has not been evaluated systematically, the herbaceous vegetation in both zone 3 and zone 2 had generally broken dormancy before the first runoff events after herbicide application. Zone 2 has tree and shrub species that are either evergreen or lose their leaves in the spring and would remain metabolically active year-round. Dilution occurs in a buffer zone as rainwater falling on the surface of the buffer zone mixes with runoff water carrying the herbicide. Although affected by the amount of infiltration, which is in turn affected by vegetation, dilution should occur regardless of the absence, presence, or type of vegetation. On an impermeable, non-adsorptive surface, dilution would be the only process decreasing concentration of pollutant in runoff. Misra et al. (1996) showed that higher inflow concentrations lead to higher herbicide retention. Nonetheless, these results indicate that a permanent grass buffer on a relatively well-drained soil was effective at controlling surface runoff loss of herbicides in this particular setting.

COMPARISON TO MATURE RIPARIAN FOREST BUFFER SYSTEM

The average surface runoff input concentrations for both herbicides were higher in the previous study of a mature riparian forest buffer (Lowrance et al., 1997), but the output concentrations at 38 m from the field were also higher. For the present study, atrazine input concentrations of $2.2 \mu\text{g L}^{-1}$ were reduced to an output concentration of $0.27 \mu\text{g L}^{-1}$ at 38 m downslope. The corresponding numbers for the Gibbs farm site (mature buffer) were $5.5 \mu\text{g L}^{-1}$ input and $0.99 \mu\text{g L}^{-1}$ output. The percent concentration reduction per meter was also greater in the restored buffer (this study) than in the mature buffer. Alachlor in surface runoff was reduced from $0.16 \mu\text{g L}^{-1}$ to $0.02 \mu\text{g L}^{-1}$ in the restored buffer (this study) and from $1.4 \mu\text{g L}^{-1}$ to $0.25 \mu\text{g L}^{-1}$ in the mature buffer. These results indicate that the two-year-old restored buffer provided a similar level of protection as the mature riparian buffer.

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