Constructed wetlands as a component of the agricultural landscape: Mitigation of herbicides in simulated runoff from upland drainage areas

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A R T I C L E   I N F O

Article history:
Received 21 September 2010
Received in revised form 13 January 2011
Accepted 14 January 2011
Available online 16 February 2011

Keywords:
Atrazine
Fluometuron
Water quality
Wetland

A B S T R A C T

Constructed wetlands are a recommended practice for buffering pollutant source areas and receiving waters. A wetland consisting of a sediment trap and two treatment cells was constructed in a Mississippi Delta lake watershed. A 3-h simulated runoff event was initiated (2003) to evaluate fate and transport of atrazine and fluometuron through the wetland. Water samples were collected during a runoff simulation and then afterward at selected intervals for 21 d, and analyzed for the herbicides. Breakthrough patterns for herbicide concentrations in water samples during the first 20 h after simulated runoff showed peak concentrations in the first 6 h, with gradual tailing as the herbicide pulse was diluted in the second, excavated (deeper) cell. Atrazine and fluometuron concentrations in the first (shallower, non-excavated) cell averaged 12- and 20-fold greater, respectively, than those in the second cell following simulated runoff, indicating entrapment in the first cell. Atrazine and fluometuron concentrations in the shallower cell decreased 32% and 22%, respectively, 9 d following simulated runoff, indicating either degradation or sorption to soil or wetland flora. In the excavated cell, concentrations were even lower, and atrazine declined more rapidly than fluometuron. Results indicate constructed wetlands can improve downstream water quality though sequestration or processing of pollutants.

Published by Elsevier Ltd.

1. Introduction

Wetlands are an integral part of many landscapes, often serving as transition zones between upland areas and water bodies. As such, wetlands are a sink for a variety of pollutants, given proximity to anthropogenic activities such as industry or agriculture. The integrity of a wetland, therefore, may depend upon its ability to process contaminants as they move through the system. Although the physical, biological, and chemical processes are complex, interrelated, and not completely understood, factors contributing to effective processing include the size of the wetland, system hydrology, vegetative characteristics and density, proximity to contaminant sources, and the nature of the contaminants (Mitsch and Gosselink, 2000).

Constructing artificial wetlands in vulnerable areas where wetlands do not naturally exist may provide protection from pollutants moving to water bodies from adjacent areas, and they may be more efficient in processing contaminants than natural wetlands because constructed wetlands can be tailored to meet specific needs. Significant research effort has focused on the development and assessment of constructed wetlands for treatment of waste from urban, mining, and industrial activities (e.g., Bastian and Hammer, 1993; Kadlec and Knight, 1996). In areas affected by agriculture, the application of conservation management practices such as constructed wetlands has received attention for attenuating non-point contamination of surface waters by sediment, livestock wastewater, and agrochemicals in runoff (Rodgers and Dunn, 1992; Hammer et al., 1993; Higgins et al., 1993; Kadlec and Knight, 1996; Cooper et al., 1998). As part of an integrated agricultural management system, constructed wetlands can be used in conjunction with other edge-of-field measures, e.g., vegetative buffer strips (Dabney et al., 2006).

Surface water contamination from non-point sources is a concern. Herbicides applied to the soil surface in row crop production are susceptible to loss in surface runoff, and downstream conservation measures such as vegetated constructed wetlands may help to minimize contamination of adjacent water bodies. Atrazine and fluometuron are commonly used soil-applied herbicides and are candidates for evaluations of the efficacy of constructed wetlands in remediating runoff from row crop areas. Factors that may influence the dissipation of herbicides in wetland systems include vegetation and associated decomposed litter; high soil organic carbon, anaerobic environment, and active populations of anaerobic and aerobic microbes (Stoeckel et al., 1997).
The capability for wetlands to remove atrazine from water has been reported from studies ranging from in vitro assays, through mesocosms, to functioning natural and constructed wetlands. Atrazine mitigation may be biologically mediated. Enhanced mineralization of atrazine has been documented in numerous, diverse terrestrial systems (Kruutz et al., 2010) and within a wetland after bio-augmentation of the sediment with soil from an enhanced-mineralizing atrazine spill site (Runes et al., 2001). Atrazine-degrading organisms have been isolated from other wetlands with a history of atrazine exposure (Runes et al., 2003). The molecular basis for enhanced degradation in wetland sediment was provided by in vitro mineralization assays; PCR detection of the gene trzD and PCR/Southern blot detection of the gene atzA (Anderson et al., 2002). A biological role for atrazine degradation may also be inferred from atrazine dissipation after the addition of sucrose to anaerobic sediment microcosms (Kao et al., 2001). Working with other wetland sediments, Weaver et al. (2004) detected little mineralization and noted that the rapid loss of atrazine (half-life 23 d) was the result of pH-mediated hydrolytic dechlorination of atrazine and enhanced binding to soil. Others have observed atrazine partitioning to sediments (Detenbeck et al., 1996) as well as enhanced sorption and irreversible binding of atrazine and metabolites in wetland soils as compared to agricultural soils (Mersie and Seybold, 1996). Atrazine degraded under strongly reduced conditions in wetland soils in a microcosm study (half-life 38 d) (Seybold et al., 1996), but degradation was slower (half-life 86 d) in the aqueous phase above the soil. In contrast, atrazine was not mineralized under either aerobic or anaerobic conditions in a wetland soil microcosm (Larsen et al., 2001). Other factors that may improve retention of atrazine include longer residence times in the wetland area (Alvord and Kadlec, 1995) and increased wetland buffer size (Moore et al., 2000).

In a microcosm study, fluometuron was metabolized under saturated conditions (half-life 25–27 d), but under flooded conditions, the half-life was 175 d (Weaver et al., 2004). In a laboratory study using soils collected from wetland sites, there was more rapid degradation of fluometuron in forested riparian soil as compared to field soil (Locke et al., 2002). Shankle et al. (2004) observed more fluometuron sorption in wetland soils compared to field soils, and this was attributed to increased organic matter. Similarly, Rose et al. (2006) found that organic matter and vegetation influenced fluometuron retention in an in situ wetland study (Rose et al., 2006).

Long-term monitoring of Beasley Lake, an oxbow lake in the Mississippi Delta (Locke, 2004), measured detectable concentrations of both atrazine and fluometuron, presumably from surrounding agricultural fields (Zablotowicz et al., 2006a). A wetland was constructed and established adjacent to Beasley Lake to evaluate its potential as a management practice to inhibit contamination of the lake from pesticide in runoff (Moore et al., 2007, 2009). One year after the constructed wetland was established, Weaver et al. (2004) reported changes in the vegetation and hydrology as well as shifts in the soil microbial community structure. The purpose of the study reported here is to describe the environmental fate of atrazine and fluometuron in a constructed wetland during a simulated rainfall event in order to evaluate the effectiveness of constructed wetlands in processing and sequestering pesticides and protecting downstream sites. A companion study evaluated the fate of insecticides introduced to the wetland system (Moore et al., 2007, 2009).

2. Materials and methods

2.1. Description of the study site

A constructed wetland (180 m long × 30 m wide [average]) consisting of a sediment trap (average 0.45 m depth) and two treatment cells was developed beginning in Spring, 2002 in the Beasley Lake watershed, Sunflower County, Mississippi (Figs. 1 and 2). The treatment cells included: (a) one long, shallow (average 0.3 m depth) non-excavated cell; and (b) one deeper (average 1 m depth), excavated cell. Cells were separated by earthen berms and connected by culverts. Wetland establishment was completed in Spring, 2003. The wetland was constructed at a natural inlet to Beasley Lake and was designed to accommodate drainage from an 8-ha row crop drainage area (Fig. 2). The wetland centroid was 90.668874° West, 33.403427° North, and the wetland was contained within an area of approximately 0.5 ha. The slope of the land within the constructed wetland from inlet to final outlet was 1%. The sediment trap had an estimated volume of 100 m³, the non-excavated cell volume was estimated at 822 m³, and the excavated cell volume was estimated at 3258 m³. Additional information concerning Beasley Lake watershed and the constructed wetland are found elsewhere (Locke, 2004; Weaver et al., 2004; Moore et al., 2007; Locke et al., 2008).

Floristic data in each compartment of the constructed wetland were taken visually in July, 2003. Species were counted or estimated only if bases of the plants were touching the water. For predominant species, actual plant counts were taken at four random locations per compartment and converted to percent of the total flora. For species that were incidental or infrequently encountered, percent of the flora was estimated.

![Fig. 1. Diagram showing a schematic of the constructed wetland.](image-url)
2.2. Simulated runoff experiment

A 3-h simulated runoff event was initiated on July 2, 2003 to evaluate transport of herbicides (atrazine and fluometuron) through the wetland (similar to Moore et al., 2007, 2009). Water was pumped from nearby Beasley Lake using a tractor-mounted centrifugal pump with 30-cm discharge at a rate of 1000–1500 L min$^{-1}$. Surface water was added at the entrance of the wetland through a metal flume. The day before the simulation (July 1), water was pumped for 8 h to recharge the wetland. Just prior to initiation of the experiment (on July 2), water was pumped until it reached steady-state flow with water exiting at the outflow pipes from the second cell.

After water had been pumped to fill the system and achieve a steady-state flow, 3.2 kg of potassium bromide as a conservative tracer was added in 40 L of water in ca. 2 min directly into the incoming water stream at the entrance of the wetland system. Atrazine (42 mL of 0.48 kg L$^{-1}$ Aatrex 4L™, Syngenta Crop Protection, Greensboro, NC, diluted in 1893 L), fluometuron (42 mL 0.48 kg L$^{-1}$ Cotoran 4L™, Griffin Agric. Chem. Group, Valdosta, GA, in 1893 L), suspended sediment (130 kg diluted in 1893 L), and surface water from Beasley Lake were mixed in a 7571-L nurse tank near the entrance to the wetland and kept in suspension using an electric submersible pump. At the entrance to the wetland, the herbicide-sediment mixture was continuously pumped from the nurse tank into the runoff water for 3 h at a rate of 5 L min$^{-1}$. Analysis of the lake water pumped into the wetland indicated negligible traces of atrazine (0.21 ng L$^{-1}$ average for June to July, Smith et al., 2007) and fluometuron (below detection limit, <0.05 mg L$^{-1}$, Zablotowicz et al., 2006a).

The experimental design for the study was as follows: During the 3 h of simulated runoff and for the next 21 d at selected intervals, water samples were collected from fixed points within the inlet sediment trap, non-excavated cell, and the excavated cell at selected intervals. Comparisons were made between the two full treatment cells (non-excavated and excavated) over time. For all sampling times, three replicate samples were collected from each compartment. For approximately 2 h after water pumping ceased, water flow exiting at the outlet gradually slowed to a trickle until flow stopped within 24 h of initiation of the simulation. Water samples were collected directly in front of the outlet pipe that emptied the wetland for 24 h. Samples of the vegetation in each cell were also collected in triplicate from each cell at time points up to 19 d after the simulated runoff and stored at −20°C until analysis for herbicide concentrations.

Water samples were placed on ice until transport to the laboratory, where they were refrigerated. Atrazine and fluometuron concentrations in water samples were determined by enzyme-linked immunosorbent assay (ELISA) (Envirologix, Portland, ME) using manufacturer protocols. Detection limits were 0.05 ng L$^{-1}$ and 0.04 ng L$^{-1}$ for fluometuron and atrazine, respectively. Water flow through the wetland was measured with an area velocity flow logger (Isco, Inc., Lincoln, NE). Total solids suspended in runoff were determined by measuring weight difference before and after drying a subsample. Bromide in water was measured using ion chromatography (DX 500 system, consisting of a GP 50 Gradient Pump, CD 25 Conductivity Detector, EG 40 Eluent Generator, LC 30 Chromatography Oven, AS11-HC separator column, AS 40 Automated Sampler, and KOH eluent, Dionex, Sunnyvale, CA).

Plants collected from each cell during and after the runoff event were extracted with methanol (80 mL MeOH:20 g moist weight). Extracts were diluted in water and analyzed for atrazine using ELISA (see previous). Fluometuron was analyzed using HPLC (Agilent 1100 system, Agilent Technologies, Wilmington, DE). The HPLC conditions for analysis included: Eclipse XDB C18 column, 4.6 × 250 mm; gradient mobile phase 55:45–5:95 water:acetonitrile over 20 min; 1 mL min$^{-1}$ flow mobile phase flow rate; Retention time 6.4 min; Fluorescence detection $E_x = 249$, $E_m = 402$.

The effects of treatment cell over time on the concentration of atrazine and fluometuron in water and plant samples were assessed by the General Linear Model (SAS 9.2, SAS Institute Inc., Cary, NC). For the excavated and non-excavated cells (Fig. 1), each sampling point per time was treated as a replicate, and the differences between the two treatment cells were measured by ANOVA and repeated for each sampling time.

Fig. 2. Digital elevation model of the wetland and adjacent drainage area, with Beasley Lake located southwest of the wetland.
3. Results and discussion

Water flow was monitored during the 3-h simulated run when water was pumped into the constructed wetland from Beasley Lake (Fig. 3a). After pumping was terminated, water flow in the wetland gradually declined for approximately 6 h (Fig. 3a) before stopping. Bromide was used to monitor flow through the various cell compartments (Fig. 3b). The main pulse for Br⁻ concentration in the first (non-excavated) cell ranged from 0.8 to 6 h after dosage, with the peak occurring at almost 3 h (Fig. 3b). The pattern of Br⁻ occurrence in the second (excavated cell) was less regular, and concentrations were much lower. The highest Br⁻ concentration observed in the excavated cell was 6 h after dosage (Fig. 3b).

Concentration of total suspended solids 1 h after initiation of the runoff simulation was highest to lowest in the order of sediment trap cell, non-excavated cell, and excavated cell. This would be expected during the peak of the water flow dosed with solids material. Once water flow ceased (within 24 h), suspended solids in the non-excavated (66 mg L⁻¹, s.e. 19) and excavated cells (75 mg L⁻¹, s.e. 40) were equivalent, indicating full dispersion of introduced solids material throughout the wetland. At 120 h after dosage, total solids in the non-excavated cell increased (392 mg L⁻¹, s.e. 182), presumably because of concentration due to water depletion through evaporation or infiltration in the cell or from additional sediment inputs from natural sources (e.g., senescent/decaying plant material in suspension). Solids concentration (86 mg L⁻¹, s.e. 36) remained the same in the excavated cell 120 h after dosage.

The breakthrough pattern of atrazine and fluometuron through the wetland after the simulated runoff event (Fig. 4, Table 1) showed peak concentrations during the first 6 h, with gradual tailing as the herbicide pulse reached the excavated cell and was diluted, dispersed, sorbed to sediments, or taken up by wetland flora. The herbicide concentrations followed the same pattern as the water flow and Br⁻ (Fig. 3). Samples collected at the outlet of the wetland (exit pipe from the excavated cell) numerically increased in herbicide concentration over the 24-h sampling period.
but concentrations were at or slightly above background levels. Atrazine concentration at the exit pipe increased from 0.02 ng L\(^{-1}\) near the beginning of the runoff event to a high of 0.12 ng L\(^{-1}\) 6 h after initiation of water flow. Fluometuron concentration increased from 0.025 ng L\(^{-1}\) initially to a high of 0.11 ng L\(^{-1}\) 7 h after initiation of water flow.

Atrazine and fluometuron concentrations peaked in the 6–24 h period in the non-excavated cell (Fig. 4, Table 1), while the highest observed herbicide concentrations in the excavated cell occurred 24–96 h after dosing. The delay in peak herbicide concentrations in the excavated cell as compared with Br\(^+\) was likely because, as a non-reactive chemical, Br\(^-\) would be expected to move with the water, but reactivity of the less polar herbicides with plants and other organic constituents would retard movement. Atrazine and fluometuron concentrations in the non-excavated cell averaged 12- and 20-fold greater, respectively, than concentrations in the excavated cell during the period following the initial simulated runoff (first 24 h), indicating delay due to entrapment and dilution during migration toward the second cell (see Fig. 1, non-excavated cell is 20–100 m from the wetland inlet vs. 100–180 m for the excavated cell). Atrazine and fluometuron concentrations in the non-excavated cell decreased 32% and 22%, respectively, 7 d following the runoff event, and water volume in the non-excavated (shallower) cell was decreasing due to evaporation or infiltration. This indicates that either degradation or sorption to soil or wetland flora may have occurred, thus maintaining steady state concentrations. In the excavated cell, concentrations were low, but remained relatively constant during the remainder of the sampling period. It was only possible to collect one sample from the shallow, non-excavated cell on d 21 because water in the cell had almost completely evaporated.

Adsorption/uptake by plants is one potential route of dissipation for herbicides (Moore et al., 2000). Vegetation was lush in all wetland cells, covering a majority of the area (>95% of the surface area in all cells). Fifty-two plant species were observed in the constructed wetland area. Only eight species comprised 1% or more of the area covered by plants, and these species are shown in Table 2. Of the eight species, one broadleaf plant, Alligatorweed [Alternanthera philoxeroides (Mart.) Griseb.], and two grass plants, juglerice [Echinochloa colonum (L.) Link] and barnyardgrass [Echinochloa crus-galli (L.) Beauv.], predominated, and all three species are non-native invasive weeds. Alligatorweed was the single most prevalent species in the sediment trap and the excavated cell, while alligatorweed and barnyardgrass were equivalent (48% each) in the non-excavated cell. The excavated cell was deeper, holding more water, and this may have contributed to the predominance of facultative wetland dicot species (94%) such as alligatorweed compared to that in the non-excavated cell (48%).

After extensive soil disturbance and a change in the hydrology of the excavated cell, vegetation efficiently and completely recolonized the site. This recently established vegetation, however, was of low diversity and was almost entirely composed of exotic invasive species. To avoid these results, it may be advisable to introduce perennial, adapted native plants immediately following similar disturbances.

Retention of atrazine and fluometuron was observed in plants sampled throughout the study period (Table 3). Atrazine concentrations in plant material from the non-excavated cell increased 5-fold in the first 24 h and then remained fairly constant throughout the remainder of the study period (Table 3). Similar observations were made in the excavated cell, but the increase was delayed. The highest concentrations of fluometuron in plant extracts from both cells were measured in samples taken 1 h after dosing (Table 3). Fluometuron concentrations in extracts from subsequent samplings decreased at least 12-fold and did not increase again for the remainder of the experimental period.

Although some retention of herbicide by plants was measured, there did not appear to be much long-term difference between the non-excavated and excavated cells, other than that initially caused by a delay in the herbicide movement to the excavated cell. Monocot species were a larger component of the plant population in the non-excavated cell (52% vs. 23% in the excavated cell), but...
Table 3

<table>
<thead>
<tr>
<th>Atrazine (mg kg⁻¹)</th>
<th>Time after dosage initiation (h)</th>
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<th>Excavated cell</th>
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<td>0.56 (0.20)</td>
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</tr>
<tr>
<td>456</td>
<td>0.40 (0.14)</td>
<td>0.41 (0.13)</td>
<td>ab</td>
</tr>
<tr>
<td>Fluometuron (mg kg⁻¹)</td>
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<td>0.08 (0.06)</td>
<td>ab</td>
</tr>
</tbody>
</table>

* Mean and standard error (in parenthesis) of three replicates.

** Within a cell, values in the same column with the same letter in bold are not significantly different. No significant differences were found between treatment cells.

this did not seem to influence overall herbicide retention by plants. Also, no visual symptoms of herbicide injury to plant were noted in either cell, likely because of low herbicide concentrations and uptake by plants.

During the 20-d period following dosing, an 85% and 81% reduction in maximum atrazine and fluometuron concentrations in water, respectively, was observed in the non-excavated cell, while a 70% and a 58% reduction was observed in the excavated cell (Table 1). Microbial adaptation resulting in enhanced degradation of atrazine has been reported in terrestrial soils from this region (Zablotowicz et al., 2006b). There was limited previous atrazine exposure in this system, but it is likely that the upstream watershed had a history of simazine exposure, which has led to microbial adaptation and enrichment of trzN triazine dehalogenase. In other studies using PCR techniques, all triazine degraders isolated from soils in this region contained the trzN chlorohydrolase and atzB and atzC amidohydrolases (Zablotowicz et al., 2008). The low dissipation rate of atrazine observed in the present study is not consistent with other reports of rapid triazine dissipation due to enhanced degradation, although the atrazine dissipation was just slightly faster than that of fluometuron. In a related laboratory incubation study using 14C radio-labeled atrazine in soil from the Beasley Lake constructed wetland area (Weaver et al., 2004), more than 85% of the applied radioactivity was recovered 32 d after treatment, indicating a lack of atrazine degraders, with most radioactivity characterized as bound residues.

This study demonstrated that constructed wetlands can improve water quality though entrapment or processing of pollutants. Two herbicides were partially contained in drainage water captured by the constructed wetland. Residence time was a factor in dissipation, and much of the herbicide load was entrapped in the first (non-excavated) cell, where it dissipated over time. Herbicide levels in the second (excavated) cell were lower than those in the first cell, and dissipation occurred there as well. Plants were a factor in herbicide retention, but no preferential affinity of herbicides by species was observed. Although atrazine dissipation was somewhat more rapid than that of fluometuron, little evidence was found for enhanced degradation due to microbial adaptation.

Acknowledgments

The authors are grateful for contributions from Frank Gwin, Matt Moore, and Paul Rodrigue.

References