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Mitigation of atrazine, *S*-metolachlor, and diazinon using common emergent aquatic vegetation

Matthew T. Moore, Martin A. Locke, Robert Kröger***

Water Quality and Ecology Research Unit, USDA Agricultural Research Service, National Sedimentation Laboratory, Oxford, MS 38655, USA

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ABSTRACT

By the year 2050, the population of the United States is expected to reach over 418 million, while the global population will reach 9.6 billion. To provide safe food and fiber, agriculture must balance pesticide usage against impacts on natural resources. Challenges arise when storms cause runoff to be transported to aquatic receiving systems. Vegetated systems such as drainage ditches and constructed wetlands have been proposed as management practices to alleviate pesticide runoff. Twelve experimental mesocosms (1.3 × 0.71 × 0.61 m) were filled with sediment and planted with a monoculture of one of three wetland plant species (*Typha latifolia*, *Leersia oryzoides*, and *Sparganium americanum*). Three mesocosms remained unvegetated to serve as controls. All mesocosms were amended with 9.2 ± 0.8 μg/L, 12 ± 0.4 μg/L, and 3.1 ± 0.2 μg/L of atrazine, metolachlor, and diazinon, respectively, over a 4 hr hydraulic retention time to simulate storm runoff. Following the 4 hr amendment, non-amended water was flushed through mesocosms for an additional 4 hr. Outflow water samples were taken hourly from pre-amendment through 8 hr, and again at 12, 24, 48, 72, and 168 hr post-amendment. *L. oryzoides* and *T. latifolia* had mean atrazine, metolachlor, and diazinon retentions from 51%–55% for the first 4 hr of the experiment. Aside from *S. americanum* and atrazine (25% retention), unvegetated controls had the lowest pesticide retention (17%–28%) of all compared mesocosms. While native aquatic vegetation shows promise for mitigation of pesticide runoff, further studies increasing the hydraulic retention time for improved efficiency should be examined.

Introduction

Approximately 45% of the United States is agricultural land, with over 127 million ha of harvested cropland (US Department of Agriculture, National Agricultural Statistics Service, 2014). Fernandez-Cornejo et al. (2014) estimated that nearly $12 billion was spent on pesticides in US agriculture in 2008. A wide range of pesticides are utilized on the agricultural landscape to minimize crop losses due to insects, disease and weeds. In 2012, 40.8 million ha of agricultural land was treated with insecticides, while 115.5 million ha was treated with herbicides (US Department of Agriculture, National Agricultural Statistics Service, 2014). Even with improved management practices, the proximity of agricultural land to water resources such as rivers or lakes often results in their contamination by pesticide runoff following storm or irrigation events. Such occasions have the potential to harm downstream aquatic resources if not properly mitigated.

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], a broadleaf herbicide, was first registered for use

* *Corresponding author.*
** *Corresponding author at: Covington Civil and Environmental, LLC, Gulfport, MS 39501, USA.*

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in the US in 1959. Since 2001, atrazine has been the second most used pesticide active ingredient in the US, trailing only glyphosate (Grube et al., 2011). In 2008 alone, 29.9 million kg of atrazine active ingredient was applied on 21 of the main US crops (Fernandez-Cornejo et al., 2014). Albright et al. (2013) suggested that local waterways surrounding agricultural lands may exceed the maximum contaminant level of 3 μg/L, as recommended by the US EPA, for drinking water resources. Although trends of atrazine concentrations over the last two decades have generally declined in both surface and ground water (Stone et al., 2014; Toccalino et al., 2014), frequent detection, even at low levels, can potentially produce deleterious aquatic effects (Davies et al., 1994; Detenbeck et al., 1996).

S-metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl-N-[(2S)-1-methoxy-2-propanyl] acetamide] is a pre-emergent broadleaf herbicide used on crops such as corn, soybeans, and cotton. In 2001, between 9.1 and 10.9 million kg of metolachlor active ingredient were applied in the US, ranking it as the 9th most applied pesticide. By 2008, this value had increased to 13.6–15.9 million kg of metolachlor active ingredient applied annually in the US, moving the herbicide into the 4th most applied pesticide (Grube et al., 2011). Metolachlor is one of the most frequently detected pesticides in both agricultural and mixed land use watersheds, with usage and concentration trends turning upward from 2001 to 2010 (Stone et al., 2014). The drinking water health advisory level for metolachlor is 0.525 mg/L (Rivard, 2003).

Diazinon[O,O-diethyl-O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate], an organophosphate (OP) insecticide, is part of a class of compounds originally designed to replace the more persistent organochlorine insecticides. Use of diazinon has declined over 80% between 2001 and 2008, with under 500,000 kg of active ingredient applied in 2008, yet it remains the 8th most commonly used OP insecticide (Grube et al., 2011). Between 1992 and 2001, some 45% of urban streams exceeded the diazinon aquatic-life benchmark (Stone et al., 2014). Concomitant with a decline in usage has been less frequent detections in streams, especially those in urban watersheds (Stone et al., 2014). Although diazinon's use is declining in the US, toxicity problems still arise, specifically in agricultural areas in California (de Vlaming et al., 2004).

Phytoremediation is a common management practice which emphasizes the use of vegetation to remediate pollutants. In agricultural settings, phytoremediation is utilized through such practices as riparian buffers, stiff-grass hedges, constructed wetlands, and vegetated drainage ditches. Numerous studies have reported on the positive effects of vegetation in decreasing pollutant loads, especially pesticides (Moore et al., 2007; Cejudo-Espinosa et al., 2009; Arora et al., 2010; Zhang et al., 2010; Anderson et al., 2011; Murphy and Coats, 2011; Elsaesser et al., 2011; Locke et al., 2011; Albright et al., 2013). In the current study, three rooted, emergent macrophytes were chosen for evaluation of pesticide remediation: *Typha latifolia* L. (broad-leaved cattail), *Sparganium americanum* Nutt. (American bur-reed), and *Leersia oryzoides* (L.) Sw. (rice cutgrass). *Typha latifolia* is ubiquitous within all 50 United States, as well as almost all Canada provinces (USDA, 2013). It can tolerate perennial flooding, drawdown cycles, reduced soil conditions, and moderate salinity (Stevens and Hoag, 2006). *Sparganium americanum* is distributed as far northwest as Manitoba, southwest as Texas, northeast as parts of Newfoundland and Labrador, and southeast as Florida (USDA, 2013). This perennial, obligate plant can reach up to three meters in height, prefers a pH range of 4.9–7.3, has no salinity tolerance, and prefers full sun. Leaves may be stiff and erect, but they have the ability to bend and float on the surface of the water during flowing water situations (Favorite, 2006). *Leersia oryzoides* is located in the contiguous 48 states, eight Canadian provinces, and warmer parts of Europe (Darris and Bartow, 2008; USDA, 2013). Commonly called rice cutgrass or sicklegrass, *L. oryzoides* is a popular species for erosion control in ditches. This perennial forms dense colonies, spreads *via* underground rhizomes, and is common near streams, ponds, ditches, and canals. *Leersia oryzoides* can tolerate seasonal or permanent flooding, while preferring a pH of 5.1–8.8 (Darris and Bartow, 2008). The objective of the current study was to examine *T. latifolia, S. americanum,* and *L. oryzoides* for their individual ability to mitigate atrazine, S-metolachlor, and diazinon loads in simulated storm runoff water.

1. Materials and methods

Mesocosms were constructed using twelve, 379 L high density polyethylene oval containers (1.3 m length × 0.71 m width × 0.61 m height) by layering 16 cm of Lexington silt loam atop a base of 22 cm of sand (Fig. 1) (Target study pesticides were below detection for both the silt loam and sand used in the study). Each mesocosm was then planted with monocultures of one of three, rooted, emergent aquatic plant species: cutgrass (*Leersia oryzoides* L. Sw.), broad-leaf cattail (*Typha latifolia* L.) and American bur-reed (*Sparganium americanum* Nutt.). Each plant species was represented by three replicate mesocosms, with three unvegetated mesocosms serving as controls. All plants and sediment used in the study were collected from the University of Mississippi Field Station (UMFS), Abbeville, MS. Areas used for plant collection have received no pesticide application in the last 30 years since the University took ownership of the property in 1985. An

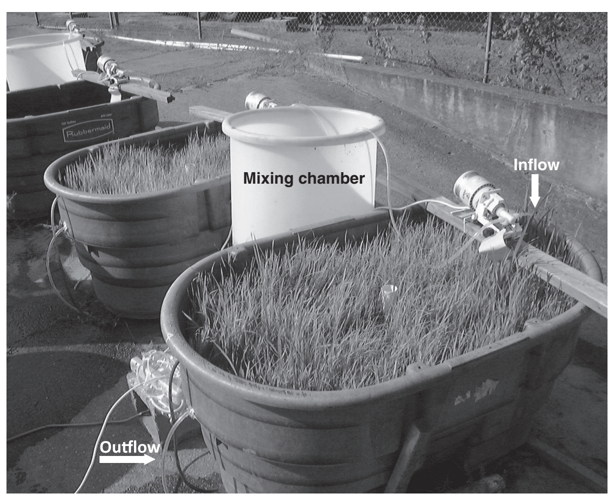

Fig. 1 – Mesocosm setup with pesticide mixing chamber, piston pump for pesticide delivery, inflow tubing, and outflow tubing for collection of sample.

equilibration period of approximately six weeks was allowed for the planted mesocosms prior to initiation of testing which began in mid-June.

1.1. Simulated runoff

Pesticide stocks (1000 mg/L) for atrazine, metolachlor, and diazinon were each prepared from commercial formulations using Bicep II Magnum™ (33% atrazine and 26.1% S-metolachlor) and Diazinon 4E™ (47.5% diazinon). Mixing chambers were prepared with a calculated volume of well water and pesticide stocks for target concentrations of atrazine (20 μg/L), S-metolachlor (16 μg/L), and diazinon (10 μg/L) to deliver a constant exposure for 4 hr. Pesticide-enriched water was pumped into individual mesocosms using Fluid Metering Inc. (FMI™) piston pumps, models QD-1 and QD-2 connected with 0.95 cm (o.d.) × 0.64 cm (i.d.) vinyl tubing to simulate a storm runoff event. Water traveled through each mesocosm, exiting at the surface through a discharge hose (0.95 cm × 0.64 cm) at the opposite end of the mesocosm. Pump flow rates were adjusted so that all mesocosms maintained a 4 hr hydraulic retention time (HRT). Mesocosms were exposed to flowing pesticide-enriched water for 4 hr, then exposed to flowing non-amended well water for an additional 4 hr to simulate flushing effects of a second storm event. Pumps were turned off after 8 hr, ceasing any outflow.

1.2. Sample collection and analysis

Water samples were collected in 1 L amber glass bottles before pesticide exposure and at 1.25, 1.5, 2, 3, 4, 5, 6, 7, 8, 12, 24, 48, 72, and 168 hr after pesticide exposure from an outflow hose at the opposite end from the inflow. When water was not flowing through mesocosms (12–168 hr), samples were collected by dipping bottles at the water surface by the outflow hose. All water samples were analyzed for concentrations of atrazine, S-metolachlor, and diazinon using an Agilent™ Model 7890A gas chromatograph (GC) equipped with dual Agilent™ 7683B series autoinjectors, dual split-splitless inlets, dual capillary columns, an Agilent™ ChemStation, and the autoinjector set at 1.0 μL injection volume for all pesticide analyses (Agilent Technologies, Wilmington, DE). Additionally, the GC was equipped with two micro-electron capture detectors (μECDs). The analytical column used for atrazine and S-metolachlor was an Agilent™ HP 5MS capillary column, 30 m × 0.25 mm i.d. × 0.25 μm film thickness. Diazinon utilized an Agilent™ HP 1MS capillary column, 30 m × 0.25 mm i.d. × 0.25 μm film thickness. Column oven temperatures for atrazine and S-metolachlor were initially at 75°C for 1 min; ramp at 10° to 175°; hold at 175° for 15 min; ramp at 10° to 225° and hold for 15 min. Diazinon column oven temperatures were initially at 85°C for 1 min; ramp at 25° to 185° and hold for 20 min. Retention times for atrazine, S-metolachlor, and diazinon were 14.79, 22.70, and 11.20 min, respectively.

Influent pesticide loads were calculated by multiplying the inflow concentration (μg/L) by the FMI™ pump rate for each mesocosm during the given time. Effluent loads were estimated by multiplying outflow concentrations by the amount of water exiting each tub over associated time periods. Percent decrease in pesticide loads exiting mesocosms after the 4 hr simulated runoff and percent of pesticide load released from mesocosms during the 4 hr clean water flush were calculated as the difference from the total influent loads and amount of each pesticide in the effluent over the given time frames. In order to help evaluate the potential of vegetation to mitigate atrazine, S-metolachlor, and diazinon from the water column, pesticide aqueous half-lives were calculated during times of stagnation (12–168 hr) using the equation $\ln(2)/k_2$, where k_2 represents the pesticide depuration rate constant. This constant was determined by plotting the ln of the aqueous pesticide mass as a function of time, then determining the slope using linear regression analysis (Bennett et al., 2005). Additionally, specific pesticide removal rates were determined for each plant species by plotting the natural $\log(C/C_o)$ *versus* time, where C is the pesticide concentration at a specific time point and C_o is the pesticide inflow concentration. Significant differences in effluent pesticide loads, half-lives, and removal rates between treatments were determined using analysis of variance and Student's *t*-test between individual treatments, with an alpha level of 0.05. Statistical analyses were completed with JMP 8.0 software (SAS, Cary, NC).

2. Results

Mean atrazine load decreases after the initial 4 hr runoff ranged from 25% ± 16% (*S. americanum*) to 53% ± 1.9% in *T. latifolia* (Table 1). Following the 4 hr non-amended water flushing event, percent pesticide loads released ranged from 29% ± 6.1% (*T. latifolia*) to 64% ± 11% (*S. americanum*). No significant differences existed among the different plant species or between the plants and the controls with regard to atrazine mitigation within the first 4 hr of exposure. *Typha latifolia* was significantly ($p = 0.0349$) more efficient than *S. americanum* at retaining atrazine during the flush period (5–8 hr). *Typha*

Table 1 – Mean loads (mg) and percent decrease (%) of loads of atrazine entering and exiting three replicate mesocosms standard error (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	0.99 ± 0.32 (0.61–1.63)	1.42 ± 0.32 (0.78–1.78)	1.17 ± 0.41 (0.37–1.75)	1.12 ± 0.38 (0.37–1.63)
0–4 hr outflow (mg)	0.65 ± 0.07 (0.54–0.78)	0.68 ± 0.17 (0.38–0.99)	0.56 ± 0.20 (0.16–0.83)	0.68 ± 0.15 (0.38–0.86)
5–8 hr flush outflow (mg)	0.57 ± 0.08 * (0.47–0.73)	0.52 ± 0.07 (0.38–0.60)	0.39 ± 0.16 * (0.07–0.55)	0.49 ± 0.15 (0.19–0.69)
% decrease 0–4 hr	25 ± 16	51 ± 6.1	53 ± 1.9	28 ± 17
% released during flush	64 ± 11	39 ± 4.8	29 ± 6.1	46 ± 4.8

* Indicates significant differences between plant species; Ranges of replicates are included in parentheses under mean ± SE values.

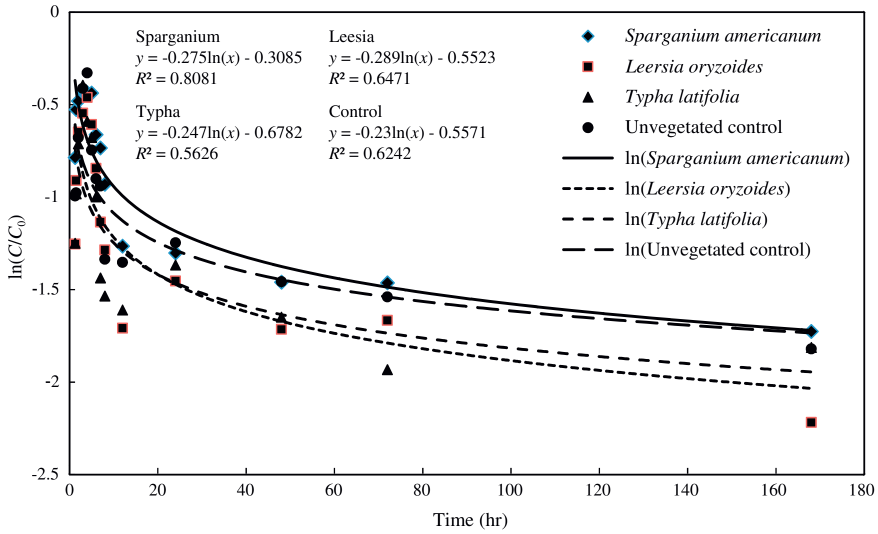

Fig. 2 – Removal rate constants of atrazine for *Sparganium americanum*, *Leersia oryzoides*, *Typha latifolia*, and the unvegetated control.

latifolia released 29% ± 6.1% of atrazine during the flush, while *S. americanum* lost 64% ± 11%. In terms of atrazine mitigation effectiveness, results were *T. latifolia* > *L. oryzoides* > unvegetated control > *S. americanum* (Table 1). Atrazine aqueous half-lives showed no significant differences, ranging from 10 ± 2.7 days (*S. americanum*) to 12 ± 10 days (unvegetated control). Likewise, there were no significant differences in removal rate constants, ranging from 0.23/hr (unvegetated control) to 0.289/hr (*L. oryzoides*) (Fig. 2).

No significant differences existed among different plant species and the unvegetated control with regard to mean S-metolachlor load decreases after 4 hr. Mean decreases ranged from 26% ± 16% (unvegetated control) to 54% ± 8.5% (*L. oryzoides*) (Table 2). Likewise, no significant differences existed between the unvegetated controls and different plant species for the mean percentage S-metolachlor lost after the flushing event. Mean percent losses during flush ranged from 29% ± 2.1% (*L. oryzoides*) to 50% ± 9.3% (*S. americanum*). Aqueous half-lives of metolachlor in mesocosms showed no significant differences among each other or against the control, ranging from 4.8 ± 1.8 days (*T. latifolia*) to 7.1 ± 1.0 days (*L. oryzoides*). No significant difference was noted between removal rate constants, since they ranged only from 0.324/hr (*L. oryzoides*) to 0.491/hr (*T. latifolia*) (Fig. 3).

No significant differences in mean percentage decrease of diazinon load following the initial 4 hr runoff were noted, which ranged between 17% ± 20% (unvegetated control) to 55% ± 8.2% (*L. oryzoides*) (Table 3). Further, no significant differences were noted in the mean percentage diazinon loss following the 4 hr flush. Loss during the flush ranged from 26% ± 3.8% (*L. oryzoides*) to 51% ± 13% (*S. americanum*) (Table 3). Aqueous diazinon half-lives were not significantly different from each other, ranging from 3.5 ± 2.2 days (unvegetated control) to 5.5 ± 1.6 days (*L. oryzoides*). No significant differences were noted in diazinon removal rate constants, ranging from 0.288/hr (*L. oryzoides*) to 0.42/hr (unvegetated control) (Fig. 4).

For all three pesticides examined, *L. oryzoides* and *T. latifolia* retained more mass during the initial 4 hr exposure and the following 4 hr flush. *Sparganium americanum* and the unvegetated control were consistently less efficient at pesticide mitigation. While no statistically significant differences were noted, this was likely due to the greater variability in data from the unvegetated control and *S. americanum* (Tables 1–3).

3. Discussion

Of the plant species examined, both *T. latifolia* and *L. oryzoides* decreased initial concentrations of atrazine, S-metolachlor, and diazinon ≥50% within the first 4 hr. Likewise, these two plant species consistently had the lowest percentage of pesticide

Table 2 – Mean loads (mg) and percent decrease (%) of loads of S-metolachlor entering and exiting three replicate mesocosms (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	1.52 ± 0.31 (0.97–2.03)	1.72 ± 0.25 (1.21–2.00)	1.36 ± 0.43 (0.52–1.94)	1.26 ± 0.40 (0.53–1.92)
0–4 hr outflow (mg)	0.94 ± 0.04 (0.88–1.01)	0.82 ± 0.24 (0.44–1.25)	0.68 ± 0.23 (0.24–1.02)	0.81 ± 0.14 (0.53–0.99)
5–8 hr flush outflow (mg)	0.70 ± 0.03 (0.66–0.76)	0.49 ± 0.05 (0.40–0.56)	0.42 ± 0.14 (0.14–0.62)	0.50 ± 0.11 (0.29–0.64)
% decrease 0–4 hr	32 ± 16	54 ± 8.5	51 ± 2.1	26 ± 16
% released during flush	50 ± 9.3	29 ± 2.1	30 ± 1.5	44 ± 7.9

Ranges of replicates are included in parentheses under mean ± SE values.

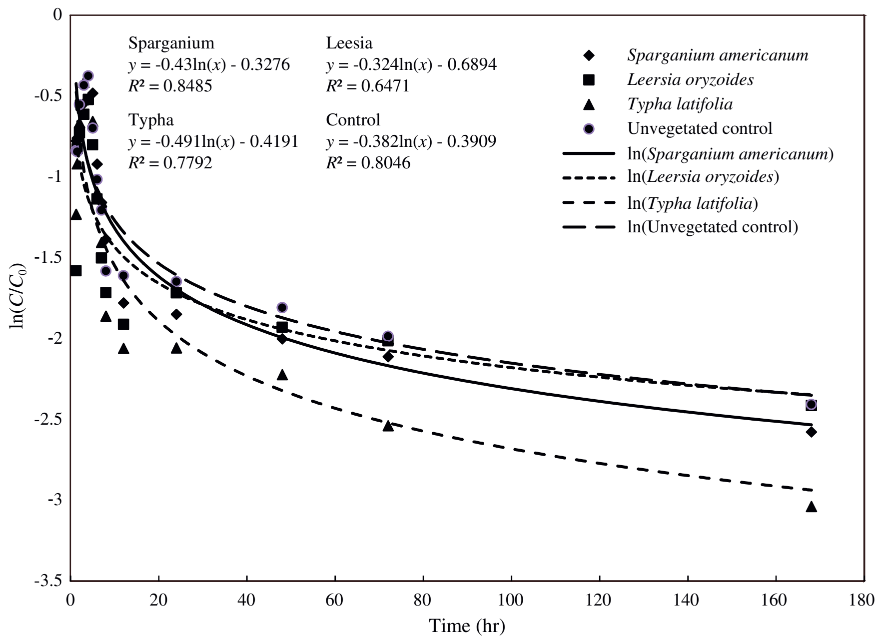

Fig. 3 – Removal rate constants of S-metolachlor for *Sparganium americanum*, *Leersia oryzoides*, *Typha latifolia*, and the unvegetated control.

released following the flush period. *Typha latifolia* has been extensively studied as a species for phytoremediation and is one of the most commonly used species in constructed wetlands (Vymazal, 2013). Marecik et al. (2012) reported that 90% of the initial atrazine concentrations (3.5 and 5 mg/L) were reduced after 50 days in hydroponic studies involving *T. latifolia*. Unlike the current study, Moore et al. (2013) reported a significant decrease in atrazine load in mesocosms planted with *T. latifolia*; however, that study utilized a 6 hr HRT with a clean water flush occurring approximately 42 hr after initial dosing had ceased. Cejudo-Espinosa et al. (2009) examined the ability of *T. domingensis* roots to remediate atrazine at concentrations from 4.17 to 30 mg/L. They determined rapid accumulation, vigorous growth, and abundant biomass of *T. domingensis* roots made this plant a successful species for phytoremediation of atrazine.

Unlike *T. latifolia, L. oryzoides* has not been extensively studied for its pesticide mitigation capacity. Moore et al. (2013) determined that the cool season grass was effective at mitigating atrazine, in addition to diazinon and permethrin. As was the case for *T. latifolia,* less mitigation efficiency for *L. oryzoides* and atrazine during the initial dose (51% ± 6%) was observed in the current study than in Moore et al. (2013) (65% ± 2%). Again, this was likely due to the (1) increased HRT from 4 to 6 hr and (2) delay in clean water flush from immediately post-amendment to 42 hr post-amendment in the study by Moore et al. (2013). While little work on pesticide mitigation with *Leersia* has been reported, several studies have examined the plant's ability to mitigate and partition nutrients (Pierce et al., 2009), chromium (Wang et al., 2012a), and arsenic (Ampiah-Bonney et al., 2007).

Even fewer pesticide studies have examined the capacity of *S. americanum* for phytoremediation. Moore et al. (2009) reported mass retentions of 67%–78% of permethrin (pyrethroid insecticide) in mesocosms with a 4 hr HRT. While this is more than the 39% initial retention reported in the current study for another strongly sorbed pesticide (diazinon), results from Moore et al. (2009) were likely a function of the physicochemical properties of the pyrethroid. A later study by Moore et al. (2013) agrees with current findings, in that *S. americanum* was much less efficient at atrazine and diazinon mitigation than *L. oryzoides*. In the current study, *S. americanum* initially

Table 3 – Mean loads (mg) and percent decrease (%) of loads of diazinon entering and exiting three replicate mesocosms (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	0.43 ± 0.09 (0.32–0.62)	0.44 ± 0.07 (0.37–0.58)	0.37 ± 0.12 (0.14–0.52)	0.33 ± 0.11 (0.14–0.51)
0–4 hr outflow (mg)	0.25 ± 0.07 (0.12–0.35)	0.19 ± 0.03 (0.14–0.23)	0.18 ± 0.06 (0.07–0.26)	0.23 ± 0.03 (0.17–0.26)
5–8 hr flush outflow (mg)	0.21 ± 0.04 (0.13–0.25)	0.11 ± 0.01 (0.11–0.12)	0.11 ± 0.04 (0.04–0.17)	0.14 ± 0.02 (0.10–0.18)
% decrease 0–4 hr	39 ± 18	55 ± 8.2	51 ± 1.0	17 ± 20
% released during flush	51 ± 13	26 ± 3.8	31 ± 1.5	50 ± 12

Ranges of replicates are included in parentheses under mean ± SE values.

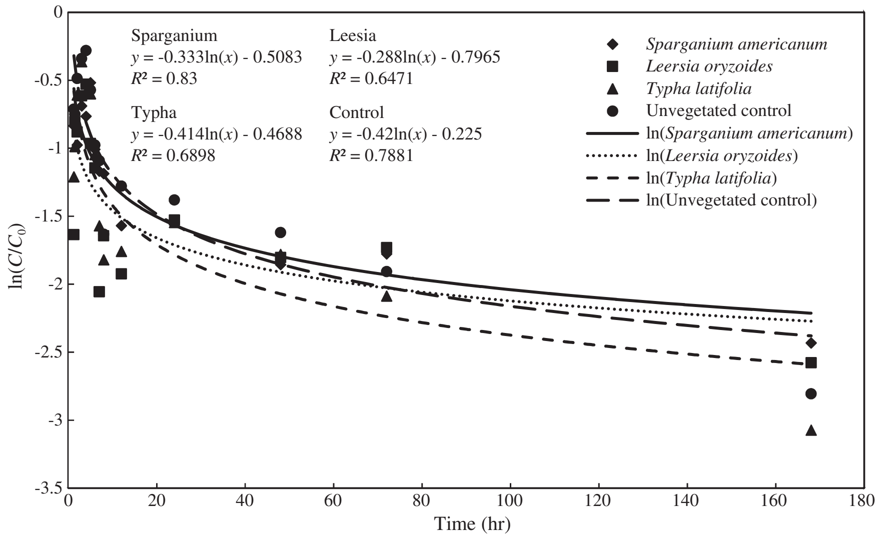

Fig. 4 – Removal rate constants of diazinon for *Sparganium americanum*, *Leersia oryzoides*, *Typha latifolia*, and the unvegetated control.

decreased atrazine and diazinon by 25% and 39%, respectively, after a 4 hr HRT. Compared to a 6 hr HRT, Moore et al. (2013) reported initial atrazine and diazinon load decreases of 59% and 64%, respectively, in *S. americanum*.

Previous research on metolachlor mitigation demonstrated that 68% of the trapping efficiency of a *Buchloe dactyloides* (buffalo grass) filter strip was attributed to chemical sorption (Krutz et al., 2004). In a later study, Krutz et al. (2009) determined that metolachlor loss after simulated rainfall was 1.4 times lower in rye cover microplots as opposed to microplots with no cover crop. Based on their soil sorption coefficients (K_{oc}), both atrazine and metolachlor are classified as "moderately sorbed" pesticides ($100 < K_{oc} < 1000$) (Rivard, 2003; Arora et al., 2010). In their literature review, Arora et al. (2010) reported that 45% of moderately sorbed pesticides were retained by vegetated buffer strips. Staddon et al. (2001) determined vegetated buffer strips had greater metolachlor sorption capacity than did bare soils. Metolachlor half-life was 10 days in vegetated buffer strips, as opposed to 23 days in bare soils. This was attributable to increased organic matter and microbial activity in the vegetated buffer strips (Staddon et al., 2001). The HRT utilized in the current study was relatively short—4 hr.

Mitigation of diazinon using aquatic macrophytes has been reported with various levels of success. Sorption to plant material accounted for 43% of the measured mass of diazinon in a Mississippi Delta constructed wetland simulated runoff study (Moore et al., 2007). Within that same study, 23% of the measured diazinon mass was associated with sediment sorption. Considered "strongly sorbed" because of its K_{oc}, Arora et al. (2010) determined that 70% of pesticides with such K_{oc} values (>1000) are retained by vegetated buffer strips. However, Moore et al. (2013) saw no significant difference in overall diazinon load retention between *T. latifolia, L. oryzoides,* and *S. americanum* in mesocosms with a 6 hr HRT. Nor was there any significant difference in pesticide load retention between vegetated systems and unvegetated controls (Moore et al., 2013). Lizotte et al. (2011) reported clear differences in survival of the amphipod *Hyalella azteca* in vegetated wetland sediments *versus* those sediments containing no vegetation exposed to diazinon and permethrin.

Other studies have examined different pesticide mitigation efficiencies of the same plant species used in the current research. A high methyl parathion removal efficiency in water and sediment was noted in mesocosms planted with *T. latifolia*. This study revealed methyl parathion half-lives were nearly eight times less in *T. latifolia* systems as opposed to unvegetated controls (Amaya-Chávez et al., 2006). Removal rate of lambda-cyhalothrin by *T. latifolia* was determined to be 0.116/day in greenhouse studies with simulated storm runoff (Lema et al., 2014).

Similarly, different plant species have been used to study mitigation of some of the pesticides used in the current study. *Acorus calamus* decreased 57% of the initial atrazine amendment (3.5 mg/L) after 6 days (Marecik et al., 2012). In hydroponic studies, Wang et al. (2012b) demonstrated the importance of emergent plants in decreasing atrazine levels in water. Using *Iris pseudacorus, Lythrum salicaria,* and *A. calamus*, between 88% and 97% of atrazine was removed in experimental systems with a pesticide half-life from 4.6–6.3 days, depending on the plant species (Wang et al., 2012b). In unvegetated systems, atrazine removal was much less (41%–48%), while half-lives were at least four times greater (Wang et al., 2012b). Switchgrass (*Panicum virgatum*) is another species reported capable of mitigating atrazine. Murphy and Coats (2011) and Albright et al. (2013) reported that switchgrass was capable of sorbing and detoxifying atrazine, while levels of the pesticide in leaf material peaked between 3 and 4 days. In a Mississippi Delta constructed wetland simulated runoff event, Locke et al. (2011) reported a decrease of 32% in atrazine surface water concentrations 9 days following the event initiation. The authors concluded that the decrease was due to either degradation or sorption to soil or wetland flora which was dominated by *Alternanthera philoxeroides* (alligator weed) and *Echinocloa crus-galli* (barnyard grass). In a 0.11 km^2 constructed wetland with *Phragmites, Eleocharis, Schloenoplectus, Baumea,* and *Typha,* Page et al. (2010) reported 60% atrazine removal, suggesting that sorption occurred onto organic sediments and biofilms within the first 2 days of contact in a system with a 7 days HRT. Although the HRT in the current study was only 4 hr, results similarly demonstrate the importance of relatively rapid sorption within 2 days of exposure, if sorption is to occur.

4. Conclusions

Leersia oryzoides and *T. latifolia* were both more effective at initially decreasing pesticide loads, as well as minimizing additional pesticide loss during the flushing event, than *S. americanum* and the unvegetated control. Because *L. oryzoides* and *T. latifolia* are capable of surviving seasonal or perennial flooding, in addition to their ubiquitous presence within the continental US, both species are feasible options to incorporate into a phytoremediation plan to mitigate atrazine, S-metolachlor, and diazinon. Although *S. americanum* was not as efficient at mitigation as *L. oryzoides* and *T. latifolia,* the plant species can still be useful in the overall mitigation design of vegetated remediation systems utilizing plant mixtures.

Although pesticide partitioning studies with various plant species may generate variable data, most scientists agree that the presence and use of vegetation is beneficial to contaminant removal (Wilson et al., 2000a, 2000b; Page et al., 2010; Elsaesser et al., 2011). Herbicides such as atrazine and S-metolachlor which have logK_{ow} values of <3 are believed to be able to move through lipid layers of plant membranes, while still soluble enough to travel in cell fluids (Cedergreen et al., 2005). Some phytoremediation systems may require several days for herbicides to be removed through biodegradation and other processes (Page et al., 2010). Even though plant sorption may take place, water quality changes (*e.g.* pH shifts) as a result of episodic storm events may cause herbicide desorption from plants and transport to downstream aquatic ecosystems. In fact, Brogan and Relyea (2013a, 2013b) suggest that the presence of aquatic vegetation alters the water quality in such a way as to encourage pesticide partitioning. The general conclusion is that many processes can influence pesticide removal through phytoremediation in aquatic systems (Vymazal and Březinová, 2015). Further evaluation of individual and multiple interacting processes will allow scientists to continue refining management practices to reduce the amount of pesticides transported in agricultural storm and irrigation runoff.

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