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Aqueous pesticide mitigation efficiency of *Typha latifolia* (L.), *Leersia oryzoides* (L.) Sw., and *Sparganium americanum* Nutt.

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HIGHLIGHTS

- *L. oryzoides* most effective at mitigating three pesticides studied.
- *T. latifolia* capable of significantly decreasing atrazine load.
- Flushing from additional simulated rainfall impacts pesticide mitigation.

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ABSTRACT

Agricultural pesticide use is necessary to help meet the increased demand for a safe and secure food supply for the United States, as well as the global community. Even with proper application and careful management, the possibility of pesticide leaching and detachment in runoff still exists following certain storm events. Several different management practices have been designed to reduce the impacts of pesticides on aquatic receiving systems. Many such practices focus on the use of vegetation to slow runoff and allow for sorption of the various contaminants. Three common drainage ditch macrophytes, *Leersia oryzoides* (cutgrass), *Typha latifolia* (cattail), and *Sparganium americanum* (bur-reed) were assessed for their ability to reduce effluent loads of atrazine, diazinon, and permethrin in simulated agricultural runoff water in 379 L individual mesocosms. Of the three macrophytes examined, *L. oryzoides* was the most effective at mitigating atrazine, and permethrin. *L. oryzoides* and *T. latifolia* significantly reduced overall atrazine loads (45 ± 7%, $p = 0.0073$ and 35 ± 8%, $p = 0.0421$, respectively) when compared to unvegetated controls (13 ± 20%). No significant differences in overall diazinon load retention were noted between plant species. Each plant species significantly decreased the initial load (after 6 h) of *trans*-permethrin, while both *L. oryzoides* and *T. latifolia* significantly reduced the overall *trans*-permethrin loads (88 ± 5%, $p = 0.0022$ and 88 ± 5%, $p = 0.0020$, respectively) when compared to unvegetated controls (68 ± 8%). Reversible adsorption of atrazine and diazinon to plants, noted during the flushing events, was greater than that observed in either *cis*- or *trans*-permethrin. These results demonstrate the ability of native ditch vegetation to mitigate pesticides associated with agricultural runoff. Likewise, they provide farmers and action agencies with supportive data for selection of vegetation in drainage ditches used as management practices.

1. Introduction

The Lower Mississippi River region's dominant land use is agriculture, accounting for over $6.8 billion in annual revenues (Black et al., 2004). To sustain national and international demands for food and fiber, much of the region's 8.9 million ha are treated with various pesticides throughout the planting and growing seasons. Additionally, some 2.4 million ha of irrigated farmland in the region use 4.5 million m^3 of surface water daily to maintain crop health (Black et al., 2004). The mixture of pesticides and water, whether through storm or irrigation runoff, has the potential to harm downstream aquatic resources.

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], a broadleaf herbicide, ranks second in use in the United States only behind glyphosate, with an estimated 33–35 million kg of active ingredient applied annually (Grube et al., 2011). Results from a 1998 study of over 100 samples collected from Midwestern US streams indicated that atrazine was detected in all samples at a median concentration of 3.97 $\mu g\,L^{-1}$ and a maximum concentration of 224 $\mu g\,L^{-1}$ (Battaglin et al., 2000). The US Geological Survey's National Water Quality Assessment (NAWQA) Program reported that out of approximately 2000 samples, atrazine had an 89.93% detection rate, while close to 9% of samples were

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$>1\ \mu g\ L^{-1}$ (Gilliom et al., 2006). Concentrations as high as $691\ \mu g\ L^{-1}$ have been reported in stream samples following storm events soon after planting (Langan et al., 1993).

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. In the early 2000s, diazinon ranked third among the most commonly used OP insecticides with 1.8–2.5 million kg of active ingredient applied annually (Grube et al., 2011). Following the phase out of non-agricultural diazinon products at the end of 2004, its use dropped to approximately 455 000 kg of active ingredient annually in the US based on 2006–2007 market estimates (Grube et al., 2011). Data from the NAWQA Program indicated a 13.34% detection rate of diazinon from among 1990 collected water samples, with a maximum concentration of $3.8\ \mu g\ L^{-1}$ (Gilliom et al., 2006). Even with reduction in use, diazinon still appears in surface water samples, especially in intensive agricultural areas in California (de Vlaming et al., 2000, 2004). Some 57 000 kg of active ingredient was applied in California during 2010 to a variety of crops including almonds, broccoli, cherries, spinach, and processing tomatoes (California Department of Pesticide Regulation, 2011).

Permethrin [3-phenoxybenzyl-(1*RS*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] is part of a class of pyrethroid insecticides designed to replace OP insecticides. Because of its physicochemical properties such as solubility and relatively short environmental half-life, permethrin is not detected in surface water as often as atrazine or diazinon. NAWQA data reported that, out of some 2000 samples, there was less than a 0.2% detection rate for *cis*-permethrin, with a maximum observed concentration of $0.019\ \mu g\ L^{-1}$ (Gilliom et al., 2006). Peak permethrin expected environmental concentrations range from $0.54\ \mu g\ L^{-1}$ in California alfalfa fields to $5.32\ \mu g\ L^{-1}$ in Maine potato fields (USEPA, 2006a). California alone, in 2010, applied 133 845 kg of permethrin active ingredient on over 236 000 ha of cropland (California Department of Pesticide Regulation, 2011).

Many best management practices (BMPs) have been suggested to remediate pesticides associated with storm or irrigation runoff. A common factor among most of the practices is utilization of vegetation, whether it be in a constructed wetland, drainage ditch, grassed waterway, buffer or stiff-grass hedge. Improved financial and research investments are being made in the field of phytoremediation which uses plants to help remediate contaminated soil and water resources (Suresh and Ravishankar, 2004). Several recent studies have demonstrated the ability of emergent vegetation to mitigate pesticides (Anderson et al., 2011; Elsaesser et al., 2011; Locke et al., 2011). The challenge for scientists is to search for specific plant(s) species which provide the greatest remediation potential in a wide array of environmental circumstances. For the current study, three emergent macrophytes were chosen for evaluation: *Typha latifolia* L. (broad-leaved cattail), *Sparganium americanum* Nutt. (American bur-reed), and *Leersia oryzoides* (L.) Sw. (rice cutgrass). *Typha* is ubiquitous across the entire United States and all ten provinces of Canada (USDA, 2013). The perennial, rhizomatous *T. latifolia* can tolerate perennial flooding as well as reduced soil conditions (Stevens and Hoag, 2006). *Sparganium* is found in 35 states of the continental US and at least seven Canadian provinces (USDA, 2013). A relative of the cattail but shorter in stature, leaves of the perennial *Sparganium* can be stiff and erect, but they also will become limp and float on the water surface in moving water situations (Favorite, 2006). As with *Typha*, *Leersia* is ubiquitous across the continental United States and is located in eight Canadian provinces (USDA, 2013). This rhizomatous, cool-season, perennial grass is valuable for erosion control because of its extensive root system. Mature *Leersia* can tolerate seasonal to permanent flooding situations (Darris and Bartow, 2004).

Bouldin et al. (2004) reported that *L. oryzoides* occurred in 25–80% of drainage ditches surveyed in the lower Mississippi Delta, while *T. latifolia* was present in 13–40%. It is plausible, then, given the numerous examples of atrazine, diazinon, and permethrin being detected in water samples of agricultural watersheds, that these pesticides could come into contact with drainage ditch vegetation. The objective of the current study was to examine *T. latifolia*, *S. americanum*, and *L. oryzoides* for their individual ability to mitigate atrazine, diazinon, and permethrin concentrations in simulated storm-induced agricultural runoff water.

2. Materials and methods

Using twelve, 379 L Rubbermaid oval high density polyethylene containers (1.32 m × 0.70 m × 0.66 m), mesocosms were constructed by layering 16 cm of Lexington silt loam atop a base of 22 cm of sand. Mesocosms were then planted with plant stocks from one of three, rooted, emergent aquatic plant species: cutgrass (*L. oryzoides* L. Sw.), broad-leaf cattail (*T. latifolia* L.) or bur-reed (*S. americanum* Nutt.). Plant stocks and sediment were both collected from the University of Mississippi Field Station, Abbeville, MS. Three replicate mesocosms were used for each plant species, as well as unvegetated sediment controls. All mesocosms were randomly arranged. Plants within the mesocosms were allowed 6 wk to equilibrate prior to test initiation.

2.1. Simulated runoff

Pesticide stocks ($1000\ mg\ L^{-1}$) for atrazine, diazinon, and permethrin (Table 1) were each prepared from commercial formulations using Atrazine 4L, Diazinon 4E, and Hi-Yield 38 Plus (permethrin). Mixing chambers were prepared with a calculated volume of well water and target concentrations of atrazine ($20\ \mu g\ L^{-1}$), diazinon ($20\ \mu g\ L^{-1}$), and permethrin ($10\ \mu g\ L^{-1}$) to deliver a constant exposure for 6 h. Prior to exposure, water depth in each mesocosm (ranging from 8.1–22 cm) was reduced to 2/3 of the original volume (ranging from 5.4–15 cm depth) to simulate hydraulic effects of low-grade weirs commonly used in Mississippi Delta drainage systems (Kröger et al., 2008).

Pesticide-enriched water was pumped into individual mesocosms using Fluid Metering Incorporated (FMI) piston pumps, models QD-1 and QD-2 connected with 0.95 cm (od) × 0.64 cm (id) vinyl tubing to simulate a storm runoff event. Water travelled through each mesocosm, exiting at the surface through a clear vinyl 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 6 h hydraulic retention time (HRT). Mesocosms were

Table 1

Selected physicochemical parameters of atrazine, diazinon, and permethrin.

	Atrazine	Diazinon	Permethrin
Molecular weight ($g\ mol^{-1}$)[a]	215.7	304.35	391.3
Vapor pressure (mm Hg)[a]	3.0×10^{-7}	7.28×10^{-7}	3.38×10^{-7}
Water solubility ($mg\ L^{-1}$)[a]	33	40	0.2
log K_{ow}[a,b]	2.68	3.3	6.1
log K_{oc}[b,c]	1.4–2.2	3.0–3.3	4.0–4.9
Photolysis ($T_{1/2}$) (d)[c,d,e,f]	335	88	110
Hydrolysis ($T_{1/2}$) (d)[g,h]	244	138	37.7

[a] EXTOXNET (1996).

[b] USDA ARS (1995).

[c] Ciba-Geigy Corporation (1994).

[d] Solomon et al. (1996).

[e] Frank et al. (1991).

[f] Laskowski (2002).

[g] Li and Feldbeck (1972).

[h] Kegley et al. (2007).

exposed to flowing pesticide enriched water for 6 h, allowed to sit undisturbed for 42 h, then exposed to flowing unamended well water for an additional 6 h to simulate flushing effects of a second storm event. Individual discharge hoses were placed in catchment basins (208 L) to collect remaining outflow.

2.2. Sample collection and analysis

Water samples were collected in 1 L amber glass bottles before pesticide exposure and at 2, 2.5, 3, 3.5, 4, 5, 6, 8, 10, 12, 24, 48, 49, 51, 54, 72 and 168 h after pesticide exposure from a clear vinyl outflow hose at the opposite end from the inflow. When water was not being pumped through mesocosms, samples were collected by dipping bottles at the water surface by the outflow hose. All water samples were analyzed for concentrations of atrazine, diazinon, and permethrin using an Agilent Model 7890 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. Additionally, the GC was equipped with two micro-electron capture detectors. The analytical column used for atrazine was an Agilent HP 5MS capillary column, 30 m × 0.25 mm id × 0.25 μm film thickness. Both diazinon and permethrin utilized an Agilent HP 1MS capillary column, 30 m × 0.25 mm i.d. × 0.25 μm film thickness. Column oven temperatures for atrazine were initially at 75 °C for 1 min; ramp at 10–175°; held at 175° for 15 min; ramp at 10–225° and held for 15 min. Diazinon column oven temperatures were initially at 85 °C for 1 min; ramp at 25–185° and held for 20 min. Column oven temperatures for permethrin were initially at 75 °C for 1 min; ramp at 35–230° and held for 15 min. Retention times for atrazine, diazinon, *cis*-permethrin and *trans*-permethrin were 14.79, 11.20, 15.43, and 15.89 min, respectively. Permethrin concentrations were reported separately as either the *cis*- or *trans*-isomer, since the former is considered more toxic than the latter (EMEA, 1998).

Water quality parameters (dissolved oxygen, temperature, pH, and conductivity) were measured in each mesocosm before the experiment, and at 4, 9, 12, 24, 48, 72, and 168 h after initiation of the experiment using an Oakton pH meter and YSI 85 multiprobe meter. Influent pesticide loads were calculated by multiplying the inflow concentration ($\mu g\ L^{-1}$) 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 6 h simulated runoff, percent of pesticide load released from mesocosms during the clean water flush, and total percentage decrease in pesticide loads (2–168 h) exiting mesocosms were calculated from the total influent loads and amount of each pesticide in the effluent over the given time frames. In order to evaluate the potential of vegetation to mitigate atrazine, diazinon, and permethrin from the water column during times of stagnation, percent decreases in concentration were calculated for periods when water was not flowing through the mesocosms (6–48 and 54–168 h after initiation of the experiment) when inflow and effluent loads could not be calculated. Significant differences in effluent pesticide loads between treatments were determined using analysis of variance (ANOVA) between individual treatments, with an alpha level of 0.05.

3. Results

Dissolved oxygen and pH levels within mesocosm replicates were similar in vegetated systems, while unvegetated controls had increased levels of both water quality parameters. Mean dissolved oxygen concentrations in vegetated mesocosms ranged from 1.2 ± 0.47 mg L^{-1} (*L. oryzoides*) to 3.9 ± 1.4 mg L^{-1} (*T. latifolia*). Unvegetated controls had a mean dissolved oxygen concentration of 7.8 ± 1.2 mg L^{-1}. Ranges of pH were 5.7–6.3 (*L. oryzoides*) to 5.7–6.7 (*S. americanum*), while unvegetated controls had pH ranging from 5.8–8.7.

Mean atrazine load decreases after the initial 6 h runoff ranged from 51 ± 6% (unvegetated control) to 65 ± 2% in *L. oryzoides* (Table 2). Following the 6 h unamended water flushing event, percent loads released ranged from 19 ± 6% (*L. oryzoides*) to 38 ± 16% (unvegetated control). Total percentage load decreases among the different plant species were 31 ± 4, 35 ± 8, and 45 ± 7% for *S. americanum*, *T. latifolia*, and *L. oryzoides*, respectively (Fig. 1). The unvegetated control had a total percentage load decrease of 13 ± 20%, which was significantly different from *T. latifolia* ($F_{(3,8)} = 4.4254$; $p = 0.0411$) and *L. oryzoides* ($p = 0.0073$).

No significant differences existed among different plant species and the unvegetated control with regard to mean diazinon load decreases after 6 h. Mean decreases ranged from 41 ± 45% (*T. latifolia*) to 69 ± 4% (*L. oryzoides*) (Table 3). Likewise, no significant differences existed between the unvegetated controls and different plant species for the mean percentage diazinon lost after the flushing event or the total percentage load decrease. Overall percentage load decreases ranged from 25 ± 47% (*T. latifolia*) to 61 ± 7% (*L. oryzoides*).

No significant differences in mean percentage decrease of *cis*-permethrin load following the initial 6 h runoff were noted, which ranged between 73 ± 7% (unvegetated control) to 88 ± 2% (*T. latifolia*) (Table 4). Further, no significant differences were noted in the total percentage load decrease, especially with the minimal decrease from each treatment following the 6 h flush. Total percentage load decreases ranged from 72 ± 6% (unvegetated control) to 87 ± 1% (*T. latifolia*) (Table 4).

S. americanum, *L. oryzoides*, and *T. latifolia* each demonstrated a significant difference in mean percentage decrease of *trans*-permethrin load following the initial 6 h runoff ($F_{(3,8)} = 10.5662$; $p = 0.0404$, 0.0017, and 0.0011, respectively) when compared to the unvegetated control. Mean percentage decreases ranged from 70 ± 6% (unvegetated control) to 89 ± 6% (*T. latifolia*) (Table 5). As with *cis*-permethrin, there was little variation and no significant differences in the mean percentage of *trans*-permethrin load released following the 6 h flushing event. However, both *L. oryzoides* ($p = 0.0022$) and *T. latifolia* ($p = 0.0020$) were significantly better at decreasing the percentage of total effluent load of *trans*-permethrin when compared to the unvegetated control ($F_{(3,8)} = 9.1543$) (Table 5).

4. Discussion

Of the three plant species examined, *L. oryzoides* was most effective at mitigating atrazine, diazinon, *cis*-permethrin and *trans*-permethrin. This cool season grass is better known for its erosion control capabilities (due to dense colony formation) and wildlife habitat improvement than its phytoremediation potential. Perhaps one of the reasons for the mitigation success of *L. oryzoides* has to do with its ubiquitous presence and ability to adapt to changing hydrological regimes. Few studies are available on using *L. oryzoides* for phytoremediation, although Ampiah-Bonney et al. (2007) reported arsenic phytoextraction coefficients up to 2.8 over a 16 wk exposure for the plant. Moore et al. (2009) reported similar mitigation results for *cis*- and *trans*-permethrin and *L. oryzoides* (71 ± 2 and 81 ± 1%, respectively) as those discovered in the current study. In the 2009 study, Moore et al. utilized a 4 h HRT (as opposed to the 6 h HRT in the current study) immediately followed by an 8 h flush of unamended water (as opposed to the current study where 42 h passed before flushing occurred.).

Table 2
Mean loads and percent decrease of loads of atrazine entering and exiting mesocosms (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	1.62 ± 0.73	1.23 ± 0.64	1.01 ± 0.39	1.31 ± 0.60
0–6 h outflow (mg)	0.68 ± 0.22	0.44 ± 0.15	0.37 ± 0.06	0.62 ± 0.13
48–51 h flush outflow (mg)	0.46 ± 0.11	0.24 ± 0.08	0.27 ± 0.05	0.45 ± 0.06
Total outflow (mg)	1.14 ± 0.56	0.68 ± 0.39	0.64 ± 0.18	1.07 ± 0.30
% Decrease after 6 h	59 ± 6	65 ± 2	62 ± 8	51 ± 6
% Released after flush	29 ± 3	19 ± 6	27 ± 3	38 ± 16
Total% decrease	31 ± 4^{ab}	45 ± 7^{b}	35 ± 8^{b}	13 ± 20^{a}

Significant differences denoted by lowercase letters.

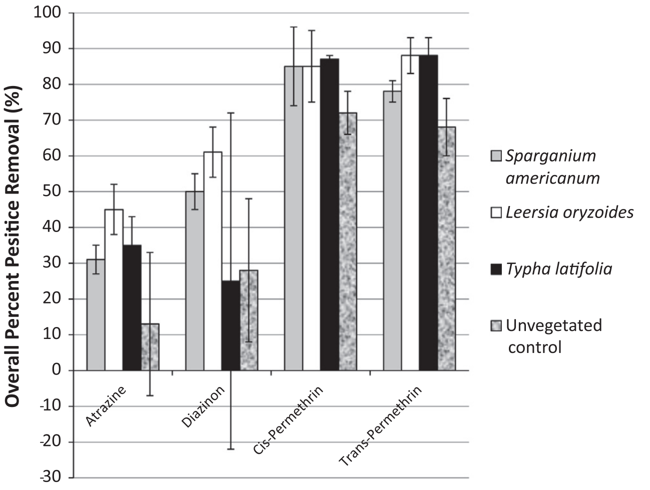

Fig. 1. Mean (±SE) total system removal of atrazine, diazinon, *cis*-permethrin and *trans*-permethrin by aquatic vegetation and the unvegetated control.

T. latifolia was somewhat less successful than *L. oryzoides*, although it did demonstrate a significant difference from the unvegetated control with respect to total percent decrease in atrazine load in the current study. The obvious danger in using plants to mitigate herbicides is that the chemical itself will damage the plants, rendering them ineffective. Langan and Hoagland (1996) reported high levels of atrazine (1500 $\mu g\ L^{-1}$) significantly affected the growth of *T. latifolia* for a 10 wk period, although slightly enhanced plant growth was noted in atrazine treatments of 10 $\mu g\ L^{-1}$. Concentrations in the current study were within the 0–20 $\mu g\ L^{-1}$ range, and no observable effects on plant growth were noted. Page et al. (2011) determined the mean atrazine removal rate to be 50% over a 3 yr period in a constructed wetland vegetated with *Typha*, *Phragmites*, *Eleocharis*, *Schoenoplectus*, and *Baumea*.

In the current study, *T. latifolia* significantly decreased *trans*-permethrin in the initial effluent loads. Likewise, Moore et al. (2009) reported *cis*- and *trans*-permethrin overall mass retentions of 67 ± 6 and 78 ± 2%, respectively, with *T. latifolia*.

Various studies have also examined the ability of *T. latifolia* to remediate other pesticides in addition to atrazine. Noting that *T. latifolia* is potentially a good candidate for phytoremediation, Wilson et al. (2000) reported a reduction of 65% in simazine activity after 7 d (simazine is another triazine herbicide in the same family as atrazine). In a two-cell wetland dominated by *T. latifolia* and *Phalaris arundinacea*, Elsaesser et al. (2011) reported a decrease in toxicity of dimethoate, dicamba, trifloxystrobin and tebuconazole by 95% in vegetated cells versus 79% in the non-vegetated cell. Within this same study, the vegetated cells reduced toxic effects within a distance of 40 m, while 64 m was required for the same removal efficiency in the non-vegetated cell.

As with *L. oryzoides*, little data is available for *S. americanum* with regard to pesticide mitigation. *S. americanum* was a small component of the overall vegetative structure reported by Elsaesser et al. (2011) which successfully mitigated dimethoate, dicamba, trifloxystrobin, and tebuconazole concentrations. Moore et al. (2009) found overall mass retentions of 67 ± 8 and 76 ± 4%, respectively, for *cis*- and *trans*-permethrin and *S. americanum*, similar to the 85 ± 11 and 78 ± 3%, respectively, reported in the current study.

Table 3
Mean loads and percent decrease of loads of diazinon entering and exiting mesocosms (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	0.59 ± 0.23	0.49 ± 0.28	0.26 ± 0.12	0.41 ± 0.12
0–6 h outflow (mg)	0.21 ± 0.04	0.15 ± 0.04	0.12 ± 0.02	0.20 ± 0.03
48–51 h flush outflow (mg)	0.07 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.09 ± 0.01
Total outflow (mg)	0.29 ± 0.09	0.18 ± 0.08	0.16 ± 0.05	0.28 ± 0.06
% Decrease after 6 h	64 ± 2	69 ± 4	41 ± 45	53 ± 10
% Released after flush	14 ± 5	8.0 ± 3	16 ± 5	24 ± 12
Total% decrease	50 ± 5	61 ± 7	25 ± 47	28 ± 20

Table 4
Mean loads and percent decrease of loads of *cis*-permethrin entering and exiting mesocosms (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	0.16 ± 0.02	0.13 ± 0.02	0.10 ± 0.03	0.14 ± 0.05
0–6 h outflow (mg)	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.0	0.04 ± 0.01
48–51 h flush outflow (mg)	2×10^{-3} ± 0	3×10^{-3} ± 0	2×10^{-3} ± 0	2×10^{-3} ± 0
Total outflow (mg)	0.02 ± 0.02	0.02 ± 0.01	0.01 ± 0	0.03 ± 0.01
% Decrease after 6 h	86 ± 10	87 ± 7	88 ± 2	73 ± 7
% Released after flush	1.0 ± 1	2.0 ± 3	2.0 ± 2	1.0 ± 1
Total% decrease	85 ± 11	85 ± 10	87 ± 1	72 ± 6

Table 5
Mean loads and percent decrease of loads of *trans*-permethrin entering and exiting mesocosms (±SE).

	S. americanum	*L. oryzoides*	*T. latifolia*	Unvegetated
Total inflow (mg)	0.12 ± 0.01	0.10 ± 0.01	0.08 ± 0.03	0.10 ± 0.04
0–6 h outflow (mg)	0.02 ± 0	0.01 ± 0	0.01 ± 0	0.03 ± 0.01
48–51 h flush outflow (mg)	$1 \times 10^{-3} \pm 0$	0.0 ± 0	$1 \times 10^{-3} \pm 0$	$2 \times 10^{-3} \pm 0$
Total outflow (mg)	0.03 ± 0	0.01 ± 0.01	0.01 ± 0.01	0.03 ± 0.01
% Decrease after 6 h	79 ± 2^{b}	88 ± 5^{b}	89 ± 6^{b}	70 ± 6^{a}
% Released after flush	1.0 ± 1	0.0 ± 0	1.0 ± 1	1.7 ± 3
Total% decrease	78 ± 3^{a}	88 ± 5^{b}	88 ± 5^{b}	68 ± 8^{a}

Significant differences denoted by lowercase letters.

Researchers have examined additional plant species' abilities to mitigate atrazine, diazinon, and permethrin. Above-ground leaf biomass of switchgrass (*Panicum virgatum*) was capable of detoxifying atrazine at concentrations of 10 μg g^{-1} (Murphy and Coats, 2011). Locke et al. (2011) reported a 70% reduction in maximum aqueous atrazine concentration in a wetland cell 90% covered with *Alternanthera philoxeroides* (alligator weed), and 89% atrazine reduction in a wetland cell with 48% *A. philoxeroides* and 48% *Echinocloa crusgalli*. A constructed wetland vegetated with *Phragmites australis*, *Eleocharis sphacelanta*, *Schoenoplectus validus*, *Baumea articulate*, and *Typha orientalis* retained 49% of the mean measured atrazine mass after 7 d (Page et al., 2010).

Phytoremediation of diazinon-contaminated waters has been the focus of several studies, particularly those in California where the OP is still detected in storm and irrigation runoff. Experimental ditches vegetated with *Hordeum vulgare* (barley), *Lolium multiflorum* (annual ryegrass), and *Chenopodium album* (lamb's quarter) reduced the inflow diazinon concentration by half after 55 m travel distance in the ditch, whereas the non-vegetated ditch required a distance of 158 m to decrease the pesticide concentration by half (Moore et al., 2008). Ditch pH ranged from 7.1–7.6 for both vegetated and non-vegetated systems, and the dissolved oxygen concentration ranged from 6.2–9.5 mg L^{-1} (Moore et al., 2008). Anderson et al. (2011) determined treatment systems containing *Juncus phaeocephalus*, *Juncus patens*, and *Hydrocotyle* spp. were partially effective at removing diazinon concentrations, although an OP-hydrolyzing enzyme was necessary to effectively remove any remaining diazinon. In a constructed wetland vegetated primarily by *A. philoxeroides* bordering Beasley Lake in the Mississippi Delta, 43% of the measured diazinon mass from a simulated storm runoff event was associated with the plants, while 23% was in sediments, and 34% remained in the water column (Moore et al., 2007).

Garcinuño et al. (2006) studied effects of permethrin on *Lupinus angustifolius* in hydroponic solutions. Results indicated that 55% of permethrin mass was either degraded or irreversibly bound to *L. angustifolius*. Additionally, no permethrin was detected in cotyledon tissue, preventing the plant from becoming a source of contamination for the duration of its life cycle (Garcinuño et al., 2006). Within plant material, permethrin is believed to be degraded through hydrolysis followed by rapid conjugation with sugars. Factors such as light, heat, and humidity may also contribute to the pesticide degradation within vegetation (Garcinuño et al., 2006). Moore et al. (2008) reported approximately 33% of measured *cis*- and *trans*-permethrin mass associated with plant material (*H. vulgare*, *L. multiflorum*, and *C. album*). Additionally, vegetated ditches had a permethrin half-distance of 21–22 m, while the non-vegetated ditch had a permethrin half-distance of 50–55 m (Moore et al., 2008).

Other pyrethroids have been examined for their ability to be successfully remediated by plants. Due to fast adsorption to *Lemna* spp. roots and fronds, both cypermethrin concentration and toxicity to *Hyalella curvispina* decreased faster in planted microcosms than in ones without the vegetative cover (Mugni et al., 2011). Water quality in these systems ranged in temperature from 17.5–19 °C; pH from 7.0–7.7; and dissolved oxygen from 2.0–6.5 mg L^{-1} (Mugni et al., 2011). Comparing high, intermediate, and low plant densities, Leistra et al. (2003) reported lambda-cyhalothrin concentrations in plant material up to 50% of the maximum dose after 24 h. The higher the plant density, the lower the percentage of lambda-cyhalothrin tended to be found in sediment. Value of pH reported by Leistra et al. (2003) were much higher (7.6–10) than those observed in the current study.

Physicochemical properties of the examined pesticides also play a significant role in their environmental fate within the wetland system. With a high water solubility and low K_{oc}, atrazine has a surface water half-life of >200 d (USDHHS, 2003). Although diazinon is highly water soluble as well (Table 1), it possesses a greater sorption constant than atrazine. In sterile, acidic (pH 5) water, diazinon's half-life was 12 d, while increasing to 138 d in sterile, neutral water (USEPA, 2006b). Additionally, Bondarenko et al. (2004) reported 2–4 times increased degradation of diazinon in water at 21 °C than at 10 °C. Current experiments were conducted in the summer with water temperatures at or above 20 °C; however the aqueous pH ranged from 5.7–8.7. Given the temperature and slightly acidic conditions in the vast majority of the mesocosms, it is estimated that the aqueous half-life of diazinon would likely be somewhere closer to 12 d instead of the138 d time period. Permethrin, on the other hand, has an aqueous half-life of 19–27 h (Imgrund, 2003). Its high K_{oc} value, one order of magnitude greater than diazinon, makes permethrin a likely candidate for rapid sorption onto any available organic carbon source. Because of these two characteristics, one would expect to see less permethrin in the water column than either atrazine or diazinon.

Alkaline hydrolysis in the surface water near aquatic vegetation (*Myriophyllum spicatum*, *Elodea nuttalli*, and *Sagittaria sagittifolia*) was considered the main dissipation process for lambda-cyhalothrin (Leistra et al., 2003). Similar conclusions have been drawn by Brogan and Relyea (2013). In a study using the submerged macrophytes *Elodea canadensis*, *M. spicatum*, *Ceratophyllum demersum*, and *Vallisneria americana*, Brogan and Relyea (2013) concluded the toxicity of malathion was mitigated not by sorption, but instead through the plants' effects on water quality (increasing pH), causing rapid hydrolysis and detoxification of the pesticide in water. Values of pH in Brogan and Relyea (2013) were much higher (9.2–9.4) than those observed in the current study.

5. Conclusions

L. oryzoides was the capable of significantly decreasing a portion of most of the pesticide loads associated with the storm runoff event. It was able to decrease the initial atrazine load (62 ± 8%); minimize atrazine load lost after flushing (19 ± 6%); significantly decreased the overall atrazine load lost during the experiment (45 ± 7%); decrease the amount of diazinon lost after flushing (8 ± 3%); significantly decrease initial loads of *trans*-permethrin (88 ± 5%); and significantly decrease the overall *trans*-permethrin load lost during the experiment (88 ± 5%). With its widespread abundance and adaption to a variety of habitats, *L. oryzoides* is a feasible macrophyte to incorporate into a phytoremediation scheme for runoff containing atrazine, diazinon, and permethrin. *T. latifolia* successfully reduced the total amounts of both atrazine (35 ± 8%) and *trans*-permethrin (88 ± 5%) loads lost during the experiment, while also significantly reducing the initial load of *trans*-permethrin (89 ± 6%). *S. americanum* only demonstrated significant success at decreasing the initial *trans*-permethrin load (79 ± 2%). Although *T. latifolia* and *S. americanum* were not as efficient mitigators as *L. oryzoides*, they can still be useful in the overall mitigation design of vegetated remediation systems. The loss of pesticide following the flushing event demonstrated that plant sorption is at least partially reversible, depending on both the plant species and pesticide chemistry. Atrazine demonstrated the most reversibility among the pesticides studied, while both permethrin isomers had very little loss following the flush. This indicated more of an irreversibly bound relationship among plants and pesticides.

The concept that vegetation can play an essential role in contaminant removal is widely recognized among the scientific community, even though available plant partitioning studies demonstrate wide variability among pesticides. Although direct uptake by plant cells would be the normal method for metabolism of organic contaminants such as pesticides, physicochemical properties of the pesticides, as well as biochemical characteristics of the plant will affect contaminant uptake and distribution. Without question, considering the current study and other available phytoremediation research, vegetation plays a role in not only the direct, but also indirect, removal processes of pesticides in aquatic systems.

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References

Ampiah-Bonney, R.J., Tyson, J.F., Lanza, G.R., 2007. Phytoextraction of arsenic from soil by *Leersia oryzoides*. Int. J. Phytoremediation 9, 31–40.

Anderson, B., Phillips, B., Hunt, J., Largay, B., Shihadeh, R., Tjeerdema, R., 2011. Pesticide and toxicity reduction using an integrated vegetated treatment system. Environ. Toxicol. Chem. 30, 1036–1043.

Battaglin, W.A., Furlong, E.T., Burkhardt, M.R., Peter, C.J., 2000. Occurrence of sulfonylurea, sulfonamide, imidazoline, and other herbicides in rivers, reservoirs and ground water in the Midwestern United States, 1998. Sci. Total Environ. 248, 123–133.

Black, R., Hutchison, S., Warshaw, C., 2004. Economic Profile of the Lower Mississippi River Region. Industrial Economics, Cambridge, MA. p. 158.

Bondarenko, S., Gan, J., Haver, D.L., Kabashima, J.N., 2004. Persistence of selected organophosphate and carbamate insecticides in water from a coastal watershed. Environ. Toxicol. Chem. 24, 2121–2127.

Bouldin, J.L., Farris, J.L., Moore, M.T., Cooper, C.M., 2004. Vegetative and structural characteristics of agricultural drainages in the Mississippi Delta landscapes. Environ. Pollut. 132, 403–411.

Brogan III, W.R., Relyea, R.A., 2013. Mitigating with macrophytes: submersed plants reduce the toxicity of pesticide-contaminated water to zooplankton. Environ. Toxicol. Chem. 32, 699–706.

California Department of Pesticide Regulation, 2011. Summary of Pesticide Use Report Data 2010: Indexed by Chemical. <http://www.cdpr.ca.gov/docs/pur/pur10rep/chmrpt10.pdf>.

Ciba-Geigy Corporation, 1994. Environmental Fate Reference Data Source Book for Atrazine. Ciba-Geigy Corporation, Greensboro, NC.

Darris, D., Bartow, A., 2004. Plant Fact Sheet for Rice Cutgrass (*Leersia oryzoides*). USDA-Natural Resources Conservation Service, Plant Materials Center, Corvallis, OR.

de Vlaming, V., Connor, V., DiGiorgio, C., Bailey, H.C., Deanovic, L.A., Hinton, D.E., 2000. Application of whole effluent toxicity test procedures to ambient water quality assessment. Environ. Toxicol. Chem. 19, 42–62.

de Vlaming, V., DiGiorgio, C., Fong, S., Deanovic, L.A., de la Paz Carpio-Obeso, M., Miller, J.L., Miller, M.J., Richard, N.J., 2004. Environ. Pollut. 132, 213–229.

Elsaesser, D., Blankenberg, A.G.B., Geist, A., Mæhlum, T., Schulz, R., 2011. Assessing the influence of vegetation on reduction of pesticide concentration in experimental surface flow constructed wetlands: application of the toxic units approach. Ecol. Eng. 37, 955–962.

EXTOXNET, 1996. Pesticide information profiles. Extension Toxicology Network. <http://extoxnet.orst.edu/pips/ghindex.html>.

European Medicines Agency (EMEA), 1998. Committee for Veterinary Medicinal Products Permethrin Summary Report, London, UK, EMEA/MRL/112/96-Final.

Favorite, J., 2006. Plant Fact Sheet for American Bur-reed (*Sparganium americanum*). USDA-Natural Resources Conservation Service, National Plant Data Center, Baton Rouge, LA.

Frank, R., Braun, H.E., Chapman, N., Burchat, C., 1991. Degradation of parent compounds of nine organophosphorus insecticides in Ontario surface and ground waters under controlled conditions. Bull. Environ. Contam. Toxicol. 47, 374–380.

Garcinuño, R.M., Hernando, P.F., Cámara, C., 2006. Removal of carbaryl, linuron, and permethrin by *Lupinus angustifolius* under hydroponic conditions. J. Agric. Food Chem. 54, 5034–5039.

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaik, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., Wolock, D.M., 2006. The Quality of Our Nation's Waters – Pesticides in the Nation's Streams and Ground Water, 1992–2001. US Geological Survey Circular 1291, Reston, VA. p. 172.

Grube, A., Donaldson, D., Kiely, T., Wu, L., 2011. Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates. US Environmental Protection Agency, Washington, DC.

Imgrund, H., 2003. Environmental fate of permethrin. <http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/permethrin.pdf>.

Kegley, S., Hill, B., Orme, S. 2007. PAN Pesticide Database, Pesticide Action Network, North America. San Francisco, CA. <http://www.pesticideinfo.org>.

Kröger, R., Cooper, C.M., Moore, M.T., 2008. A preliminary study of an alternative controlled drainage strategy in surface drainage ditches: low-grade weirs. Agric. Water Manage. 95, 678–684.

Laskowski, D.A., 2002. Physical and chemical properties of pyrethroids. Rev. Environ. Contam. Toxicol. 174, 49–170.

Langan, M.M., Hoagland, K.D., 1996. Growth responses of *Typha latifolia* and *Scirpus acutus* to atrazine contamination. Bull. Environ. Contamin. Toxicol. 57, 307–314.

Langan, M.M., Hoagland, K.D., Everson, A.R., 1993. Pesticide levels in storm runoff from agricultural stream sites with different riparian buffer strips. In: Proceeding of the Platte River Basin Ecosystem Symposium, December 7–8, 1993, Grand Island, NE. pp. 223–233.

Leistra, M., Zweers, A.J., Warinton, J.S., Crum, S.J.H., Hand, L.H., Beltman, W.H.J., Maund, S.J., 2003. Fate of the insecticide lambda-cyhalothrin in ditch enclosures differing in vegetation density. Pest Manage. Sci. 60, 75–84.

Li, G.C., Feldbeck, G.T., 1972. Atrazine hydrolysis as catalyzed by humic acids. Soil Sci. 114, 201–209.

Locke, M.A., Weaver, M.A., Zablotowicz, R.M., Steinriede, R.W., Bryson, C.T., Cullum, R.F., 2011. Constructed wetlands as a component of the agricultural landscape: mitigation of herbicides in simulated runoff from upland drainage areas. Chemosphere 83, 1532–1538.

Moore, M.T., Cooper, C.M., Smith Jr., S., Cullum, R.F., Knight, S.S., Locke, M.A., Bennett, E.R., 2007. Diazinon mitigation in constructed wetlands: influence of vegetation. Water Air Soil Pollut. 184, 313–321.

Moore, M.T., Denton, D.L., Cooper, C.M., Wrysinski, J., Miller, J.L., Reece, K., Crane, D., Robins, P., 2008. Mitigation assessment of vegetated drainage ditches for collecting irrigation runoff in California. J. Environ. Qual. 37, 486–493.

Moore, M.T., Kröger, R., Cooper, C.M., Smith Jr., S., 2009. Ability of four emergent macrophytes to remediate permethrin in mesocosm experiments. Arch. Environ. Contam. Toxicol. 57, 282–288.

Mugni, H., Demetrio, P., Bulus, G., Ronco, A., Bonetto, C., 2011. Effect of aquatic vegetation on the persistence of cypermethrin toxicity in water. Bull. Environ. Contamin. Toxicol. 86, 23–27.

Murphy, I.J., Coats, J.R., 2011. The capacity of switchgrass (*Panicum virgatum*) to degrade atrazine in a phytoremediation setting. Environ. Toxicol. Chem. 30, 715–722.

Page, D., Dillon, P., Mueller, J., Bartkow, M., 2010. Quantification of herbicide removal in a constructed wetland using passive samplers and composite water quality monitoring. Chemosphere 81, 394–399.

Page, D.W., Khan, S.J., Miotlinski, K., 2011. A systematic approach to determine herbicide removals in constructed wetlands using time integrated passive samplers. J. Water Reuse Desalination 1, 11–17.

Solomon, K.R., Baker, D.B., Richards, R.P., Dickson, K.R., Klaine, S.J., LaPoint, T.W., Kendall, R.J., Weisskopf, C.P., Giddings, J.M., Giesy, J.P., Hall Jr., L.W., Williams, W.M., 1996. Ecological risk assessment of atrazine in North American surface waters. Environ. Toxicol. Chem. 15, 31–76.

Stevens, M., Hoag, C., 2006. Plant Fact Sheet for Broad Leaved Cattail (*Typha latifolia*). USDA-Natural Resources Conservation Service, Plant Materials Center, Aberdeen, ID.

Suresh, S., Ravishankar, G.A., 2004. Phytoremediation – a novel and promising approach for environmental clean-up. Crit. Rev. Biotechnol. 24, 97–124.

USDA, 2013. Plants Database. US Department of Agriculture. <http://www.plants.usda.gov>.

USDA ARS, 1995. ARS pesticide properties database. US Department of Agriculture, Agricultural Research Service. <http://www.ars.usda.gov/Services/docs.htm?docid=14199>.

USDHHS, 2003. ToxGuide™ for Atrazine. <http://www.atsdr.cdc.gov/toxguides/toxguide-153.pdf>.

USEPA, 2006a. Reregistration Eligibility Decision (RED) for Permethrin. US Environmental Protection Agency. Washington, DC. EPA 738-R-06-017.

USEPA, 2006b. Reregistration Eligibility Decision (RED) for Diazinon. US Environmental Protection Agency. Washington, DC. EPA 738-R-04-006.

Wilson, P.C., Whitwell, T., Klaine, S.J., 2000. Metalaxyl and simazine toxicity to and uptake by *Typha latifolia*. Arch. Environ. Contamin. Toxicol. 39, 282–288.