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Influence of varying nutrient and pesticide mixtures on abatement efficiency using a vegetated free water surface constructed wetland mesocosm

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The nutrient and pesticide abatement efficiency of varying mixtures was examined in a vegetated free water surface constructed wetland. Three different agricultural chemical pollutant mixture conditions were assessed: nutrients only (N and P); pesticides only (atrazine, S-metolachlor and permethrin); and a mixture of nutrients and pesticides. With nutrients only, 672 h nutrient mitigation of 77–91% total phosphorous (TP) and 74–98% total nitrogen (TN) was associated with distance from the injection point and rainfall, whereas with nutrient and pesticide mixtures, 672 h nutrient mitigation of 11–71% TP and 84–98% TN were associated with distance and time. With pesticides only, 672 h pesticide mitigation of 50–99% was associated with distance and time, whereas with nutrients and pesticide mixtures, 672 h pesticide mitigation of 48–99% was associated primarily with distance. Dissipation half-lives were 2–10 times greater for P and 1.5–5 times greater for N when pesticides were present. Pesticide dissipation half-lives showed no clear differences with or without nutrients. While vegetated free water surface constructed wetlands can be effective best management practice tools to trap and abate agricultural run-off during rainfall events, efficiencies can be affected by different types of complex pollutant mixtures and wetland design and implementation should accommodate varying efficiencies.

Keywords: best management practices; mitigation; nitrogen; phosphorus; atrazine; S-metolachlor; permethrin

1. Introduction

Mechanised modern agricultural techniques have allowed us to maximise row-crop productivity to feed and clothe an ever increasing global population, a need that will intensify as global demand for agricultural products continues to increase.[1] However, these techniques can come at a potentially high ecological cost by posing a significant increased risk to aquatic ecosystems and drinking water resources.[2,3] Such risks originate from the growing use of man-made fertiliser (N, P) and pesticides to control and maintain high agricultural row-crop production. Tilman et al. [4] estimated an increase of 2.4–2.7-fold in global fertiliser (N, P) and pesticide use by 2050, with a concomitant impact on downstream aquatic ecosystems via eutrophication and habitat destruction. As a result, there is a need for effective conservation management strategies to be implemented.

One strategy to mitigate downstream impacts due to global increased fertiliser and pesticide use has been to implement constructed wetlands to intercept run-off from intensively cultivated

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landscapes. Use of free water surface constructed wetlands has increased globally in the last decade in countries such as China, [5–7] South Africa, [8,9] France, [10] Norway, [11] Spain, [12] and the USA.[13-17] Although constructed wetlands are recognised as reliable technology for wastewater treatment, [18,19] the technology has only recently begun to be widely implemented for mitigation of non-point source pollution such as agricultural run-off. [10,11,15,17,20] Previous research has addressed the use of vegetated free water surface constructed wetlands to remove nutrients of various types including N [6,12,17,21] and P.[11,15,17,21-23] In addition, other research has focused on the use of free water surface constructed wetlands to remove pesticides of various types including herbicides and insecticides either singly or in mixtures. [10,13,16,24] However, more complex mixtures of nutrients and pesticides in combination, as well as comparisons between nutrient only and pesticide only conditions have been less well studied.[8] Such mixtures can occur under various scenarios such as primarily nutrients in early spring, nutrients and pesticides in late spring to early summer, and primarily pesticides in mid- to late summer. Issues of the effectiveness of constructed wetlands in abating such complex agricultural pollutant mixtures have become increasingly important as constructed wetlands are more frequently used as conservation practices to mitigate agricultural contamination, a leading cause of increased eutrophication, ecological impacts from pesticides and overall degradation of habitat in rivers, lakes and streams.

The focus of this study was to assess the abatement efficiency of a prototypical vegetated free water surface constructed wetland receiving three different simulated agricultural pollutant mixture conditions: nutrients only (N and P); pesticides only (two herbicides and one insecticide); and a combination of both nutrients and pesticides. It is hypothesised that pollutant entrapment and dissipation from the water column will be unaffected by the presence or absence of nutrients or pesticides entering a vegetated free water surface constructed wetland.

2. Materials and methods

2.1. Constructed wetland mesocosm design

An experimental vegetated free water surface wetland mesocosm was constructed at the University of Mississippi Field Station (34°25′55″N, 89°24′00″W) in Lafayette County, Mississippi, USA. The wetland mesocosm was evenly divided and hydraulically isolated along its north–south axis with a 6 mil plastic liner placed 0.3 m below the sediment surface and standing 1.2 m above the sediment surface. The partition divided the wetland mesocosm into two sections (227 m² each) to the east and west. Both sections were naturally vegetated with emergent aquatic plants, predominantly common rush (*Juncus effusus*) and common reed (*Phragmites australis*) (Table 1) with similar species distribution and plant densities based upon Kruskal–Wallis one-way analysis of variance (ANOVA) on ranks (*J. effusus*, p = 0.434; *P. australis*, p = 0.555). The east section had a minimum and maximum water-holding capacity of 110,880 and 258,720 L, respectively, with a wetland slope of 9.2 mm m⁻¹ (0.92% grade). The west section had a minimum and maximum water-holding capacity of 99,330 and 247,170 L, respectively, with a wetland slope of 7.9 mm m⁻¹ (0.79% grade). Prior to the first treatment exposure, wetland hydrology was near mid capacity (east: $\sim 180,000$ L, west: $\sim 170,000$ L).

To simulate a variety of possible agricultural run-off event scenarios with differing contaminant inputs, we assessed three different mixture conditions: nutrients (N and P) only; pesticides (two herbicides and one insecticide) only; and a combination of both nutrients and pesticides. A fourth control condition (no amended contaminants) was included as a baseline comparison. To do this in a constructed wetland mesocosm with only two sections, the experiment was divided into two briefly temporally separate treatment exposures. During the first treatment exposure, conducted from 29 July 2009 to 26 August 2009, the east wetland section was amended over a 4-h period on

Table 1.	Plant species and densities (ramets m ⁻²) in east and west sections of a constructed
wetland n	nesocosm used to mitigate varying nutrient and pesticide mixtures.

	Distance from inflow (m)					
Plant species	0	10	20	40		
East section ^a						
Juncus effusus	286 (153)	85 (32)	223 (171)	171 (296)		
Phragmites australis	24 (25)	27 (35)	37 (64)	12 (15)		
Lythrum salicaria	4 (6)	0 (0)	0 (0)	0 (0)		
Osmunda cinnamonea	5 (8)	0(0)	0(0)	0(0)		
Acer rubrum	2 (4)	0 (0)	0(0)	0 (0)		
Leersia oryzoides	0 (0)	5 (8)	0 (0)	17 (29)		
Total	325 (163)	117 (30)	260 (172)	199 (274)		
West section ^b						
Juncus effusus	113 (19)	124 (106)	40 (69)	159 (144)		
Phragmites australis	44 (21)	36 (41)	51 (44)	0(0)		
Acer rubrum	1(2)	0 (0)	0 (0)	0 (0)		
Leersia oryzoides	0 (0)	20 (35)	0 (0)	0 (0)		
Total	158 (13)	180 (102)	91 (26)	159 (144)		

^aNutrients only and pesticides only treatments.

29 July 2009 at a continuous flow rate of 103 L min⁻¹ using a submersible groundwater well pump located at the study site with an aqueous 20 L stock solution mixture of ammonium nitrate (total of 357 g N) and triple superphosphate (total of 409 g P) delivered via piston pump (Fluid Metering Inc., Syosset, NY, USA) at 85 L min⁻¹ to a 121 L mixing chamber simultaneously receiving groundwater; the west wetland section was amended over the same 4-h period at the same flow rate with only water (control). At the conclusion of the first treatment and prior to the start of the second treatment, the wetland was drained, flushed with fresh unamended water from the same source as the first treatment for 48 h, and allowed to refill to mid capacity (east: $\sim 185,000 \, \text{L}$. west: ~ 173,000 L) per the hydrologic conditions previous to the first treatment exposure. During the second treatment exposure, conducted from 2 to 30 September 2009, the east wetland section was amended over a 4-h period on 2 September 2009 at a continuous flow rate of 103 L min⁻¹ with an aqueous mixture of atrazine [total of 0.5 kg active ingredient (a.i.)], S-metolachlor (total of 0.5 kg a.i.) and permethrin (total of 0.133 g a.i.) as commercial field formulations Bicep II Magnum[®] (atrazine + S -metolachlor) and Hi-Yield 38[®] (permethrin). Concomitantly, the west wetland section was amended over the same 4-h period and same flow rate with an aqueous mixture of ammonium nitrate (total of 357 g N), super triple phosphate (total of 409 g P), atrazine (total of 0.5 kg a.i.), S-metolachlor (total of 0.5 kg a.i.) and permethrin (total of 0.133 g a.i.) as commercial field formulations Bicep II Magnum® (atrazine + S-metolachlor) and Hi-Yield 38[®] (permethrin). Both treatments were amended from 20 L mixture stock solutions delivered via piston pump (Fluid Metering Inc) at 85 L min⁻¹ to a 121 L mixing chamber simultaneously receiving groundwater as previously described. Simulated run-off volume was based upon what would be expected from a 2.5 mm run-off from a 0.9-ha agricultural field generating a total inflow volume of 24,777 L of run-off in each section. All target nutrient and pesticide loads amended to the constructed wetland were determined from previously reported concentrations of these agricultural pollutants in row-crop agricultural run-off.[25,26]

2.2. Nutrient and pesticide analysis

Water samples (1 L) were collected every 30 min within the first 4 h; every 4 h until 48 h; and on days 5, 7, 14, 21 and 28 post amendment at distances of 10, 20 and 40 m from the

bNo treatment (control) and pesticides + nutrients treatment.

injection point within both sections of the wetland mesocosm. Samples were collected during the study using an automated pumping sampler (ISCO Model 3700, Teledyne ISCO, Omaha, NE, USA) modified from Smith.[27] Sample containers were 1 L fluorine-coated polyethylene plastic bottles fitted with a Teflon-lined screw cap, to minimise pesticide sorption. Samples were placed on ice, transported to the USDA-ARS National Sedimentation Laboratory, and stored at 4°C (typically < 24 h) for target constituent analysis. In addition, bulk surface sediments (5 cm) were collected during pesticide treatments (pesticide only and nutrient + pesticide) at 10, 20 and 40 m from the injection point on days 1, 5, 12 and 22. Although a total of \sim 162 and 193 mm rainfall occurred during both monitoring periods (28 July to 26 August 2009 and 1 to 30 September 2009), no wetland inflow or outflow occurred from either section during the study following any storm event. Thus the wetlands functioned as retention systems.

Analyses for P and N were conducted according to methods described by Eaton et al. [28] In brief, total PO_4^- -P (TP) involved persulfate digestion and analysis with an ascorbic acid colourimetric method; for soluble reactive PO_4^- -P (SRP), samples were filtered through a 0.45 μ m cellulose nitrate filter and analysed using the ascorbic acid colourimetric method; NH_4^+ -N, filtered samples were analysed using a phenate method; NO_3^- -N, filtered samples were analysed using a cadmium reduction colourimetric method; NO_2^- -N, filtered samples were analysed using a potassium permanganate colourimetric method; and total N (TN) $[NO_3^-$ -N + NO_2^- -N + total Kjeldahl N (TKN)] involved block digestion in sulfuric acid and flow injection analysis. Colourimetric analyses were performed using a ThermoSpectronic GenesysTM 10 ultraviolet (UV) spectrophotometer (Spectronic Instruments, Inc., Rochester, NY, USA). Method detection limits were: 0.01 mg L $^{-1}$, TP, SRP, NO_3^- -N and NO_2^- -N; and 0.02 mg L $^{-1}$, NH_4^+ -N and TKN.

Aqueous and sediment pesticide analyses were conducted according to Smith et al. [29] and Bennett et al. [30] In brief, pesticides were extracted using pesticide-grade ethyl acetate, dried over anhydrous Na₂SO₄ and concentrated to near dryness by rotary evaporation. The extract was then subjected to silica gel column chromatography cleanup, and concentration to 1mL volume under high purity dry nitrogen for GC analysis. Pesticide recoveries and extraction efficiencies, based on fortified samples, were $\geq 90\%$ for targeted pesticides.[29,30] Two Agilent HP model 6890 gas chromatographs (Agilent Technologies, Inc., Waldbronn, Germany) equipped with dual Agilent HP 7683 ALS autoinjectors, dual split-splitless inlets, dual capillary columns, an Agilent HP Kayak XA Chemstation, and the autoinjector set at 1.0 μL injection volume fast mode were used for all targeted pesticide analyses, according to Smith et al. [29,30] The first of the two Agilent HP 6890 GCs was equipped with two micro-electron capture detectors (µECDs) and the second 6890 with one µECD, one N-P detector (NPD) and an Agilent HP 5973 mass selective detector (MSD). The primary analytical column was an Agilent HP 5MS capillary column, $30 \,\mathrm{m} \times$ 0.25 mm i.d. × 0.25 μm film thickness. Column oven temperatures were: initial at 85°C for 1 min; ramp at 25°C to 190°C; hold at 190°C for 25 min; ramp at 25°C to 230°C and hold for 30 min. The carrier gas used was ultra-high purity (UHP) helium at 28 cm s⁻¹ and inlet temperature at 250°C. The μECD temperature was 325°C with a constant make up gas flow of 40 mL min⁻¹ UHP nitrogen. Method detection limits were: $0.1 \,\mu g \, L^{-1}$, aqueous atrazine, S-metolachlor, cispermethrin and trans-permethrin; $1 \mu g L^{-1}$, sediment atrazine, S-metolachlor, cis-permethrin and trans-permethrin.

In addition, water quality parameters of temperature, pH, conductivity and dissolved oxygen were measured *in situ* in each section of the constructed wetland mesocosm from 28 July 2009 to 26 August 2009 and again from 1 to 30 September 2009 at 10 and 40 m using four calibrated Yellow Springs Instruments (YSI) 6290 multi-parameter water quality monitoring systems (Yellow Springs, OH, USA). Water quality monitoring systems were recalibrated weekly to ensure proper working conditions and data integrity. Measurements were collected hourly during treatment days 1–6 (week 1), 7–13 (week 2), 14–20 (week 3) and 21–28 (week 4).

2.3. Data analysis

Weekly means and standard deviations (±SD) were determined for all four in situ parameters and overall means ±SD were determined for all nutrients and pesticides under control section conditions. Forward stepwise linear regressions were performed according to Berenson et al. [31] for each of the three different mixture conditions to assess multiple independent variables that could influence observed changes in concentrations of amended agricultural chemicals. Standardised dimensionless regression coefficients and coefficients of determination were computed from amended nutrients and pesticides as dependent variables and values of sampling time (time), distance from inflow (distance), J. effusus plant density (Juncus), P. australis plant density (Phragmites) and total daily precipitation (rain) as independent variables. Independent variables were added or removed using F-to-enter of 4.0 and F-to-remove of 3.9. Aqueous exponential dissipation models for each nutrient species and pesticide at 10, 20 and 40 m were constructed, when possible, using non-linear exponential decay rate regression models modified from Reddy et al. [32] for each of the three different mixture conditions. The resulting equations were used to determine aqueous dissipation half-lives $(T_{1/2})$ within the wetland. All statistical analyses were conducted using SigmaPlot® v.12.0 (Systat Software Inc., Chicago, IL, USA) statistical software.[33] Statistical significance level for all models was set at 5% ($p \le 0.05$) for all analyses.[34]

3. Results and discussion

3.1. Wetland in situ water quality and control conditions

Monitored in situ water quality of the vegetated free water surface constructed wetland mesocosm was typical of shallow freshwater wetland habitats in the south-eastern USA (Table 2) with hypoxic conditions (dissolved oxygen < 2.0 mg L) [35,36] and slightly acidic water. [37,38] Water temperatures were indicative of climatic conditions of the study site (north Mississippi) during summer, with means ranging from 22.4 to 27.3°C.[36,39] No outflow occurred from the wetland at any time during the study periods (28 July to 26 August 2009 and 1 to 30 September 2009) despite $\sim 162 \, \mathrm{mm}$ total precipitation occurring from 28 July to 26 August and 188 mm total precipitation occurring from 1 to 30 September. Prior to both the first and second treatment periods, east and west section baseline pretreatment (27 July 2009 and 31 August 2009) nutrient and pesticide concentrations indicated low levels of N and P and very low to below detection limit concentrations of atrazine, S-metolachlor and permethrin (Supplemental Table 1 available online at http://dx.doi.org/10.1080/02757540.2013.861823). In addition, during the first study period (29 July to 26 August), control section baseline nutrient and pesticide concentrations again indicated low levels of N and P, and very low to below detection limit levels of atrazine, S-metolachlor and permethrin. The control section was used to assess the degree of hydraulic isolation between divided wetland sections. Results indicated good hydraulic isolation with minimal diffusion (<6% of amended P and N) of sections containing higher gradient agricultural pollutant concentrations leaching into sections containing low to no concentrations only observed at 10 m (Table 3).

3.2. Wetland nutrients

Wetland P concentrations during nutrients only treatment peaked within 8 h at all sites, ranging from $2.83 \,\mathrm{mg} \,\mathrm{TPL^{-1}}$ at $10 \,\mathrm{m}$ to $9.42 \,\mathrm{mg} \,\mathrm{TPL^{-1}}$ at $40 \,\mathrm{m}$ and $2.02 \,\mathrm{mg} \,\mathrm{SRPL^{-1}}$ at $10 \,\mathrm{m}$ to $6.87 \,\mathrm{mg} \,\mathrm{SRPL^{-1}}$ at $40 \,\mathrm{m}$, indicating P loading at the downstream portion of the wetland (Figure 1). Aqueous TP dissipation ranged from 49 to 79% within 48 h and 77 to 91% by 672 h. Aqueous

Table 2. Mean (SD) weekly *in situ* water quality measurements within east and west sections of the constructed wetland mesocosm from 28 July 2009 to 26 August 2009 (nutrients only and control) and from 1 to 30 September 2009 (pesticides only and nutrients + pesticides).

	Temperature (°C)		Conductivit	Conductivity ($\mu S cm^{-1}$)		$Dissolvedoxygen(mgL^{-1})$		pН	
Week	10 m	40 m	10 m	40 m	10 m	40 m	10 m	40 m	
Nutrients	s only (east	section)							
1	25.5 (1.9)	24.9 (1.7)	65.9 (20.2)	216.1 (186.0)	1.7 (2.0)	3.1 (2.0)	5.8 (0.2)	5.4 (0.3)	
2	27.3 (1.2)	26.9 (0.5)	84.4 (9.3)	93.1 (12.0)	0.4(0.4)	1.2(1.5)	6.2 (0.1)	6.0 (0.1)	
3	26.9 (2.1)	25.6 (0.6)	69.7 (6.1)	93.0 (15.3)	0.5(0.2)	0.5(0.1)	6.0 (0.1)	6.1 (0.1)	
4	23.9 (2.1)	23.6 (1.5)	52.6 (7.2)	65.3 (12.3)	0.6 (0.4)	0.4 (0.2)	5.9 (0.1)	5.9 (0.1)	
Control ((west section	n)							
1	25.2 (1.8)	25.0 (1.3)	49.5 (20.0)	66.7 (24.3)	1.0(1.7)	0.3 (0.4)	5.9 (0.2)	6.0(0.3)	
2	27.0 (1.2)	26.6 (0.7)	92.5 (15.1)	108.1 (18.1)	0.3(0.1)	0.3(0.0)	6.2(0.1)	6.3 (0.1)	
3	25.8 (1.5)	25.5 (0.9)	71.5 (6.4)	95.0 (9.0)	0.4(0.1)	0.3 (0.0)	6.0(0.1)	6.1 (0.1)	
4	24.0 (2.5)	23.5 (1.7)	58.4 (4.9)	73.4 (5.4)	0.7 (0.7)	0.4 (0.2)	5.9 (0.1)	6.0 (0.1)	
Pesticide	es only (east	section)							
1	22.7 (1.9)	22.5 (1.0)	37.9 (5.3)	54.8 (3.0)	0.8(1.4)	0.4(0.3)	5.8 (0.1)	5.8 (0.1)	
2	23.9 (0.9)	23.9 (0.4)	43.1 (5.8)	56.1 (7.4)	0.5 (0.3)	0.4(0.2)	5.9 (0.1)	5.8 (0.1)	
3	23.3 (0.5)	23.4 (0.5)	59.3 (20.3)	66.7 (22.4)	0.5(0.2)	0.4(0.3)	6.1 (0.2)	6.1 (0.2)	
4	22.5 (1.6)	22.5 (1.5)	39.5 (15.8)	46.8 (19.9)	0.5 (0.5)	0.5 (0.5)	5.9 (0.2)	5.9 (0.2)	
Nutrients	s + pesticido	es (west secti	on)						
	23.0 (2.4)	22.8 (1.4)	274.9 (158.4)	67.0 (3.9)	1.2(0.9)	0.4(0.2)	5.9 (0.3)	6.0 (0.0)	
	24.0 (1.3)	23.9 (0.7)	120.0 (29.4)	74.0 (6.0)	0.6 (0.5)	0.3 (0.2)	6.5 (0.1)	6.1 (0.1)	
	23.4 (0.6)	23.3 (0.5)	84.7 (32.9)	81.5 (22.3)	0.4 (0.4)	0.3 (0.5)	6.4 (0.2)	6.5 (0.3)	
	22.5 (1.7)	22.4 (1.6)	55.2 (32.1)	66.6 (27.0)	0.4 (0.4)	0.4 (0.6)	6.1 (0.3)	6.3 (0.3)	

Table 3. Mean (SD) measured nutrient (mg L^{-1}) and pesticide (μ g L^{-1}) concentrations in the control (west section) of the constructed wetland mesocosm from 28 July 2009 to 26 August 2009. Adjacent east section received nutrients only.

Nutrient or pesticide	10 m	20 m	40 m	
TP	0.47 (0.30)	0.37 (0.17)	0.29 (0.17)	
SRP	0.21 (0.27)	0.07 (0.06)	0.05 (0.04)	
NH_4^+ -N	0.03 (0.04)	0.01 (0.02)	0.01 (0.02)	
$NO_3^{\frac{1}{2}}$ -N	0.68 (0.77)	0.08 (0.09)	0.04 (0.04)	
NO_2^{-1} -N	0.01 (0.01)	<0.01 ^a	<0.01 ^a	
TN	2.10 (1.09)	1.61 (1.44)	1.33 (0.46)	
Atrazine	0.5 (0.7)	$< 0.1^{b}$	$< 0.1^{b}$	
S-Metolachlor	$< 0.1^{b}$	<0.1 ^b	$< 0.1^{b}$	
Cis-Permethrin	0.2(0.5)	<0.1 ^b	$< 0.1^{b}$	
Trans-Permethrin	<0.1 ^b	< 0.1 ^b	<0.1 ^b	

 $^{{}^{\}rm a}$ Below detection limit of 0.01 mg L^{-1} .

SRP dissipation ranged from 45 to 77% within 48 h and 98 to 99% by 672 h. Forward stepwise regression models showed that P was influenced by plant density, precipitation and time (Table 4). Aqueous dissipation half-lives of P ranged from 13 to 34 h (Table 5). By contrast, during nutrients + pesticides treatment, aqueous P concentrations peaked at 3–44 h post amendment, ranging from 1.28 mg TP L $^{-1}$ at 40 m to 8.47 mg TP L $^{-1}$ at 10 m and 0.38 mg SRP L $^{-1}$ at 40 m to 7.24 mg SRP L $^{-1}$ at 10 m, indicating P loading in the upstream portion of the wetland (Figure 1). Aqueous TP dissipation during this treatment ranged from 13–34% within 48 h and 11–71% by 672 h. Aqueous SRP dissipation with this treatment ranged from 25 to 68% within 48 h and 79 to 99% by 672 h. Forward stepwise regression models indicated that TP during this treatment was

 $^{^{}b}$ Below detection limit of 0.1 μ g L^{-1} .

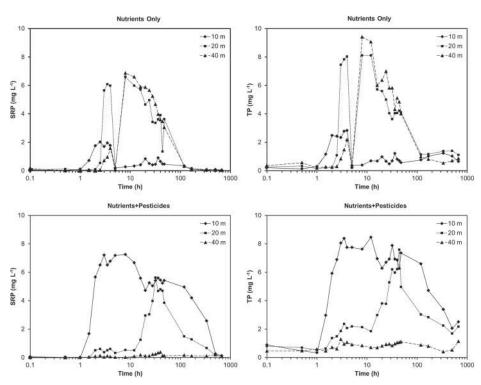


Figure 1. Phosphorus aqueous concentrations, total phosphorus (TP) and soluble reactive phosphorus (SRP), under nutrients only or nutrients + pesticides conditions in a free water surface constructed wetland mesocosm.

influenced by distance, time and rain, whereas SRP was influenced by distance, plant density and time (Table 4). Dissipation half-lives of P during nutrients + pesticides treatment were 2–10 times greater than nutrient only treatment ranging from 67 to 300 h (Table 5). Our dissipation results for P were comparable with other free water surface constructed wetlands receiving agricultural run-off during summer, showing aqueous SRP and TP dissipation ranging from < 30% [22] and 47% [23] to \sim 80%.[17] Observed associations of SRP and TP with *Juncus* sp. plant density during the summer nutrients only treatment are indicative of biological uptake of P by emergent aquatic macrophytes,[15,22,23] whereas the lack of association with plant density during the nutrients + pesticides treatment would indicate potential inhibition of biological uptake of P via growth inhibition in the presence of herbicides atrazine and *S*-metolachlor.[40,41] This, in turn, would affect the rate at which P dissipates from the water column and increase P half-life in the presence of herbicides at concentrations < 200 μ g atrazine L⁻¹ and < 300 μ g *S*-metolachlor L⁻¹.

Aqueous N concentrations in the wetland during nutrients only treatment peaked at various times across the sites. In general, concentrations peaked within 3 h at 10 m and within 16–44 h at 40 m. Peak dissolved inorganic N (DIN) concentrations were 0.82–0.92 mg NH $_4^+$ -N L $_1^-$, 3.42 – -43.83 mgNO $_3^-$ -N L $_1^-$ and 0.06–1.69 mg NO $_2^-$ -N L $_1^-$, whereas TN was in the range 7.58–116.91 mg L $_1^-$ (Figure 2). Similar to P, the greatest N loading during nutrients only treatment occurred at downstream wetland sites (Figure 2). DIN dissipation values at 48 h were in the range 4–8, 38–80 and 33–90%, and dissipation at 672 h were 100, 99–100 and 100% for NH $_4^+$ -N, NO $_3^-$ -N and NO $_2^-$ -N, respectively. Dissipation of TN ranged from 27 to 62% at 48 h and 74 to 98% at 672 h. Forward stepwise regression analysis indicated that nutrients only treatment DIN and TN were influenced by rain, plant density and distance (Table 4). Aqueous dissipation half-lives for DIN during nutrient only treatment ranged from 146 to 187 h for NH $_4^+$ -N and 22 to 58 h

Table 4. Forward stepwise linear regressions (n = 78) with standardised dimensionless regression coefficients and coefficients of determination computed using amended agrichemicals as dependent variables and values of sampling time (Time), distance from inflow (Distance), *J. effusus* plant density (*Juncus*), *P. australis* plant density (*Phragmites*) and total daily precipitation (Rain) as independent variables.

Agrichemical	Time	Distance	Juncus	Phragmites	Rain	R^2	p
Nutrients only (east	section)						
TP^a	0.260^{a}		0.291 ^a		0.292	0.256	< 0.001
SRP	-0.226		0.369		0.336	0.332	< 0.001
NH_4^+ -N	0.201a		0.347		0.344	0.296	< 0.001
NO_3^- -N			0.425^{a}		0.389	0.332	< 0.001
NO_2^3 -N		0.332			0.394	0.266	< 0.001
TN		0.270	0.259		0.452	0.408	< 0.001
Nutrients + pesticide	es (west section	1)					
TPa	0.378 ^a	-0.723^{a}			0.231	0.645	< 0.001
SRP	-0.21	-1.015		-0.430		0.551	< 0.001
NH_4^+ -N	-0.192	-0.624^{a}				0.426	< 0.001
NO_3^- -N	-0.239	-0.884^{a}		-0.398		0.426	< 0.001
NO_2^{-1} -N		-0.454				0.206	< 0.001
TN^{a}	-0.358	-0.645				0.545	< 0.001
Pesticides only (east	section)						
Atrazine	0.205 ^a	-0.527^{a}				0.320	< 0.001
S-Metolachlor ^a	0.393^{a}	-0.662^{a}				0.593	< 0.001
Cis-Permethrin	-0.260^{a}		-0.433^{a}			0.254	< 0.001
Trans-Permethrin	-0.261^{a}		-0.425^{a}			0.249	< 0.001
Nutrients + pesticide	es (west section	n)					
Atrazine	0.296^{a}	-0.489^{a}				0.327	< 0.001
S-Metolachlor	-0.189	-0.690	0.334			0.411	< 0.001
Cis-Permethrin	-0.216^{a}	-0.361^{a}				0.177	< 0.001
Trans-Permethrin		-0.645		-0.434		0.150	0.001

^aLog₁₀ transformed variable. Bold font indicates the largest standardised coefficient in each regression and blank cells indicate variables were dropped from stepwise regression due to a lack of significance.

for NO_3^- -N and NO_2^- -N, whereas TN ranged from 60–70 h (Table 5). In comparison, during nutrients + pesticides treatment, wetland aqueous N concentrations peaked within 8 h at 10 m and within 40–44 h at 40 m. Peak DIN concentrations during this treatment were 0.03–0.57 mg NH_4^+ -N L^{-1} , 0.80–33.76 mg NO_3^- -N L^{-1} and 0.02–0.29 mg NO_2^- -N L^{-1} , whereas TN ranged from 6.31 to 79.53 mg L^{-1} (Figure2). Greatest N loading during nutrients + pesticides treatment occurred at the 10 m site, again similar to patterns of P loading during this treatment. DIN dissipation values at 48 h during this treatment were 16–67, 29–64 and 27–55%, and dissipation values at 672 h were 100, 88–100 and 100% for NH_4^+ -N, NO_3^- -N and NO_2^- -N, respectively. Dissipation of TN ranged from 34 to 59% at 48 h and 84 to 98% at 672 h. During nutrients + pesticides treatment, forward stepwise regression models revealed NH_4^+ -N was influenced by distance and time, NO_3^- -N was influenced by distance, plant density and time, NO_2^- -N was influenced by distance only, and TN was influenced by distance and time (Table 4). During nutrients + pesticides treatment, dissipation half-lives of aqueous N were 1.5–5 times greater than in the nutrients only treatment. DIN nutrients + pesticides treatment half-lives were 146–230 h for NH_4^+ -N, 32–65 h for NO_3^- -N and NO_2^- -N, and TN half-lives ranged from 44 to 408 h (Table 5).

Nitrogen dissipation from a wetland water column can occur via complex processes of several biogeochemical pathways including nitrification, denitrification and organism uptake (animal, plant, algae, bacteria).[6,18,41] Dissipation of wetland water column DIN in this study was comparable with other studies assessing free water surface constructed wetland vegetated with emergent aquatic macrophytes.[6,14] Díaz et al. [14] showed 85–99% dissipation of NO₃⁻-N from the water column during the growing season (April–September) in wetlands having 50–60%

Table 5. Aqueous exponential dissipation model coefficients and calculated aqueous dissipation half-lives for nutrients in east and west sections of a constructed wetland mesocosm.

Distance	TP	SRP	NH_4^+ -N	NO_3^- -N	NO_2^- -N	TN
Nutrients only (east	section)					
10 m						
Coefficient (b)	0.0013	0.0523*	0.0022	0.0311*	0.0025	0.0013
Half-life (h) $T_{1/2}$	NC^a	13	NC	22	NC	NC
20 m						
Coefficient (b)	0.0203*	0.0210*	0.0047*	0.0197*	0.0053	0.0115*
Half-life (h) $T_{1/2}$	34	33	146	35	NC	60
40 m						
Coefficient (b)	0.0196*	0.0202*	0.0037*	0.0120*	0.0128*	0.0099*
Half-life (h) $T_{1/2}$	35	34	187	58	54	70
Nutrients + pesticid	es (west section)				
10 m		,				
Coefficient (b)	0.0023*	0.0035*	0.0030*	0.0218*	0.0053*	0.0158*
Half-life (h) $T_{1/2}$	300	197	230	32	130	44
20 m						
Coefficient (b)	0.0032*	0.0103*	0.0047*	0.0126*	0.0080*	0.0083*
Half-life (h) $T_{1/2}$	216	67	146	55	86	84
40 m						
Coefficient (b)	0.0005	0.0011	0.0040*	0.0105*	0.0090*	0.0017*
Half-life (h) $T_{1/2}$	NC	NC	173	65	77	408

^{*}Statistically significant model coefficient of determination $(R^2) < 0.05$.

vegetation coverage of Typha latifolia or Echinochloa crus-galli compared with only 22% dissipation with only 5% vegetation. Lu et al. [6] observed a broader range of NO₃⁻-N dissipation reporting an average of $60.9 \pm 132.7\%$ during summer (June–September) in a wetland vegetated with Phragmites australis and Zizania caduciflora. In addition, Lu et al. [6] in the same study, measured dissipation of NH_{$^{+}$}-N during summer reporting an average of 63.6 \pm 49.5%, which is comparable with the results of the current study. Dissipation of TN is considered a valuable metric because it incorporates both inorganic and organic forms of N and is most consistently associated with the eutrophication of aquatic systems. Previous studies of TN dissipation in free water surface constructed wetlands receiving agricultural run-off during the growing season (April–September) range from as low as 20% to as much as 90%, and varied greatly [6,12,14,17] with greater dissipation percentages occurring with greater coverage of emergent aquatic macrophytes.[14] The results of the current study had comparable TN dissipation (74-98%) and showed that TN dissipation was associated with emergent aquatic plant density (Juncus sp.) during nutrients only treatment. By contrast, TN dissipation during nutrients + pesticides treatment was not associated with emergent aquatic plant density and might indicate the potential inhibition of plant uptake of N via growth inhibition in the presence of the herbicides atrazine and S-metolachlor, [41,42] which would account for the slightly longer half-lives (1.5–5-fold) during this treatment. Lytle and Lytle [43] showed J. effusus growth to be significantly inhibited by atrazine concentrations as low as 96 µg L⁻¹, specifically new shoot development. Similarly, Moore and Locke [44] observed that mixtures of atrazine and S-metolachlor significantly reduce radicle development in Typha latifolia seedlings at concentrations as low as $31 \,\mu g \, L^{-1}$ of the mixture, noting that S-metolachlor is a long-chain fatty acid inhibitor.[44] If plant growth and possibly plant metabolism slow in the presence of both atrazine and S-metolachlor, N metabolism will also be inhibited and concomitantly reduce N uptake rates. This would, in turn, affect the rate at which N dissipates from the water column and increase agricultural run-off storage time needed for a wetland to process and remove N before exiting into a river or stream.

^aNC, not calculated due to insignificant model coefficient of determination (R^2) .

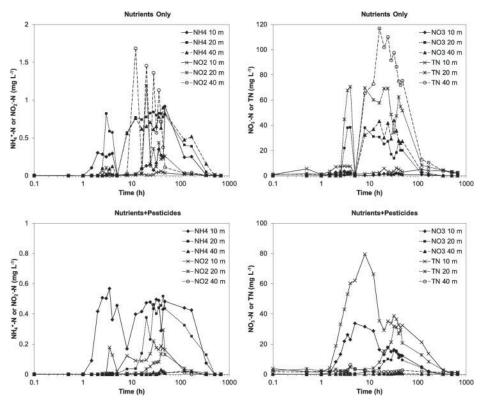


Figure 2. Nitrogen aqueous concentrations, NH₄⁺-N, NO₂⁻-N, NO₃⁻-N and total nitrogen (TN), under nutrients only or nutrients + pesticides conditions in a free water surface constructed wetland mesocosm.

3.3. Wetland pesticides

Patterns of wetland herbicide concentrations during pesticides only treatment showed that peak concentrations occurred within 8-16 h at 10 m ranging from 196.9 µg atrazine L⁻¹ to 287.5 µg S-metolachlor L^{-1} and within 168 h at 40 m ranging from 8.3 μ g S-metolachlor L^{-1} to 14.9 μ g atrazine L^{-1} , indicating loading in the first 10 m of the wetland (Figure 3). Herbicide dissipation during pesticides only treatment at 48 h ranged from 19 to 49% for atrazine and 56 to 58% for S-metolachlor, whereas at 672 h dissipation ranged from 50 to 97% for atrazine and 67 to 99% for S-metolachlor. Surface sediment herbicide concentrations peaked within 24-120 h at 10 m ranging from $16 \,\mu g$ S-metolachlor kg⁻¹ to $21 \,\mu g$ atrazine kg⁻¹ and within 120– $288 \,h$ at $40 \,m$ with concentrations of 20 µg S-metolachlor kg⁻¹ to 36 µg atrazine kg⁻¹ (Figure 4). Forward stepwise regression analysis revealed that atrazine and S-metolachlor were influenced by distance and time variables (Table 4). Dissipation half-lives of herbicides during pesticides only treatment were 154–204 and 62–265 h for atrazine and S-metolachlor, respectively (Table 6). During nutrients + pesticides treatment, patterns of herbicide distribution similar to those in pesticides only treatment were observed. Peak herbicide concentrations occurred within 3-12 h at 10 m, ranging from 191.8 μ g atrazine L⁻¹ to 315.5 μ g S-metolachlor L⁻¹, and again within 168 h at 40 m ranging from $8.5 \,\mu g$ S-metolachlor L⁻¹ to $15.8 \,\mu g$ atrazine L⁻¹, indicating loading in the first 10 m of the wetland (Figure 3). Sediment herbicide concentrations during this treatment peaked within 24–288 h at 10 m ranging from 37 μ g S-metolachlor kg⁻¹ to 38 μ g atrazine kg⁻¹ and within 24 h at 40 m with concentrations of $9 \mu g kg^{-1}$ for both herbicides (Figure 4). Nutrients + pesticides

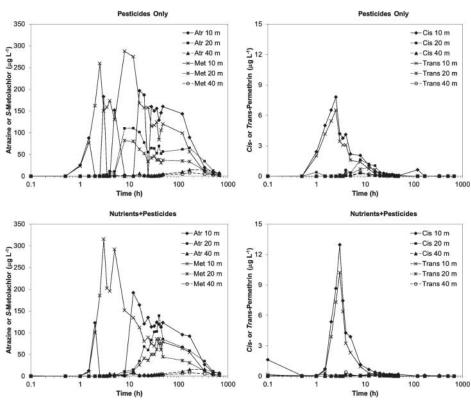


Figure 3. Herbicides atrazine and S-metolachlor and insecticide isomers *cis*-permethrin and *trans*-permethrin aqueous concentrations under pesticides only and nutrients + pesticides conditions in a free water surface constructed wetland mesocosm.

treatment forward stepwise regressions showed atrazine was influenced by distance and time variables, whereas S-metolachlor was influenced by distance, plant density and time (Table 4). Dissipation half-lives of herbicide during nutrients + pesticides treatment were 150 and 16–276 h for atrazine and S-metolachlor, respectively (Table 6). Herbicide water column dissipation in the current study was comparable with other studies in similar wetland systems. [45–49] In previous studies, water column atrazine dissipation in free water surface constructed wetlands has been reported to range from as low as 34–37% after 35 days [45] to as high as 70–89% after 20 days, [49] whereas the current study observed a range of atrazine dissipation of 50-97%. Dissipation of metolachlor from wetland water column has been reported to range from 48 to 83% [46] and is similar to the results of this studyof 67–99%. Observed herbicide concentrations within selected sediment samples indicate a significant fraction of both herbicides sorbed to wetland bed sediments at concentrations comparable with those reported by Belden et al. [50] in southern playa wetland sediments receiving agricultural run-off. Wide ranges in reported half-lives of metolachlor (408– 1464 h) were concentration dependent, with lower concentrations having shorter half-lives. [45] This explains the wide range of observed half-lives of S-metolachlor in the present study (16– 276 h). In this study, dissipation did not appear to be affected by the absence or presence of nutrients with herbicides.

Insecticide permethrin concentrations in wetland water during pesticides only treatment had peak concentrations occurring within 2.5–12 h at all sites, with concentrations of 6.5–7.8 μ g L⁻¹ at 10 m, 0.9–1.6 μ g L⁻¹ at 20 m and 0.3 μ g L⁻¹ at 40 m for *cis*- and *trans*-isomers (Figure 3). Permethrin dissipation during pesticides only treatment was rapid, with 98–100% dissipation

Table 6. Aqueous exponential dissipation model coefficients and calculated aqueous dissipation half-lives for pesticides in east and west sections of a constructed wetland mesocosm.

Distance	Atrazine	S-Metolachlor	cis-Permethrin	trans-Permethrin
Pesticides only (east	section)			
10 m				
Coefficient (b)	0.0045*	0.0109*	0.3567*	0.4943*
Half-life (h) $T_{1/2}$ 20 m	154	62	2	1.4
Coefficient (b)	0.0033*	0.0073*	0.1007*	0.0847*
Half-life (h) $T_{1/2}$ 40 m	209	94	6.9	8.1
Coefficient (b)	0.0012	0.0026*	0.0878*	0.1056*
Half-life (h) $T_{1/2}$	NC^a	265	7.9	6.5
Nutrients + Pesticid 10 m	es (West Section	1)		
Coefficient (b)	0.0046*	0.0432*	0.8458*	0.9337*
Half-life (h) $T_{1/2}$ 20 m	150	16	0.8	0.7
Coefficient (b)	0.0046*	0.0058*	0.0575*	0.0917*
Half-life (h) $T_{1/2}$ 40 m	150	120	12	7.5
Coefficient (b)	0.0014	0.0025*	0.0455*	1.3114*
Half-life (h) $T_{1/2}$	NC	276	15	0.5

^{*}Statistically significant model coefficient of determination $(R^2) p < 0.05$.

within 48 h. Variables influencing permethrin during this treatment were plant density and time (Table 4). Permethrin dissipation half-lives during this treatment ranged from 1.4 to 7.9 h (Table 6). In comparison, permethrin concentrations during nutrients + pesticides treatment peaked at 3 h at 10 m, but at 16-20 h at 20-40 m. Measured permethrin concentrations during this treatment were comparable with pesticides only treatment with $10.2-13.0 \,\mu g \, L^{-1}$ at $10 \, m$, $0.1-0.2 \,\mu g \, L^{-1}$ at 20 m and $0.1 \,\mu g \, L^{-1}$ at 40 m for cis- and trans-isomers (Figure 3). Surface sediment samples analysed for permethrin showed that nearly all samples were below detection for this pesticide. Only a single sample within the nutrients + pesticides treatment at 10 m at 288 h measured 1 μg permethrin kg⁻¹, indicating that minimal amounts of this pesticide reached wetland surface sediments (Figure 4). Forward stepwise regression analysis showed that permethrin during nutrients + pesticides treatment was influenced by distance, plant density and time (Table 4). Permethrin dissipation half-lives during this treatment ranged widely from 0.8 to 15 h for the cis isomer and from 0.7 to 7.5 h for the trans-isomer (Table 6). Comparisons of water column permethrin dissipation in this study with other previously reported studies within similar vegetated wetland systems [13,48,51] showed similarity in abatement efficiency. Budd et al. [13] observed 90-94% dissipation of permethrin after 5 h in a free surface water wetland vegetated primarily with Paspulum distichum, Polygonum lapathifolium and Echinochloa crus-galli, and receiving agricultural run-off after rainfall events from May to August. Moore et al. [51] observed dissipation of permethrin after 12 h in free surface water wetland mesocosms vegetated with emergent aquatic macrophytes Typha latifolia (67-78%) and Leersia oryzoides (71-81%). The lack of observed permethrin in wetland surface sediment in the current study is in contrast to other wetland studies showing significant sorption of permethrin to sediment [51,52] and indicated that permethrin within the study wetland likely sorbed to numerous other plant surfaces, algae, dissolved organic carbon and other particulates suspended in the water column prior to reaching bed sediments. Although the present study reports a 48 h permethrin dissipation of 98-100%, the short half-life reported (0.8–15 h) would make our results comparable with both reported studies. As

 $^{^{}a}$ NC, not calculated due to insignificant model coefficient of determination (R^{2}).

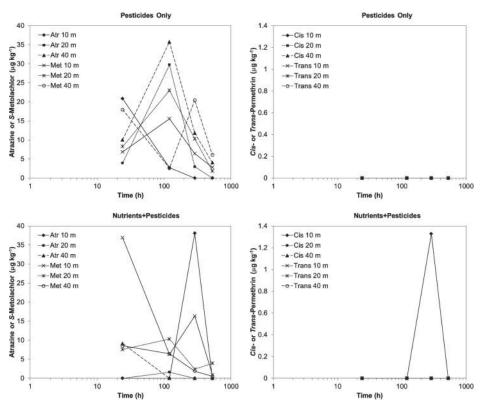


Figure 4. Herbicides atrazine and S-metolachlor and insecticide isomers *cis*-permethrin and *trans*-permethrin surface sediment (top 5 cm) concentrations under pesticides only and nutrients + pesticides conditions in a free water surface constructed wetland mesocosm.

with herbicides, permethrin dissipation did not appear to be affected by the absence or presence of nutrients.

4. Conclusions

Non-point source agricultural run-off is, by nature, a mixture of various pollutants that includes nutrients and pesticides.[13,14] Because of this, the current study is increasingly important in understanding the abatement efficiency and increased use of free surface water constructed wetlands as an agricultural best management practice in mitigating water quality impacts in rivers, lakes and streams. Emergent aquatic vegetation density plays an important role in the abatement of both nutrients and pesticides. However, nutrient abatement could be inhibited in the presence of herbicides. Further study is needed to better understand the interactions of agricultural pollutants on the efficacy of vegetated free water surface constructed wetlands in abating agricultural run-off.

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