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Effects of a Simulated Agricultural Runoff Event on Sediment Toxicity in a Managed Backwater Wetland

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Abstract We examined the effects of an amended mixture of three pesticides, atrazine (72.7 g), *S*-metolachlor (54.5 g), and permethrin (both *cis* and *trans* isomers; 11.4 g), on 10-day sediment toxicity to *Hyalella azteca* in a managed natural backwater wetland after a simulated agricultural runoff event. Sediment samples were collected at 10, 40, 100, 300, and 500 m from inflow 13 days prior to amendment and 1, 5, 12, 22, and 36 days post-amendment. Background pesticide concentrations ranged from <1 to 977, <1 to 119, and <1 to 2 μg kg^{-1}, for atrazine, *S*-metolachlor, and permethrin, respectively. Average post-amendment atrazine and *S*-metolachlor were 2,915–3,927 and 3–20 μg kg^{-1}, respectively at 10–40 m and 538–872 and <1 μg kg^{-1}, respectively at 300–500 m. Average post-amendment permethrin was 65–200 μg kg^{-1} at 10–40 m and 1–10 μg kg^{-1} at 300–500 m. *H. azteca* 10-day survival varied spatially and temporally up to 100 m from inflow. Animal growth, independent of survival, was reduced 40 and 100 m from inflow on day 36, showing continued sediment toxicity of up to 100 m from inflow more than 1 month after amendment. Animal survival and growth were unaffected at 300 and 500 m from inflow throughout the study period. Correlations of pesticide concentrations and *H. azteca* responses indicated that observed sediment toxicity was primarily from permethrin with potential additional synergistic toxicity from atrazine and methyl parathion. Study results indicate that natural backwater wetlands can be managed to ameliorate pesticide mixture 10-day sediment toxicity to *H. azteca* within 300 m of inflow and smaller wetlands (≤100 m) may require several months of effluent retention to mitigate effects.

Keywords Atrazine · *S*-metolachlor · Permethrin · Pesticides · Riverine wetland · *Hyalella azteca*

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1 Introduction

Importance of agriculture in providing proper nutrition and fiber for the world's growing human population continues to increase (Swinton et al. 2007). As modern agriculture increasingly relies upon new technologies such as chemical fertilizers and pesticides to improve productivity and efficiency in order to meet this growing need (Cooper and Dobson 2007), there can be ecological trade-offs. One such ecological trade-off is degradation of water quality and aquatic habitat in rivers, lakes, and streams resulting from agricultural nonpoint source pollution (Knight and Welch 2004; Vondracek et al. 2005). Currently, several strategies

exist to lessen the impact of nonpoint source agricultural pollution including placement of conservation practices within agricultural fields such as conservation tillage and/or edge of fields such as vegetated buffer strips, sediment basins, and vegetated constructed wetlands (Reichenberger et al. 2007; Locke et al. 2008; Dunn et al. 2011). However, concerns exist regarding decreased agricultural productivity when implementing agricultural conservation practices (Pannell et al. 2006). Such concerns increase the value of utilizing existing riverine backwater wetland systems that are of poor to limited value for agricultural production but that can be modified and managed to maximize their natural filtering capabilities and become a viable conservation practice. Under the aforementioned conditions, these wetland systems already receive nonpoint source agricultural pollution such as pesticides (López-Flores et al. 2003; Lizotte et al. 2009; Knight et al. 2009a) and nutrients (Shields et al. 2010). While backwater wetland systems can be managed to intercept and trap nonpoint source agricultural pollution and improve downstream water and habitat quality for many aquatic organisms including isolated riverine bendways (Lizotte et al. 2009; Shields and Pearce 2010) and shallow floodplain depressions (Ibelings et al. 2007; Jeppesen et al. 2007), it is less clear how wetland organisms will be affected.

One such wetland organism, *Hyalella azteca* (Saussure), is a light brown to greenish colored freshwater species of Amphipoda, occurring through out much of North America into South America (Gonzalez and Watling 2002) where they are associated with substrates in both lentic and lotic clear unpolluted waters (Anteau and Afton 2008). *H. azteca* passes through at least nine instars during development before reaching a maximum length of about 8 mm, and the adult female is capable of hatching 15 broods or more, each about 10 days apart (De March 1977; De March 1978). Adults continue to molt numerous times with frequency dependent on food availability, temperature, and favorability of other environmental conditions (De March 1977; De March 1978; France 1987). *H. azteca* is a voracious omnivore, capable of consuming both animal and plant tissues (Koslucher and Minshall 1973; Rowell and Blinn 2003), and is probably most often observed grazing on the microscopic community associated with surfaces of living and dead aquatic vegetation (Rowell and Blinn 2003) in relatively warm-water habitats. *H. azteca* are prey for fish, but also some birds, amphibians, and predatory invertebrates (Anteau and Afton 2008; Anteau et al. 2011). For these reasons, *H. azteca* was selected as a sentinel species for this study.

The objective of the current study was to examine the use of a managed natural riverine backwater wetland in mitigating the ecological impacts of agricultural runoff on sediment-associated aquatic organisms. To do this, we first examined the responses of a sentinel epibenthic invertebrate, *H. azteca*, in standard 10-day sediment bioassays using survival and growth endpoints. Next, we assessed associations between observed organism responses and measured sediment-associated pollutant levels in order to link ecological effects with corresponding agricultural runoff.

2 Materials and Methods

2.1 Study Site Description

The study area was a reach of the Coldwater River about 20 km downstream from Arkabutla Lake Dam in northwestern Mississippi. The backwater wetland site was a segment of a backwater riverine bend about 2.5 km long and 20–40 m wide in Tunica County, Mississippi. Located inside the Coldwater River mainstem flood control levee, the backwater is the result of a 0.4-km cutoff constructed in 1941–1942. Land use surrounding the backwater wetland is row-crop cultivation, with a buffer of natural vegetation 5–100 m wide on both banks. The backwater wetland receives agricultural runoff from approximately 100 ha of cultivated lands, primarily through an intermittent slough hydraulically connected to a network of drainage ditches (Shields and Pearce 2010). The backwater wetland study area was managed using water control weirs upstream (34°40′05.85″ N, 90°13′38.77″ W) and downstream (34°40′16.67″ N, 90°13′35.05″ W), creating a larger, deeper segment managed as a lake habitat and a smaller, shallower segment, 500-m long, 20-m wide, that supported wetland and terrestrial plants managed as a wetland (Fig. 1). In addition, the backwater wetland had a large slough draining the majority of adjacent agricultural acreage into the system between 10 and 40 m; a smaller slough extending to the southeast via gulley erosion entering between 40 m and 100 m and an intermediate slough directly to the east entering between 100 and 300 m (Fig. 1).

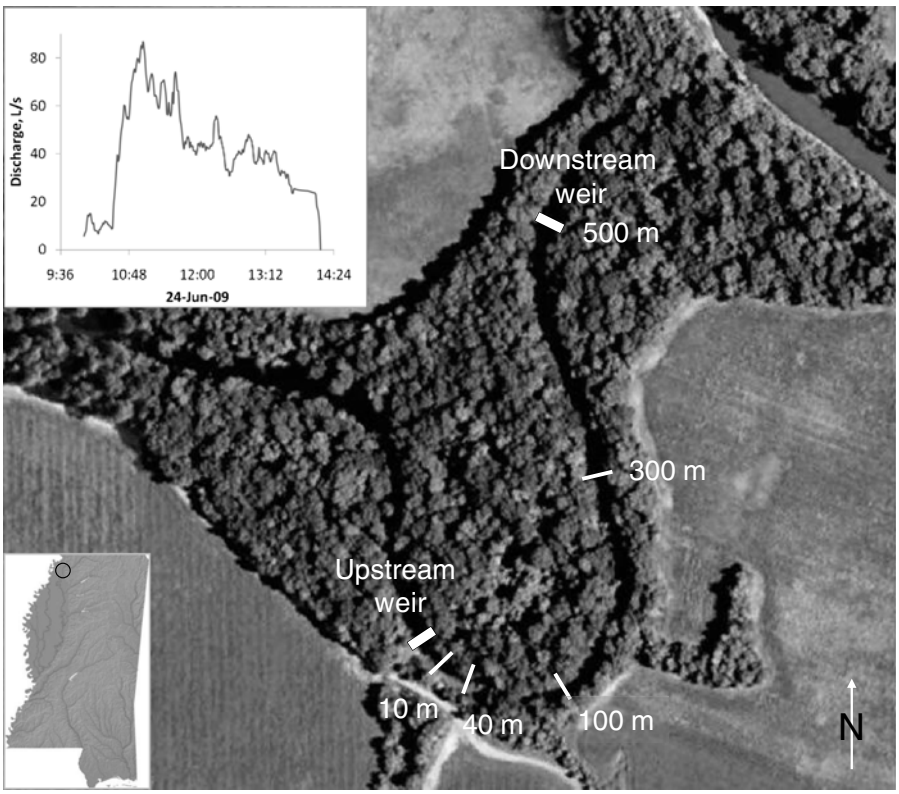


Fig. 1 Aerial photograph of the location and configuration of the Coldwater River-managed backwater wetland in Tunica County, Mississippi, with both upstream and downstream weirs and sampling locations. *Inset* of hydrograph during simulated agricultural runoff event on 24 June 2009

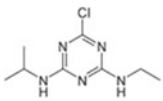
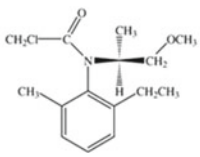
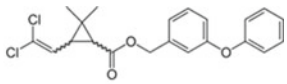
2.2 Simulated Agricultural Runoff Event

To simulate the rainfall event, the release of approximately 720 m^3 of water from the upstream lake segment of the backwater into the managed wetland segment occurred over a 4-h period on 24 June 2009. A hydrograph for the artificial event (Fig. 1, inset) was designed by scaling an observed hydrograph from the tributary slough (Shields and Pearce 2010) so that the peak flow was equal to the maximum discharge that could be obtained by releasing water from the lake cell through the drainage structure into the wetland (90 L s^{-1}). During the event, the hydrograph was generated by removing and replacing flashboards from the drainage structure at set times. Flow rates were continuously recorded by measuring the depth of flow over the weir and converting flow depth to discharge using a rating curve provided by the manufacturer. Flow rates were verified using acoustic and electromagnetic devices in the discharge channel. Outflow from the wetland was monitored throughout the experiment using a logging pressure transducer to record the depth of flow over the weir structure. No outflow occurred during simulated event, and no outflow occurred during the period following the event. A mixture comprising suspended sediment, nitrogen (34 % NH_4NO_3), phosphorus (42 % triple super phosphate P_2O_5), atrazine, *S*-metolachlor, and permethrin (Table 1) was amended for 1 h simulating a 1 % pesticide and nutrient loss, respectively, in agricultural runoff (Willis and McDowell 1982; McDowell et al. 1989) during a 1.27-cm rainfall event from a 16-ha cultivated field. A total of 270.8 kg sediment, 6.1 kg NH_4NO_3, 3.6 kg P_2O_5, 72.7 g active ingredient (ai) atrazine with 54.5 g ai *S*-metolachlor (Bicep II Magnum®), and 11.4 g ai permethrin (Hi-Yield 38®) were amended during 1 h at the upstream weir.

2.3 Sediment Sampling

Surface bulk sediment samples (top 5 cm) were collected 13 days prior to amendment and on days 1, 5, 12, 22, and 26 post-amendment. Samples were collected at distances from upstream weir inflow of 10, 40, 100, 300, and 500 m (adjacent to downstream weir) (Fig. 1). An exception was made at 100 m where samples were not collected on days 5 and 12 due to the absence of overlying water at the site. Approximately

Table 1 Physical and chemical properties of amended pesticides atrazine, *S*-metolachlor, and permethrin

Property	Atrazine[a,b]	*S*-metolachlor[a,c]	Permethrin[a,d]
Type	Herbicide	Herbicide	Insecticide
Class	Triazine	Acetanilide	Pyrethroid
CAS No.	1912-24-9	87392-12-9	52645-53-1
Molecular formula	$C_8H_{14}ClN_5$	$C_{15}H_{22}ClNO_2$	$C_{21}H_{20}Cl_2O_3$
Molecular structure			
Molecular weight	215.7	283.8	391.3
Density at 20 nbsp °C (g mL^{-1})	1.19	1.09	1.19
Vapor pressure (mPa)	0.04	1.7	0.045
Aqueous solubility (mg L^{-1})	32	480	0.006
Adsorption coefficient (log K_{oc})	2.0	2.4	4.2–5.7
Partition coefficient (log K_{ow})	2.3	3.4	6.1
Hydrolysis $T_{½}$ at pH 7 (day)	30	>200	Stable
Aerobic soil $T_{½}$ (d)	146	9	30–38
Anaerobic soil $T_{½}$ (d)	159	37–81	108

[a] EXTOXNET (1996)
[b] Bouldin et al. (2006)
[c] Moore et al. (2001)
[d] Dasgupta et al. (2008)

2 kg whole bulk wet sediment samples were collected by hand obtained using an acetone-washed stainless steel trowel and transferred to 1 L acetone/hexane triple-washed amber-colored glass jars fitted with a Teflon™-lined screw cap. Sample jars were preserved on wet ice and transported to the USDA-ARS National Sedimentation Laboratory (NSL), Oxford, Mississippi for analysis.

2.4 Sediment Characterization and Pesticide Analysis

After arrival at the NSL, bulk sediment from each site and control sediment from the University of Mississippi Field Station (UMFS) was thoroughly homogenized and an aliquot (~200 g, *w*/*w*) was subsampled and air-dried for 48 h for sediment characterization, nutrient, and pesticide analysis. Portions of the sample

were run on a Horiba model LA-910 laser scattering particle size analyzer (Horiba Scientific, Kyoto-shi Kyoto, Japan) to obtain particle size distribution data. Small portions of sediment from different areas of the sample material were added to the analyzer until laser transmittance was reduced to within the recommended operating range, approximately 85 %. Sample material was dispersed in approximately 200 ml water with 0.02 % sodium hexametaphosphate (Calgon) surfactant to aid dispersion, and then subjected to 30 s of ultrasonic treatment (40 W, 39 kHz) by the Horiba LA-910 prior to measurement. Light scattering was measured using both a He–Ne laser (632.8 mm, 1 mW) and tungsten halogen lamp (50 W) with a set of six 18-division, ring-shaped silicone photo-diode detectors. Particle sizes were calculated based on Mie scattering theory, using a relative refractive index of 1.32-000.

Sediment samples for carbon and nitrogen analysis were allowed to air dry and were then finely ground. Samples were then representatively subsampled to obtain approximately 1 g (±0.1 g). Subsamples were analyzed using a Vario Max CNS instrument from Elementar Analysensysteme GmbH (Hanau, Germany) in CN mode with precision of less than or equal to 0.5 % relative measurement, employing a thermal conductivity detector for measurements following tungsten catalytic tube combustion of samples, and separation of gases to acquire desired components. Sediment phosphorus was not measured since the focus of the study was on sediment toxicity and because phosphorus either within the water column or bound to sediments is not considered toxic to animals (Carpenter et al. 1998) and as a result would not contribute to any toxicity observed in the current study. Nutrient recovery (in percent) and precision (relative standard deviation (%RSD)), based on fortified samples, were evaluated. Carbon showed acceptable mean recoveries of 99–100 % with RSD of 0.1 %; nitrogen also had good mean recoveries of 94–96 % with RSD of 1.1 % based upon standard quality assurance/quality control (QA/QC) practices (Eaton et al. 2005).

In addition to the amended pesticides (atrazine, *S*-metolachlor, and permethrin), an additional suite of 13 non-amended pesticides and metabolites (Table 2) were analyzed in sediments due to the open nature of the study wetland which allowed runoff to enter from adjacent agricultural fields (Shields and Pearce 2010) and further contaminating the sediment. Pesticides were extracted using pesticide-grade ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated to near dryness by rotary evaporation. Next, the extract was subjected to silica gel column chromatography cleanup, and concentrated to 1 mL volume under high purity dry nitrogen for GC analysis. Pesticide analysis was conducted using an Agilent Model 7890A gas chromatograph (Agilent Technologies, Inc., Waldbronn, Germany) 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 were used according to Smith and Cooper (2004) and Moore et al. (2009). The Agilent 7890A GC was equipped with two microelectron capture detectors (μECDs), and the analytical column was an Agilent HP 1MS capillary column, 30 m×0.25 mm (i.d.)×0.25 μm film thickness. Carrier gas used was ultrahigh purity (UHP) helium at 28 mL min^{-1} and inlet temperature at 250 °C. The μECD temperature was 325 °C with a constant make-up gas flow of 60 mL min^{-1} UHP nitrogen. Analytical detection limits for all pesticides were 1 μg kg^{-1}. Pesticide recovery (in percent) and precision (%RSD), based on fortified samples, were evaluated. For non-amended pesticides (Table 2), acceptable recoveries of 99–104 % with RSDs of 2.4–14.9 % for herbicides occurred; good recoveries of 89–102 % with RSDs of 3.4–11.7 % for insecticides occurred; and acceptable recoveries of 92–98 % with RSDs of 5.3–16.3 % for organochlorine pesticides were reported. For amended pesticides, atrazine showed acceptable recoveries of 109–111 % with RSDs from 6.4 to 10.2 %; *S*-metolachlor showed acceptable recoveries of 102–103 % with RSDs from 5.6 to 8.7 %; permethrin also had good recoveries of 98–121 % with RSDs from 1.9 to 9.6 % based upon standard QA/QC practices (Eaton et al. 2005).

2.5 Sediment Bioassays

Static nonrenewal bulk sediment bioassays lasting 10 days and using 7–8 days old *H. azteca* were conducted according to US Environmental Protection Agency (US EPA 2000) protocols, with the following modifications. In brief, four replicate exposures consisted of 20 g wet weight wetland sediment sample with 180 mL overlying hardness adjusted water (free from priority pollutants) from the UMFS (Deaver and Rodgers 1996) placed in exposure chambers (240 mL polypropylene plastic beakers). Exposure chambers were aerated for 30 min at test initiation to maintain oxygen levels. Ten *H. azteca* were placed in each exposure chamber along with two, 6-mm-diameter

Table 2 Mean sediment characteristics (in percent) and mean concentrations (in micrograms per kilogram) of amended and non-amended pesticides in sediments (U, below detection limit of 1 μg kg^{-1})

Characteristic or pesticide	Control	Distance from wetland inflow				
		10 m	40 m	100 m	300 m	500 m
Particle size						
Sand	85.9±2.2	33.3±29.1	44.5±21.9	49.3±33.4	48.0±12.2	23.7±25.5
Silt	14.1±2.2	63.9±28.0	52.9±20.5	45.6±29.6	49.6±11.5	71.7±22.0
Clay	0.0±0.0	2.8±1.4	2.5±1.4	5.0±3.9	2.4±0.7	5.2±5.0
Nutrient						
TOC	0.79±0.40	1.80±0.54	1.85±0.21	1.39±0.61	1.70±0.33	1.68±0.12
TN	0.04±0.05	0.15±0.06	0.17±0.03	0.11±0.06	0.15±0.04	0.14±0.01
Pesticide						
Atrazine (pre)	U	U	13	U	977	267
Atrazine (post)	1±3	3,927±6,251	2,915±3,382	U	872±617	538±771
S-metolachlor (pre)	U	21	119	U	U	U
S-metolachlor (post)	U	3±8	20±49	1±3	1±2	7±16
Permethrin (pre)	U	U	U	U	U	2
Permethrin (post)	U	200±192	65±62	10±14	10±10	1±1
Trifluralin	U	28±29	78±83	U	51±38	58±76
Methyl parathion	8±4	394±560	633±714	U	144±249	47±95
Alachlor	U	U	142±346	U	348±567	U
Chlorpyrifos	2±4	253±618	79±182	U	82±185	U
Cyanazine	4±7	3±7	71±167	U	9±23	2±5
Pendimethalin	U	U	U	U	U	U
Fipronil	U	5±6	3±3	U	2±1	1±1
Dieldrin	U	1±1	1±1	U	1±1	1±1
p,p′-DDE	U	8±14	4±3	U	3±2	3±2
Fipronil sulfone	U	2±2	7±11	U	2±1	1±1
p,p′-DDD	1±0	6±6	5±3	U	3±2	2±1
Bifenthrin	U	U	U	U	U	U
λ-cyhalothrin	U	U	U	U	U	U

pre pre-amendment background pesticide concentrations (n=1), *post* post-amendment pesticide concentrations (n=1)

maple leaf discs as substrate and food. Additional feeding of 0.1 mL of a 1:1 suspension rabbit chow/Tetramin® flake food at 2 gL^{-1} occurred every 2 days during the exposure period. Toxicity tests were conducted in a Powers Scientific, Inc. Animal Growth Chamber with a 16:8 (light/dark)-h photoperiod and a temperature of 23±1 °C. Standard physical and chemical water characteristics for sediment bioassays (temperature, pH, dissolved oxygen, conductivity, hardness, alkalinity, ammonium-*N*, nitrate-*N*, and nitrite-*N*) were measured according to Eaton et al. (2005). Bioassay endpoints measured were survival and growth (in micrograms dry weight).

2.6 Data Analysis

H. azteca 10-day survival and growth data were analyzed using a one-way analysis of variance (ANOVA) with Dunnett's multiple range tests versus controls or Kruskal–Wallis ANOVA on ranks with Dunn's multiple range tests versus controls when data failed to meet parametric assumptions (Steel et al. 1997). When significant survival effects were observed at a specific site, growth data from that site were excluded from the overall analysis of growth effects versus controls according US EPA (2000) protocols for data analysis. Effects of time after amendment (day), and distance

from wetland inflow within the wetland were analyzed using a two-way repeated-measure ANOVA on ln(x+1) transformed *H. azteca* survival data with Tukey's multiple comparison test (Steel et al. 1997; Schulz et al. 2003). Pearson product moment correlations of *H. azteca* survival and growth versus sediment pesticide concentrations in the managed backwater wetland were conducted. Because total organic carbon (TOC) can influence sediment pesticide toxicity (Nebeker et al. 1989), reported pesticide concentrations are often adjusted to the fraction of organic carbon content of the sediment (in micrograms pesticide per gram OC). For these analyses, pesticide concentrations were either unadjusted, adjusted to sediment total organic carbon (OC), or adjusted to sediment silt fraction (silt) to determine the strongest association between observed animal responses and measured pesticides. No attempt was made to associate measured nitrogen concentrations and animal responses since observed overlying water ammonium-*N*, nitrate-*N*, and nitrite-*N* occurred in concentrations below known-effects concentrations for *H. azteca* of 1.2, 142.4, and 12.5 mg L^{-1}, respectively (Borgmann and Borgmann 1997; Pandey et al. 2011; Soucek and Dickinson 2012).

3 Results

3.1 Sediment Characteristics and Pesticide Concentrations

Managed backwater wetland sediments were predominantly silt loam in soil texture (Reddy and DeLaune 2008) except at 40 m where soil texture was characterized as sandy loam (Table 2). Wetland sediments had low clay fractions ranging from <1 to 10 %, TOC fractions ranging from 1 to 2 %, and TN fractions ranging from 0.1 to 0.2 %. All control sediment samples had loamy sand soil textures with <1 % TOC and <0.1 % TN and had a few, low detectable amounts of any target pesticides, specifically methyl parathion, chlorpyrifos, cyanazine, and *p*,*p*′-DDD (Table 2). Analysis of a suite of un-amended pesticides in sediment samples revealed a variety of contamination longitudinally within the wetland (Table 2). The herbicide pendimethalin and two pyrethroid insecticides bifenthrin and λ-cyhalothrin were not detected in any sediment sample. In addition, all sediment samples at 100 m from inflow had no detectable concentrations of un-amended pesticides assessed in this study. Sediment from all remaining sites had detectable concentrations of at least 8 of the 13 un-amended pesticides analyzed (Table 2) with the organophosphate insecticides methyl parathion and chlorpyrifos occurring in the greatest concentrations and fipronil and dieldrin, the lowest. For amended pesticides, herbicides atrazine and *S*-metolachlor were detected in sediment prior to amendment (day 13) whereas the insecticide permethrin (either *cis* or *trans* isomers) was not detected (Fig. 2a–d). For amended pesticides, four pre-amendment samples detected either atrazine or *S*-metolachlor in backwater wetland sediments and were likely sourced from nearby adjacent agricultural fields. Peak concentrations of atrazine in sediment occurred 12 days after amendment upstream (10 and 40 m) but 5 days after amendment further downstream (300 and 500 m). A similar pattern was observed for sediment permethrin concentrations (both *cis* and *trans* isomers) (Fig. 2c, d). In contrast, sediment *S*-metolachlor concentrations were greatest prior to amendment at upstream sites (10 and 40 m) with only four samples having detectable concentrations after amendment (Fig. 2b).

3.2 Sediment *H. azteca* Bioassays

Sediment bioassay overlying water-quality parameters were within acceptable limits for 10-day bioassays according to US EPA (2000) protocol . Mean±SD water-quality data were as follows: temperature, 23.5±0.3 °C; pH 7.8±0.4; dissolved oxygen, 6.9±0.1 mg L^{-1}; conductivity, 367±42 μS cm^{-1}; alkalinity, 41.6±10.3 mg L^{-1} as $CaCO_3$; hardness, 79.6±19.0 mg L^{-1} as $CaCO_3$; ammonium-N, 0.2±0.2 mg L^{-1}; nitrate-N, 0.4±0.3 mg L^{-1}; nitrite-N, 0.03±0.007 mg L^{-1}. *H. azteca* 10-day survival in pesticide-contaminated wetland sediment varied spatially and temporally after pesticide amendment but not before (Table 3). Prior to amendment (day 13), all sites had ≥90 % mean *H. azteca* survival and were comparable with control survival. After amendment of the atrazine, *S*-metolachlor, and permethrin mixture, clear trends were observed in animal survival with lowest mean survival, 0–65 %, occurring upstream near the point of amendment (10 m) and highest mean survival, 93–98 %, occurring furthest downstream (500 m). Specifically, significant (p<0.05) reduction in mean survival (versus controls) occurred on day 1 as far as 100 m downstream, on days 5 and 12 as far as 40 m downstream, and through day 36 at 10 m downstream (Table 3). Within the 36-day

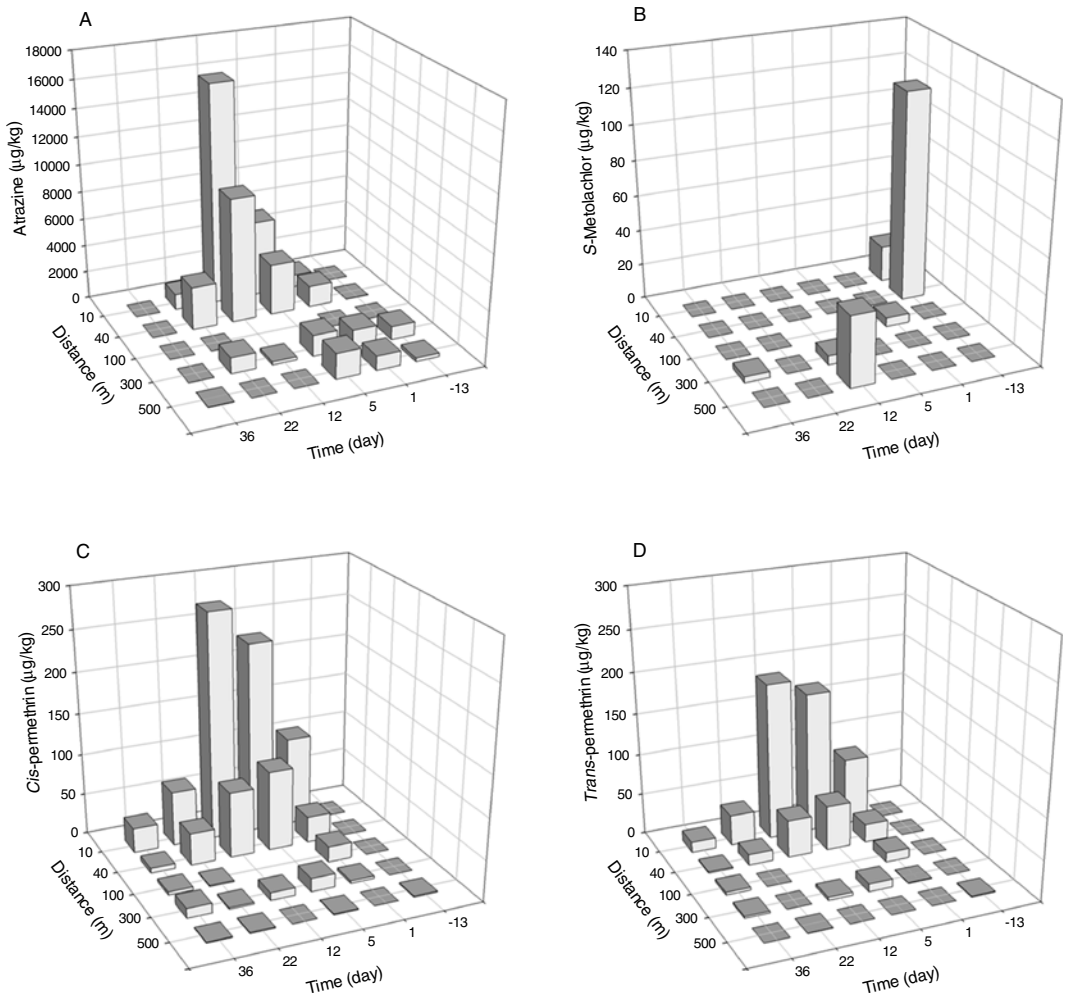


Fig. 2 Sediment concentrations (in micrograms per kilogram) of amended pesticides, **a** atrazine, **b** *S*-metolachlor, **c** *cis*-permethrin, and **d** *trans*-permethrin during/after the simulated agricultural runoff event in a managed backwater wetland

study period, survival recovery was observed at all sites with significant survival reductions. At 10 m, mean survival improved from 0 on day 5 to 65 % by day 22. At 40 m, mean survival improved from 20 on day 1 to 83 % by day 22, and at 100 m, mean survival increased from 48 on day 1 to 98 % by day 22.

Results of the two-way repeated-measure ANOVA with sampling day ($p<0.0001$), distance from wetland inflow ($p<0.0001$) showed significant temporal and spatial variation in mean *H. azteca* survival (Table 4). Mean survival significantly increased over time and across distance downstream from wetland inflow. As a result, significant interactions occurred between sampling day×distance from wetland inflow ($p<0.0001$) clearly indicating increased sediment toxicity at sites with increasing proximity to wetland inflow within the first two weeks after pesticide amendment (Table 5).

Observed pesticide mixture effects on *H. azteca* growth were limited due to significant survival effects. From days 1 to 22 where animal survival was not significantly affected, growth was also unaffected (Table 3). On day 36, sites 40 and 100 m had significantly ($p<0.05$) reduced growth (independent of survival effects) compared with animal growth in control sediments. Decrease in mean animal mass was greatest at 40 m where growth was reduced by 83 % compared with controls, whereas mean animal mass at 100 m decreased by 47 % compared with controls (Table 3).

Table 3 Mean *Hyalella azteca* 10-day survival and growth responses to sediment exposures from a modified wetland

Endpoint	Day	Control	Distance from wetland inflow				
			10 m	40 m	100 m	300 m	500 m
Survival (%)	−13	95±6	95±6	90±14	90±12	93±10	90±8
	1	100±0	23±13*	20±18*	48±25*	95±6	93±5
	5	93±10	0±0*	28±13*	NS[a]	85±6	93±10
	12	93±10	30±24*	33±13*	NS	88±19	98±5
	22	100±0	65±5*	83±17	98±5	98±5	98±5
	36	95±6	48±10*	78±13	95±5	88±19	95±6
Growth (μg)	−13	35±5	48±16	37±19	53±11	32±9	28±10
	1	46±10	23±18[b]	35±65[b]	35±10[b]	40±22	54±10
	5	62±9	N/A[c]	35±24[b]	NS	64±22	39±15
	12	47±13	25±10[b]	16±6[b]	NS	53±10	48±20
	22	39±13	18±15[b]	42±15	49±23	53±13	69±7
	36	55±15	16±16[b]	9±11*	29±9*	39±15	39±7

*$p<0.05$, significantly different from control

[a] Not sampled at site when water was not present

[b] Not included due to significant survival effects

[c] Not applicable

3.3 Pesticide-Bioassay Endpoint Associations

Because of the broad suite of pesticides measured in wetland sediment, associations between bioassay endpoints (i.e., survival and growth) and measured concentrations were important in elucidating and clarifying stressor–response patterns. Significant associations ($p<0.05$) between unadjusted pesticide concentrations and *H. azteca* survival occurred with permethrin (*cis* and *trans* isomers and ∑permethrin), atrazine, methyl parathion, fipronil, and *p,p′*-DDD, respectively (Table 6). Highest correlation coefficients occurred with sediment concentrations of the insecticides permethrin (*cis* and *trans* isomers and ∑permethrin; $r=-0.907$, −0.908, and −0.916) and methyl parathion ($r=-0.613$) concentrations normalized for organic carbon levels. Highest correlation coefficient for the herbicide atrazine and *H. azteca* survival occurred with concentrations adjusted for sediment silt fraction ($r=-0.611$). In contrast, *S*-metolachlor was not associated with animal survival regardless of unadjusted or adjusted concentrations (Table 6). *H. azteca* growth was significantly ($p<0.05$) associated with sediment permethrin (*cis* and *trans* isomers and ∑permethrin) only. Highest correlation coefficients occurred with unadjusted *cis* and *trans* isomers and ∑permethrin with *r* values of −0.515, −0.519, and −0.518, respectively (Table 6).

4 Discussion

There is a limited but growing body of literature examining the effects of agricultural contaminants on benthic aquatic invertebrates in wetlands designed to trap and process runoff (Milam et al. 2004; Bouldin et al. 2007). However, these studies have focused on a single contaminant: a single insecticide. Milam et al. (2004) observed no significant effects of the organophosphate insecticide methyl parathion in wetland sediment, either vegetated or without vegetation, on survival or growth on *Chironomus tentans* after 10-day exposures whereas Bouldin et al. (2007) showed a decrease in 10-day survival of *Chironomus dilutus*

Table 4 *Hyalella azteca* 10-day sediment survival (ln (x+1) transformed) two-way repeated measures analysis of variance with sampling day (day) and distance from wetland inflow (distance)

Variable	Degrees of freedom	Sum of squares	*F* statistic	*p* value
Day	5	0.20	28.9	<0.0001
Distance	3	0.40	299.1	<0.0001
Day × distance	15	0.20	9.5	<0.0001

Table 5 Results of Tukey's test multiple comparison procedure: differing capital letters represent statistically significant survival differences by distance from wetland inflow within sampling day; differing lower case letters represent statistically significant survival differences by sampling day within distance from wetland inflow ($p \leq 0.05$)

Day	Distance from wetland inflow			
	10 m	40 m	300 m	500 m
−13	Aa	Aa	Aa	Aa
1	Bd	Bb	Aa	Aa
5	Ce	Bb	Aa	Aa
12	Bcd	Bb	Aa	Aa
22	Bab	ABa	Aa	Aa
36	Bbc	Aa	Aa	Aa

exposed to diazinon contaminated wetland sediment collected from 2 to 14 days after amendment. There remains a paucity of research on the effects of agricultural contaminant mixtures to benthic invertebrates in wetland systems (Bouldin et al. 2005; Moore et al. 2007), even though mixture contamination from agricultural runoff is common (Belden et al. 2006; Smith et al. 2008). As a result, assessments of contaminant mixture sediment toxicity instead of single contaminant sediment toxicity are more appropriate. As contaminant mixtures from agricultural runoff enter the wetland system and are removed from the water column, fractions of these contaminants enter different compartments of the system including physical compartments (gravimetric settling of suspended sediments; sorption of P and pesticides to sediment surface particles: sand, silt, and clay) and biological compartments (uptake of N and P by plants and algae; sorption of pesticides to plants, algae) at varying rates depending upon physicochemical properties of the contaminants (Reddy and DeLaune 2008). In the present study, sediment nutrient TN concentrations were unaffected by aqueous nitrogen amendments with TN highly similar across most sites ranging from 0.15 to 0.20 % at 10–300 m and 0.12 to 0.15 % at 500 m except 100 m which ranged from 0.07 to 0.08 % and where no water was present after day 1 but before day 22 sampling periods and could be the result of intermittent water inundation. The broad suite of non-amended pesticides detected in the backwater wetland sediments is typical of this intensive agricultural region (Knight et al. 2009b). Influx of these non-amended pesticides can come from three primary sources: a large slough draining the majority of the acreage

Table 6 Pearson product moment correlation coefficients (r) of *Hyalella azteca* 10-day survival (n=34) and growth (n=33) versus pesticides in sediment of a managed backwater wetland

Pesticide	Survival			Growth		
	ng g^{-1}	μg g $silt^{-1}$	μg g OC^{-1}	ng g^{-1}	μg g $silt^{-1}$	μg g OC^{-1}
Trifluralin	−0.370	−0.142	−0.267	0.038	0.126	0.111
Methyl parathion	−0.596*	−0.518*	−0.613*	−0.173	−0.043	−0.116
Alachlor	−0.053	−0.001	−0.071	0.186	0.152	0.173
Chlorpyrifos	−0.286	−0.452	−0.337	−0.170	−0.247	−0.190
Cyanazine	0.001	−0.203	−0.073	−0.006	−0.180	−0.031
Fipronil	−0.573*	−0.451	−0.450	−0.324	−0.220	−0.255
Dieldrin	−0.168	0.065	0.071	0.003	0.168	0.090
p,p′-DDE	−0.461	−0.366	−0.344	−0.085	−0.070	−0.080
Fipronil sulfone	−0.372	−0.293	−0.295	−0.108	−0.196	−0.164
p,p′-DDD	−0.530*	−0.373	−0.409	−0.142	−0.027	−0.087
Atrazine	−0.514*	−0.611*	−0.546*	−0.201	−0.245	−0.212
Metolachlor	0.180	0.146	0.179	0.138	0.038	0.106
cis-permethrin	−0.872*	−0.803*	−0.907*	−0.515*	−0.424	−0.500*
trans-permethrin	−0.913*	−0.785*	−0.908*	−0.519*	−0.417	−0.480
∑permethrin	−0.873*	−0.811*	−0.916*	−0.518*	−0.430	−0.504*

*$p \leq 0.0033$, statistically significant correlation after Bonferroni adjusted

into the backwater wetland between 10 and 40 m, a smaller slough extending to the southeast via gulley erosion entering between 40 and 100 m, and an intermediate slough directly to the east entering between 100 and 300 m (Fig. 1). These drainage areas explain the greater concentrations and frequency of occurrence of non-amended pesticides at 10, 40, and 300 m. Non-detection of any of these non-amended pesticides at 100 m can be attributed to intermittent inundation. Amended permethrin, both *cis* and *trans* isomers, readily adsorbed to backwater wetland sediments within 24 h and continued through 12 days post-amendment (Table 1). Permethrin concentration peaks occurred upstream at 10 and 40 m with concomitant decreases in concentrations downstream.

Previous research showed permethrin to rapidly adsorb to soils and sediments (Sharom and Solomon 1981; Allen et al. 2005; Gan et al. 2005; Xu et al. 2008). Physical and chemical properties of permethrin such as relatively high adsorption and partition coefficients (K_{oc} and K_{ow}) and low water solubility (Table 2) are the primary reasons. Furthermore, factors such as overlying water pH, soil pH, clay, and TOC content have been shown by Gan et al. (2005) to significantly influence sediment permethrin distribution. Sediments with lower clay and TOC content (<5 and <2.5 %, respectively) in slightly basic soils (7.5–8.0) were observed to sorb less permethrin than those with greater clay and TOC (Gan et al. 2005). Wetland sediment in the current study had relatively low clay and TOC (<5.3 and <2 %, respectively) (Table 2) and the pH of soils in the region (i.e., Mississippi Delta) range from slightly acidic to slightly basic (5.5–7.3) (Zablotowicz et al. 2006, 2007). In addition, the overlying water within the wetland had a circumneutral pH (6.5–7.5) (Lizotte et al. 2012). These conditions resulted in the observed sediment-sorbed permethrin ranging from <1 to 464 μg kg^{-1} in wetland sediments. Similarly, amended atrazine was observed compartmentalizing into the sediment phase by clear concentration peaks occurring upstream at 10 and 40 m with concomitant decreases in concentrations downstream. Factors such as TOC and clay content have been shown by Ling et al. (2006) and Lima et al. (2010) to significantly influence sediment atrazine sorption. Sediments with lower TOC and clay content (<2 and <20 %, respectively) in slightly acidic soils (6.1–6.5) were observed to sorb less atrazine than those with greater TOC and clay (Ling et al. 2006; Lima et al. 2010). Despite wetland sediment in this study having relatively low TOC and clay (<2 and <5.3 %, respectively) (Table 2), a significant amount of atrazine (>1,000 μg kg^{-1}) was found to sorb to several samples of this sediment (Fig. 2). In contrast, observed *S*-metolachlor was detected sporadically in only a few samples and with no clear pattern. Despite similar partition coefficients and soil adsorption coefficients (Zheng and Cooper 1996; Gao et al. 1998; Nemeth-Konda et al. 2002) (Table 1), atrazine and *S*-metolachlor clearly differentiated in their adsorption to backwater wetland sediments. Zheng and Cooper (1996) also observed that soil clay and sand content significantly influenced metolachlor adsorption. They found soils with higher silt content (fluvisols) had the least tendency to adsorb metolachlor. In the present study, sediments from the backwater wetland were characterized as silty to sandy loam, having 45–71 % silt (Table 2). As a result, adsorption of *S*-metolachlor to sediments was likely decreased allowing the herbicide to remain compartmentalized in other phases (e.g., aqueous and dissolved organic carbon) within the wetland system (Table 1).

Recently, there have been an increasing number of studies assessing pesticide toxicity in wetlands used for risk reduction (Schulz et al. 2003; Milam et al. 2004; Bouldin et al. 2007; Moore et al. 2007; Hunt et al. 2008; Brown et al. 2010). However, the majority of such studies have focused on only a single contaminant and only a few have addressed risk associated with mixture toxicity (Moore et al. 2007; Hunt et al. 2008; Brown et al. 2010). In the present study, differences in *H. azteca* 10-day survival and growth showed clear spatial and temporal patterns within managed backwater sediments throughout the 36-day study period. Animal survival was consistently greater at sites >100 m downstream from the point of amendment through 12 days post-amendment compared with the upstream site closest to the point of amendment (10 m). Similar spatial and temporal patterns were observed in *H. azteca* aqueous survival by Schulz et al. (2003) and Milam et al. (2004) in constructed wetlands amended with an organophosphate insecticide, methyl parathion. However, such patterns were not apparent in 10-day wetland sediment exposures assessing *C. tentans* survival and growth in wetlands amended with organophosphate insecticides such as methyl parathion and diazinon (Milam et al. 2004; Bouldin et al. 2007) but were apparent in wetland

sediment exposures assessing *H. azteca* survival in a constructed wetland amended with pyrethroid insecticides (Moore et al. 2007). These differences in responses can be attributed to two factors: first, organophosphate insecticides adsorb to sediments less readily than pyrethroid insecticides (Bondarenko and Gan 2004; Gan et al. 2005); and second, the more sensitive nature of *H. azteca* to sediment bound pyrethroids than *C. tentans* (Maund et al. 2002). As a result, future toxicity assessments of pesticide-contaminated wetland sediments should include at least *H. azteca*, but preferably both *H. azteca* and *C. tentans*.

Associations of wetland sediment *H. azteca* survival and pesticide mixtures revealed between three and five different negative correlations. The greatest total number of associations was with unadjusted pesticide concentrations whereas the highest correlation coefficients were with pesticide concentrations adjusted for organic carbon content. Organic carbon adjusted permethrin, including both *cis* and *trans* isomers, had the highest negative correlation coefficients ($r>0.9$). This coincided with Σpermethrin concentrations ranging from 5 to 20 μg g^{-1} OC and mean animal survival ranging from 0 to 65 %. Our observed Σpermethrin effects concentrations are similar to those observed by Amweg et al. (2005) who reported a 10-day *H. azteca* LC_{50} of 4.9 μg permethrin g^{-1} OC in California sediments. Organic carbon adjusted methyl parathion, having the second highest negative correlation coefficient with animal survival, had concentrations ranging from 22 to 83 μg g^{-1} OC that coincided with 0–33 % mean animal survival. Our observed methyl parathion effects concentrations are comparable with Ding et al. (2011) who observed a 10-day *H. azteca* LC_{50} of 12.7 μg methyl parathion g^{-1} OC. Coinciding with peak methyl parathion concentrations, and associated animal survival effects, were peak atrazine concentrations. In our study, atrazine was also significantly negatively correlated with decreased animal survival at concentrations ranging from 200 to 794 μg g^{-1} OC. Currently there are no known reported sediment atrazine effects concentrations for *H. azteca*. Wan et al. (2006) reported a 28-day *H. azteca* no-observed effect concentration for atrazine of 125 μg g^{-1} OC, below our reported peak concentrations. While atrazine has not been considered potently toxic to aquatic organisms (Solomon et al. 1996), the herbicide has been observed to interact synergistically with organophosphate insecticides such as methyl parathion, increasing the insecticides' potency to *H. azteca* (Anderson and Lydy 2002). As a result, it is possible that some of the observed toxicity in the present study was attributable to synergistic interactions among these two pesticides co-occurring in backwater wetland sediments. Although significant negative correlations were observed between unadjusted wetland sediment fipronil and *p,p′*-DDD concentrations and *H. azteca* survival, it is unlikely that these pesticides contributed to the observed sediment toxicity. This conclusion is based upon reported effects concentrations for both compounds. Reported fipronil sediment 10-day *H. azteca* LC_{50} of 4.1 μg g^{-1} OC (Hintzen et al. 2009) is well below our observed peak fipronil sediment concentrations of <1 μg g^{-1} OC and reported *p,p′*-DDD 10-day *H. azteca* LC_{50} of 1,300 μg g^{-1} OC (Weston et al. 2004) more than three orders of magnitude below our peak *p,p′*-DDD concentrations of <1 μg g^{-1} OC. The sublethal response of *H. azteca* growth in this study was negatively correlated with unadjusted permethrin, including both *cis* and *trans* isomers. While significant, the correlation coefficients for this endpoint were lower than those for survival. Amweg et al. (2005) also observed significant growth impairment when *H. azteca* was exposed to a variety of pyrethroids, including permethrin. This same study also noted that significant growth impairment (>35 % decrease in biomass) can occur at approximately one half median lethal concentrations (LC_{50}) and our results are comparable. Future research might include the use of pore water analysis to improve understanding of the bioavailable fraction of each pesticide in a pesticide mixture, allowing for use of more available data on aqueous effects concentrations (i.e., LC_{50}) to elucidate observed toxicity.

5 Conclusions

Results of our study showed managed backwater wetlands can rapidly and effectively trap and process agricultural runoff during moderate rainfall events, mitigating impacts to sediment-associated aquatic invertebrates in receiving aquatic systems. Mitigation of mixture pesticide sediment toxicity to the 10-day survival of the epibenthic crustacean, *H. azteca*, in the 500 m managed backwater wetland occurred within 22 days of amendment and at distances of >40 m within the system. Similarly, mitigation of mixture

pesticide sediment toxicity to 10-day *H. azteca* growth occurred at distances of >100 m through 36 days post-amendment. When properly managed, such naturally occurring floodplain wetlands have the potential to be used as an agricultural conservation practice to intercept and process agricultural runoff and improve downstream sediment quality.

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