ECOHYDROLOGY
Ecohydrol. **2**, 287–293 (2009)
Published online 8 May 2009 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/eco.52

Efficiency of a modified backwater wetland in trapping a pesticide mixture†

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ABSTRACT

The pesticide trapping efficiency of a modified backwater wetland amended with a mixture of three pesticides, atrazine, *S*-metolachlor, and fipronil, using a simulated runoff event, was examined. The 700-m long, 25-m wide wetland, located along the Coldwater River in Tunica County, Mississippi, USA, was modified for hydrologic control via weirs at both ends. A pesticide mixture was amended into the wetland at the upstream weir simulating a 1-h, 1·27-cm-rainfall event from a 16 ha agricultural field. Water samples (1 l) were collected hourly within the first 24 h and again on days 2, 5, 7, 15, 21, 28 and 56, post-injection at both ends of the wetland for pesticide analysis. Peak pesticide concentrations were observed upstream 1 h after injection. Rapid pesticide removal from upstream water occurred with 63, 51 and 61% decrease of atrazine, *S*-metolachlor and fipronil, respectively, by 24 h. By day 7, 79, 80 and 87% decreases from peak concentrations occurred. After day 28, all pesticide concentrations were $<0{\cdot}3\ \mu g\ l^{-1}$, and after day 56, no target pesticides were detected. Downstream, atrazine occurred in trace amounts ($<0{\cdot}4\ \mu g\ l^{-1}$) within 24 h and after day 28 was not detectable. *S*-Metolachlor occurred once downstream on day 21 ($0{\cdot}249\ \mu g\ l^{-1}$), and fipronil was detected on days 15–56 in trace amounts ($<0{\cdot}05\ \mu g\ l^{-1}$). Results indicate that modified backwater wetlands can efficiently trap pesticides in runoff from agricultural fields during small to moderate rainfall events, mitigating impacts to receiving waters in the main river channel. Published in 2009 by John Wiley & Sons, Ltd.

KEY WORDS river floodplain; atrazine; *S*-metolachlor; fipronil; simulated runoff; mitigation

Received 19 December 2008; Accepted 25 February 2009

INTRODUCTION

Backwater wetlands occurring along river channels have important economic and ecological functions such as providing habitat, natural buffers, and acting as filters for suspended sediment, nutrients and pesticides entering from adjacent agricultural fields. Backwater wetlands may be modified via hydrologic manipulation to more efficiently utilize their natural filtering capabilities (Mitsch *et al.*, 2002). Both natural and constructed wetlands have been shown to be effective in mitigating contaminants in agricultural runoff (Moore *et al.*, 2002, 2007a). The intensively cultivated Mississippi Delta contains numerous floodplain water bodies such as backwater wetlands that receive significant inflows of water and associated pollutants from cultivated lands. As a result these backwater wetlands, with modification, could be used as an additional, region-specific tool or best management practice (BMP) for reducing pesticide loads from non-point sources (Wauchope *et al.*, 2004).

In 2007, US Congress increased corn (*Zea mays* L.) subsidies for biofuel production, and as a result, a dramatic increase in corn production has occurred. Concomitant with this increased corn acreage is a likely increase in corn-related pesticide use. Herbicides such as atrazine and metolachlor are commonly used in mixtures for corn crops and sold under the trade name Bicep II Magnum® produced by Syngenta (Table I). The phenylpyrazole insecticide, fipronil, sold under the trade name Regent 4SC® produced by BASF (Table I) has been marketed for corn crops to replace organophosphate insecticides such as chlorpyrifos and methyl parathion because of fipronil's effectiveness at low field application rates against insect pests that have become resistant to organophosphates (Bobe *et al.*, 1997). According to NASS (2008), in 2003 (the most recent year with complete data) approximately 24·3 million kg of atrazine, 2·9 million kg of metolachlor, and 63 000 kg of fipronil were used on corn crops in the US for pest management. As a result, the current study examined the trapping efficiency of a modified backwater wetland amended with a mixture of three pesticides, atrazine, *S*-metolachlor, and fipronil, using a simulated runoff event. The 700-m long, 25 m-wide backwater wetland, located within a cutoff bend-way along the Coldwater River in Tunica County, Mississippi, USA, was modified for hydrologic control by adding weirs at both ends.

Site Description

A reach of the Coldwater River about 20 km downstream from Arkabutla Lake Dam in northwestern Mississippi was selected because of the presence of more than 20 severed backwater meander bends and other floodplain water bodies. A severed compound meander bend backwater in Tunica County about 2·5-km long and 40-m wide

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Table I. Physical and chemical properties of atrazine, *S*-metolachlor, and fipronil.

Property	Atrazine[1,2]	*S*-Metolachlor[2,3]	Fipronil[4]
Use Type	Herbicide	Herbicide	Insecticide
Class	Triazine	Acetanilide	Phenylpyrazole
CAS no.	1912-24-9	87392-12-9	120068-37-3
Molecular weight	215·7	283·8	437·2
Density@20 °C (g mL^{-1})	1·19	1·09	1·24
Water solubility (mg l^{-1})	32	480	1·9–2·4
Vapour pressure (mPa)	0·04	1·7	3·7E-4
Adsorption coefficient (log K_{oc})	2·0	2·4	2·9
Partition coefficient (log K_{ow})	2·3	3·4	3·5
Hydrolysis $T_{1/2}$ (d)	30	>200	>100
Water $T_{1/2}$ (d)	58	47	28
Aerobic soil $T_{1/2}$ (d)	146	9	188
Anaerobic soil $T_{1/2}$ (d)	159	37–81	19·3–22·2

[1] Bouldin *et al.* (2006)
[2] EXTOXNET (1996)
[3] Moore *et al.* (2001a)
[4] Gunasekara *et al.* (2007)

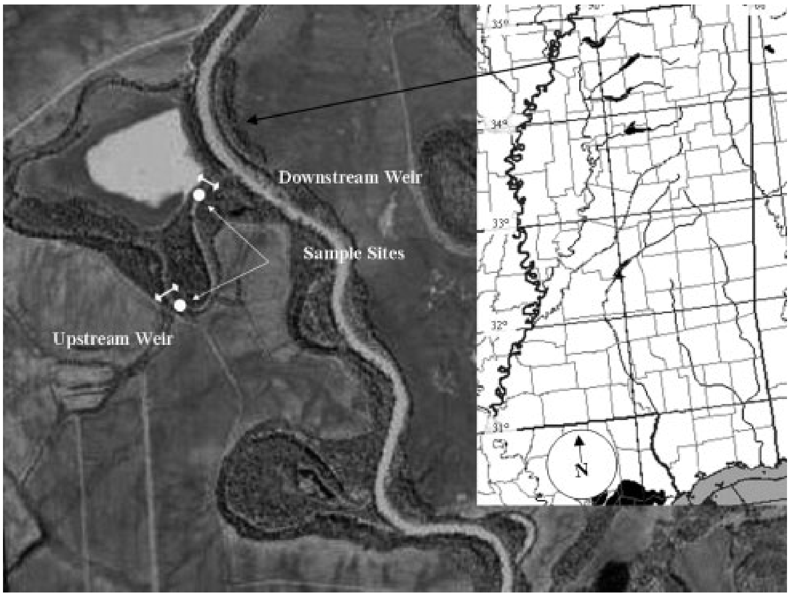

Figure 1. Aerial photo and map showing the location of the Coldwater River modified backwater wetland in Tunica County, Mississippi, USA, with both upstream and downstream weirs and sampling locations.

was selected for this study (Figure 1). The backwater is inside the mainstem flood control levee, and is the result of a 0·4 km cutoff constructed in 1941–1942. Land-use both inside and outside the bend are in row-crop cultivation, but there was a buffer of natural vegetation 5–100 m wide on both banks. The backwater receives runoff from about 100 ha of cultivated lands, primarily through an intermittent slough connected to a series of drainage ditches. The backwater study site was modified with two water control weirs (34°40′04·93″N, 90°13′38·09″W, and 34°40′15·15″N, 90°13′35·36″W), creating a larger, deeper cell managed as a lake-type aquatic habitat and a smaller, shallower cell, 700-m long, 25-m wide, that supports wetland and terrestrial plants managed as a wetland (Figure 1). A mean water depth of 28 cm was measured in the wetland cell when water was present. The weir controlling the lake cell was located such that most runoff from adjacent fields was diverted into the wetland cell. Both weirs were designed with adjustable crest drainage structures protected by 'Clemson' beaver exclusion screens at their upstream intakes. Weirs were protected with riprap to allow for overflow in either direction.

MATERIALS AND METHODS

On 20 June 2007, a mixture consisting of atrazine, *S*-metolachlor and fipronil was amended once simulating a 1-hour 1·27-cm rainfall event with a conservative (0·1%) pesticide loss in runoff (Willis and McDowell, 1982) from a 16 ha agricultural field. A total of 6600 mg active ingredient (a. i.) atrazine with 5220 mg a. i. *S*-metolachlor (Bicep II Magnum®), and 630·4 mg a. i. fipronil (Regent 4SC®) were injected into the backwater wetland at the upstream weir for 1·3 h. To simulate the rainfall event, water was released from the upstream lake cell portion of the backwater into the modified wetland cell portion over a 4-h period. 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 until a 74-mm rain on day 20.

Water samples (1 l) were collected hourly within the first 24 h and again on days 2, 5, 7, 15, 21, 28 and 56 post-injection at upstream and downstream sites adjacent to respective weirs. First 24-h hourly samples were collected using an automated pumping sampler (ISCO Model 3700) modified from Smith (1993). Sample containers were 1l polyethylene plastic bottles fitted with a Teflon-lined screw cap. Samples were placed on ice, transported to the USDA-ARS National Sedimentation Laboratory, Oxford, MS, USA, and stored at 4 °C (typically <24 h) for target pesticide analysis. Samples collected after 24 h were grab samples placed in 1-l glass jars fitted with a Teflon lined screw cap and treated as described previously.

Target pesticide analysis was conducted via a modified gas chromatography (GC) method similar to one described by Bennett *et al.* (2000) and Smith and Cooper (2004). In brief, pesticides were extracted using pesticide-grade ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated to near dryness by rotary evaporation. The extract was then subjected to silica gel column chromatography cleanup, and concentration to 1 ml volume under high purity dry nitrogen for GC analysis. Pesticide recoveries and extraction efficiencies, based on fortified samples, were ≥90% for targeted pesticides (Smith *et al.*, 2007).

Two Agilent HP model 6890 gas chromatographs (GCs) 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 and Cooper (2004) and Smith *et al.* (2007). One of the two Agilent HP 6890 GCs was equipped with two micro electron capture detectors (μECDs) and the second 6890 with one μECD, one nitrogen phosphorus detector (NPD), and an Agilent HP 5973 mass selective detector (MSD). The primary analytical column was an Agilent HP 5MS capillary column, 30 m × 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–190 °C; hold at 190 °C for 25 min; ramp at 25 °C–230 °C and hold for 30 min. 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. Average extraction efficiencies using fortified samples were >90% for all three pesticides. Levels of detection for atrazine, *S*-metolachlor and fipronil were 1, 10 and 1 ng l^{-1}, respectively.

Water quality parameters of temperature, pH, dissolved oxygen and turbidity were measured *in-situ* in the backwater wetland at the downstream site using a Yellow Springs Instruments (YSI) 6600 multi-parameter water quality monitoring system (Yellow Springs, Ohio, USA). Measurements were collected every 30 min for the first 24 h and on days 2, 21 and 56 whereas on days 5, 7, 15 and 28 measurements were collected every 4 h to provide baseline water quality data.

Coefficients for exponential decay formulas for pesticide concentrations at the upstream site were generated by running non-linear regressions using SigmaStat® v.2·03 statistical software (SPSS, 1997). The resulting formulas were used to determine aqueous half-lives ($T_{1/2}$) within the wetland. Statistical significance level for all models was set at 5% ($p \leq 0{\cdot}05$) for all analyses (Glantz, 1997).

RESULTS

During the simulated rainfall event, approximately 730 m^3 of water was released from the upstream lake cell portion of the backwater into the modified wetland cell portion over about 4 h (Figure 2). Measured water quality was typical of shallow backwater water bodies in the southeastern US (Table II). Water temperature was indicative of climatic conditions in northern Mississippi during June ranging from 24 to 28 °C. Mean daily pH was slightly acidic ranging from about 6·3 to 7 and dissolved oxygen ranged from 3 to 5 mg l^{-1}. Turbidity fluctuated in conjunction with weather conditions, clearer during dry periods and more turbid after rainfall events of 41 mm on days 11–12, and 74 mm on day 20.

Pesticide concentrations were not detectable in water samples collected prior to pesticide amendment at either the upstream or downstream sites. In addition, no target pesticide concentrations were observed in the source

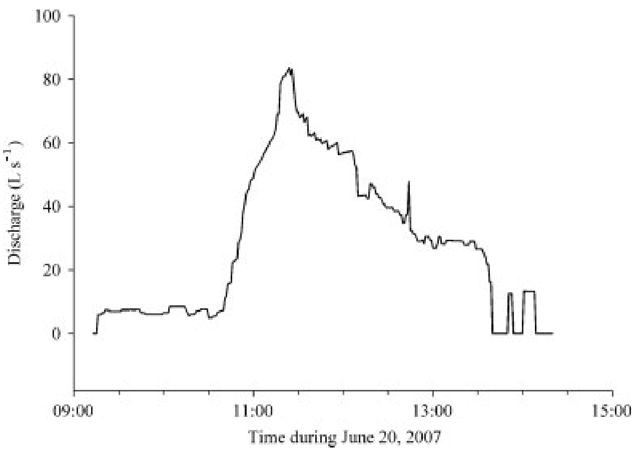

Figure 2. Measured discharge (l s^{-1}) during the simulated rainfall event. Water was released from the lake cell into the wetland cell of the modified backwater.

DOI: 10.1002/eco

Table II. Mean (±SD) *in-situ* water quality characteristics of the wetland during the study period: 20 June–15 August 2007.

Day	Date	Temperature (°C)	pH	Dissolved oxygen (mg l^{-1})	Turbidity (NTU)
0	6/20/2007	25·9 ± 1·3	6·78 ± 0·04	5·21 ± 2·05	18·5 ± 5·1
1	6/21/2007	25·4 ± 1·1	6·80 ± 0·04	4·09 ± 1·53	22·7 ± 4·7
2	6/22/2007	25·2 ± 1·2	6·78 ± 0·03	3·01 ± 1·19	34·5 ± 13·8
5	6/25/2007	26·1 ± 0·9	6·71 ± 0·03	3·46 ± 0·52	14·2 ± 1·6
7	6/27/2007	25·9 ± 0·9	6·72 ± 0·05	3·40 ± 0·73	42·0 ± 69·8
15	7/5/2007	26·4 ± 1·3	6·72 ± 0·04	3·08 ± 0·83	16·6 ± 3·3
21	7/11/2007	23·9 ± 0·2	6·37 ± 0·09	5·32 ± 0·82	121·6 ± 74·9
28	7/18/2007	24·9 ± 0·4	6·61 ± 0·02	No Data	9·4 ± 0·9
56	8/15/2007	27·9 ± 1·3	7·24 ± 0·08	3·92 ± 2·12	6·7 ± 2·4

water from the lake cell used to simulate the rainfall event. Although several rainfall events occurred during the study period (days 11, 12 and 20), including events prior to sampling days 15 and 21, rainfall did not appear to significantly affect pesticide concentrations within the wetland. Peak pesticide concentrations (12·997, 6·658 and 0·817 μg l^{-1} of atrazine, *S*-metolachlor, and fipronil, respectively) were observed 1·25 h after initial amendment at the upstream injection site during the simulated rainfall event and were used as a baseline to determine trapping efficiency within the wetland during the 56-day study period.

Pesticide concentrations fluctuated during the first 24 h following injection at the upstream site (Figure 3). During the first 2 h after pesticide amendment ceased and while the simulated runoff continued, measured pesticide concentrations at the upstream site significantly decreased (90%) as target pesticides atrazine, *S*-metolachlor and fipronil were further diluted by 48, 27 and 37%, respectively. Approximately 2 h after the simulated runoff ended, atrazine, *S*-metolachlor and fipronil concentrations consistently increased as water began to oscillate back towards the upstream site, peaking after 3 h. Observed pesticide concentrations then showed a consistent trend of oscillating every 3 h for the next 15 h. At the 700-m downstream site, atrazine was detected within the first 24 h of pesticide amendment (Figure 3). This pesticide was observed at <0·500 μg l^{-1} during dosing and again 6, 13, 14, 18 and 21 h after amendment ceased. *S*-Metolachlor and fipronil were not detected in any downstream samples within the first 24 h after amendment.

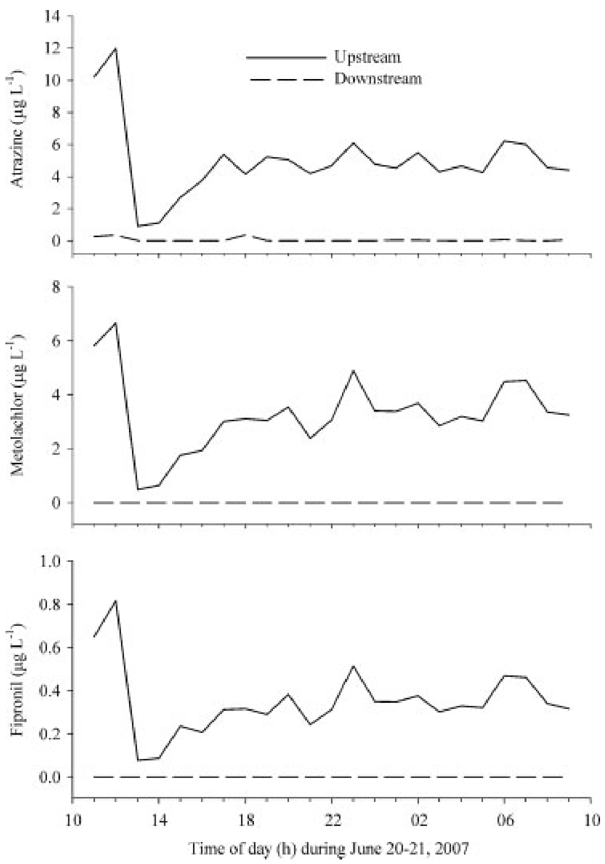

Figure 3. Atrazine, metolachlor and fipronil concentrations (μg l^{-1}) 24 h post-amendment in a modified backwater wetland.

Long term observations (56 days) of the target pesticides showed most water column detections occurred at the upstream sampling site (Figure 4). Two days after pesticide amendment, aqueous concentrations decreased by 65, 51 and 62% for atrazine, *S*-metolachlor, and fipronil respectively. Concentrations decreased by approximately 80% on days 5, 7 and 15 for fipronil, metolachlor and atrazine, respectively, and >90% reduction was observed on days 15, 15 and 21 for fipronil, *S*-metolachlor and atrazine, respectively. Atrazine and fipronil were detected up to 28 days post-injection upstream whereas *S*-metolachlor was detected only up to 21 days. No target pesticides were detected at the upstream site after 56 days. At 700 m downstream, atrazine was detected on days 2, 7, 15 and 21 at 0·251, 0·100, 1·020 and 0·485 μg l^{-1}, respectively. *S*-Metolachlor was detected only on day 21 at 0·249 μg l^{-1} and fipronil was detected on days 15, 21, 28 and 56 at 0·042, 0·040, 0·044 and 0·014 μg l^{-1}, respectively (Figure 4). Although pesticide concentrations at the downstream site were never >9·5% of peak upstream concentrations, the highest downstream concentrations coincided with rainfall events on 1 and 2 July 2007 (day 11–12, 41 mm) and 10 July 2007 (day 20, 74 mm).

Results of regression fits of upstream site concentrations to exponential decay formulas are shown in Table III. Calculated aqueous half-lives were 5·39, 3·01 and 1·33 days for atrazine, metolachlor and fipronil, respectively, at the upstream site. Predictions based on the regression formulas indicate that these pesticides would

DOI: 10.1002/eco

Table III. Exponential decay model results and calculated aqueous half-lives ($T_{1/2}$) for atrazine, metolachlor, and fipronil in a modified backwater wetland.

	Atrazine	S-Metolachlor	Fipronil
Exponential decay coefficient (b)	0·1288	0·2305	0·5201
Half-life (d) ($T_{1/2}$)	5·39	3·01	1·33
r^2	0·7157	0·9317	0·9091
F-value	20·1	109·1	80·0
p-value	0·0020	<0·0001	<0·0001

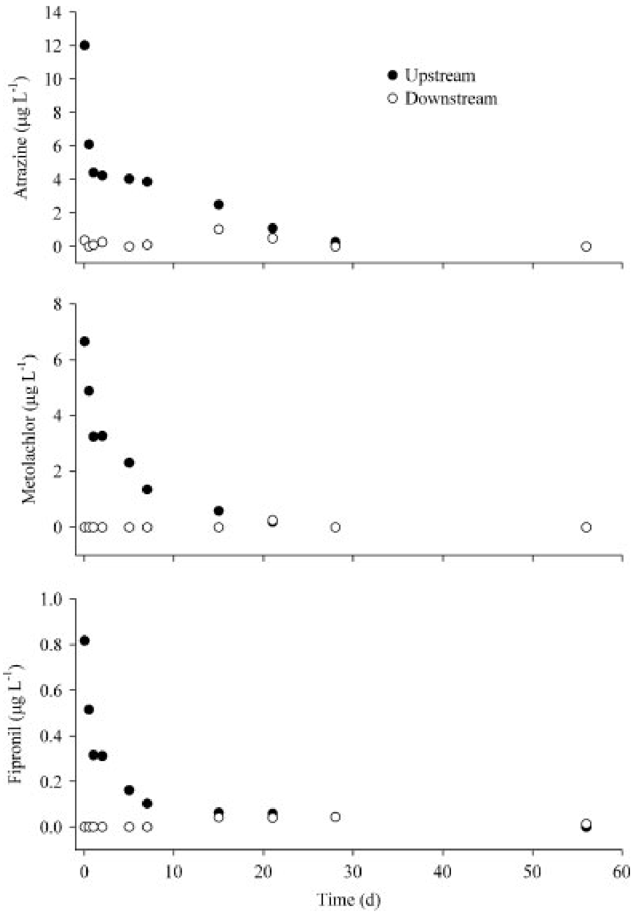

Figure 4. Atrazine, metolachlor and fipronil concentrations (µg l^{-1}) 56 days post-amendment in a modified backwater wetland.

be trapped and processed in this wetland within a short period of time (days to weeks).

DISCUSSION

Pesticides in runoff from agricultural fields often occur in mixtures (Smith *et al*., 2006). As a result, studies such as the current one focusing on pesticide mixtures are increasingly important in understanding the use and efficiency of wetlands as a potential BMP in mitigating contaminant impacts on water quality in receiving systems. Several studies have shown the effectiveness and efficiency of constructed wetlands in trapping and processing pesticides (Moore *et al*., 2000, 2001a, 2002, 2007a). However, much less is known about how more natural wetland systems occurring along backwaters and floodplains of large rivers might be utilized as a BMP. This study simulated atrazine, *S*-metolachlor and fipronil contamination that has been previously observed in rivers, lakes and streams occurring in intensively cultivated regions of the Mississippi Delta and the loess hills of north and central Mississippi (Table IV), particularly during growing season runoff events (Smith *et al*., 2006).

Several factors influence the capability of a wetland to efficiently trap pesticides. These include wetland size (primarily distance travelled), presence of vegetation and/or detritus, soil characteristics, water chemistry (pH and dissolved oxygen) and hydraulic retention time (Rodgers and Dunn, 1992; Moore *et al*., 2007b). The current study used a large backwater wetland (700-m long) during a small runoff event that was contained within both weirs (no discharge from the backwater wetland). In addition the wetland had a mixture of wetland vegetation throughout with a silty loam soil. Overlying water pH was slightly acidic and was not chronically anoxic (Table II). Under these conditions, atrazine, *S*-metolachlor and fipronil were removed from the water column relatively rapidly compared with other studies. Moore *et al*. (2000) observed atrazine to be trapped and removed from the water column within 100–280 m of the runoff source and had a calculated half-life in water of 9 days compared with 5–6 days in the current study. Moore *et al*. (2001b) trapped metolachlor within 100–400 m and had a calculated half life in water of 8–13 days compared with 3 days in this study. Shan *et al*. (2003) calculated a fipronil half-life in water of 4–5 days in a paddy field mesocosm compared with 1–2 days in our study.

Pesticides such as herbicides atrazine and metolachlor can be frequently observed in a variety of aquatic ecosystems with the potential for causing ecological damage. Wetlands used as BMPs could mitigate environmental impacts and ecological risks of pesticide mixtures in agricultural runoff. Vascular and non-vascular plants alike, as well as phytoplankton can potentially be affected by herbicide runoff into aquatic ecosystems. Hartgers *et al*. (1998) showed a mixture of herbicides atrazine, metolachlor and diuron at 1·6, 1·7 and 0·5 µg l^{-1} decreased phytoplankton communities. Ecological risks to aquatic animals, fish and invertebrates, would come from exposure to the insecticide fipronil. Fipronil is highly toxic to freshwater fish (LC50 83–250 µg l^{-1}); however, crustaceans and aquatic insects are much more sensitive (Gunasekara *et al*., 2007). Reported fipronil LC50s for water fleas and crayfish ranged from 14 to 20 µg l^{-1} and LC50s for midge and mosquito larvae ranged from 0·35 to 23 µg l^{-1} (Gunasekara *et al*., 2007). Less is known regarding mixture toxicity of fipronil and herbicides. Key *et al*. (2007) showed additive toxicity of fipronil and atrazine to larval grass shrimp (*Palaemonetes pugio*). Within the current study, acute ecological impacts most likely occurred at or near the upstream site within the

Table IV. Observed peak aqueous concentrations (μg l^{-1}) of atrazine, metolachlor, and fipronil in surface waters of selected Mississippi lakes and streams.

Water body	Year	Atrazine	Metolachlor	Fipronil
Deep Hollow Lake	1998–2003	0·020–0·180[1,2]	0·045–0·420[1,2]	0·007–0·008[3]
Thighman Lake	1998–2003	0·038–23·400[1,2]	0·007–14·900[1,2]	0·000–0·007[3]
Beasley Lake	1998–2005	0·125–3·045[4]	0·027–10·046[4]	0·009–0·012[4]
Little Topashaw Creek	2000–2004	0·185–72·420[5]	0·282–21·422[5]	0·128–1·803[5]

[1] Cooper *et al*. (2003)
[2] Zablotowicz *et al*. (2006)
[3] Moore *et al*. (2007b)
[4] Smith *et al*. (2007)
[5] Smith *et al*. (2006)

first 24 h of the runoff event. Based upon observed concentrations, ecological impacts at the 700–m downstream site were unlikely throughout the study period.

Results of this study indicate that modified backwater wetlands can efficiently trap pesticides in runoff from agricultural fields during small to moderate rainfall events, mitigating impacts to receiving waters in the main river channel. Greater than 90% of atrazine, *S*-metolachlor and fipronil were trapped and processed within the entire 700–m long backwater wetland with greater than 80% of these pesticides trapped and processed within the upstream site. Target pesticides were trapped and processed relatively rapidly (days to weeks) within the system.

ACKNOWLEDGEMENTS

We wish to thank M. Ursic, T. Sullivan, L. Brooks, R. Cullum, T. Welch, and S. Smith, Jr. for technical assistance and analyses. We also thank R. Kröger, M. Moore, R. Cullum, and C. Britson for many helpful comments while reviewing an earlier version of the manuscript. Mention of equipment, computer programs, or a pesticide does not constitute an endorsement for use by the US Department of Agriculture nor does it imply pesticide registration under FIFRA as amended.

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DOI: 10.1002/eco