Mitigation of chlorpyrifos runoff using constructed wetlands

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Abstract

Constructed wetlands have been proposed as a potential best management practice (BMP) to mitigate effects of pesticide-associated agricultural runoff. Wetland mesocosms (14 m × 59–73 m) were amended with chlorpyrifos to simulate a storm runoff event at concentrations of 73, 147 and 733 μg/l. Water, sediment and plant samples collected weekly for 12 weeks indicated that chlorpyrifos rapidly sorbed to sediment and plant material, with approximately 47–65% of measured chlorpyrifos mass retained within the first 30–36 m of wetland mesocosms. Of the measured mass, approximately 55% and 25% were retained by sediments and plants, respectively. A field-scale evaluation of a constructed wetland's mitigation capability was performed in the Lourens River watershed of Cape Town, South Africa. Results indicate that the wetland was able to retain and considerably decrease the concentration (and hence toxicity) of chlorpyrifos and suspended sediment entering the receiving waterbody (Lourens River). This research provides fundamental answers concerning constructed wetland capabilities that are necessary for constructing field-scale systems within agricultural watersheds. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Agricultural activities are frequently conducted in close proximity to lakes, reservoirs, and streams. Particularly in the Mississippi Delta, areas containing wetlands have been intensively used for agriculture and silviculture. This has resulted in loss of edge-of-field wetlands, which were once associated with agricultural fields (Reddy and Gale, 1994). These areas may have been in the form of riparian wetlands, hardwood swamps, relic channels or oxbow lakes. Removal of such wetlands led to the practice of "plowing with one wheel in the water" or plowing near an adjacent water body. These former wetland areas had potential functions (denitrification, nutrient processing, etc.) and values (wildlife and fish production, recreational activities, etc.). One potential function was water quality enhancement or mitigation, particularly for cropland runoff containing pesticides.

Over 500 million kg of pesticides are used each year in the United States in both agricultural and urban settings (Majewski and Capel, 1995). Of this, it is estimated that approximately 32 million kg are organophosphate insecticides, which gained wide-scale use in the late 1960s and early 1970s (Barbash and Resek, 1996). By the 1980s, organophosphates accounted for approximately 65% of total insecticide usage (Larson et al., 1997). Because of their use, it is reasonable that there may be potential risks to downstream biota should an agricultural pesticide runoff event occur. Likewise,

such risks to downstream biota may be mitigated by restoring these edge-of-field wetlands as buffer areas.

Chlorpyrifos [phosphorothioc acid O,O-diethyl O-(3, 5,6-trichloro-2-pyridinyl) ester], an acetylcholinesterase inhibitor, is the most intensively used organophosphate insecticide in agriculture (Larson et al., 1997) (Table 1). Chlorpyrifos is applied in both agricultural (cotton, grains, and fruits) and urban (lawns, commercial and domestic buildings) settings. Additionally, chlorpyrifos has been detected in air, rain, and fog (Majewski and Capel, 1995). Pulses of insecticides, including chlorpyrifos, have been reported in the San Joaquin and Sacramento Rivers in California (Kuivila and Foe, 1995). Because of its potential presence in an aquatic environment, it is important to research possible best management practices (BMPs) that could alleviate incoming runoff concentrations. Thus, there are two components to the presented research. First, the potential buffering capacity of constructed "edge-of-field" wetlands for chlorpyrifos runoff was examined using a simulated storm runoff event in replicated mesocosms in Mississippi, USA. Second, a field assessment of chlorpyrifos mitigation within an actual wetland in the Lourens River, South Africa, catchment area is presented. Objectives addressed by this research include determining: (1) effectiveness of constructed wetlands at

decreasing concentrations of chlorpyrifos prior to entering receiving systems, (2) the mass partitioning (water, sediment, and plants) of chlorpyrifos in constructed wetlands, and (3) toxicity mitigation capabilities of the Lourens River wetland.
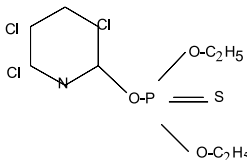
2. Materials and methods

2.1. Mississippi experimental wetlands

2.1.1. Wetland parameters

A series of eight constructed wetland cells (specifically designed to evaluate fate of pesticides in wetlands) located at the University of Mississippi Field Station were used for this research (Rodgers and Dunn, 1992). Depending upon the study focus, these wetland cells can be adjusted to serve as either flow-through or static systems. For the purpose of this research, cells were adjusted to act as flow-through systems. Four wetland cells were chosen as test cells, with one additional cell serving as an unamended control. The three remaining wetland cells were used as water sources for the simulated rainfall. Average dimensions ($\pm$S.D.) for experimental cells were 10 ($\pm$1) m width $\times$ 66 ($\pm$7) m length $\times$ 0.24 ($\pm$0.06) m depth. Wetland vegetation

Table 1
Physical properties and fate characteristics of chlorpyrifos

Structure	
Molecular weight (g/mol)[a,b]	350.62
Water solubility (mg/l)[a,c]	2
K_{ow}[a,b]	66 000
K_{oc}[a,c]	6070, 8498
Vapor pressure (mm Hg)[a,c]	2×10^{-5}
Biotransformation ($T_{1/2}$) (days)[c]	11–141
Hydrolysis ($T_{1/2}$) (days)[d,e,f,g]	18.9, 22.9, 27.8, 80
Photolysis ($T_{1/2}$) (days)[a]	21–28
Volatilization$_{water}$ ($T_{1/2}$) (days)[a]	3.5–20
Water persistence, $T_{1/2}$ (days)[h,i]	0.2–0.3, 0.5–4
Sediment persistence, $T_{1/2}$ (days)[a,b,h]	0.8–16, 7–35, 60–120
Plant persistence, $T_{1/2}$ (days)[e]	1–7

[a] EXTOXNET (1996).
[b] Racke (1993).
[c] Racke et al. (1992).
[d] Chapman and Cole (1982).
[e] Meikle and Youngson (1978).
[f] Sharom et al. (1980).
[g] Macalady and Wolfe (1983).
[h] Knuth and Heinis (1992).
[i] Kersting and van Wijngaarden (1992).

Table 2
Plant densities in Mississippi constructed wetland mesocosms

Wetland (µg/l)	Percent vegetative cover	Plant species	Plant densities (no./m^2)	Relative percent abundance
73	25	*Juncus effusus*	53	58
		Leersia sp.	28	31
		Ludwigia sp.	10	11
147A	80	*Juncus effusus*	152	97
		Leersia sp.	5	3
147B	90	*Juncus effusus*	171	93
		Leersia sp.	12	7
733	75	*Juncus effusus*	71	37
		Ludwigia sp.	60	32
		Leersia sp.	59	31

consisted mainly of *Juncus effusus*, *Leersia* sp., and *Ludwigia* sp. (Table 2). Wetland sediments were a sandy loam, with approximately 84% sand and 16% silt.

2.1.2. Experimental design

Each experimental wetland cell was randomly assigned a chlorpyrifos concentration, which represented one of three potential runoff scenarios (0.1% chlorpyrifos runoff, 0.5% chlorpyrifos runoff or 5% chlorpyrifos runoff). The concentrations of chlorpyrifos applied (as simulated runoff) were based on manufacturer's recommended application rates, as well as assumptions of an immediate, post-application 2.54 cm rainfall on the "contributing" area of 4, 40, and 400 ha agricultural fields. Because initial assumptions are based on concentrations entering wetlands, there was no added difference in concentration among the 4, 40, or 400 ha field assumptions. Calculated wetland cell volumes were used to determine appropriate chlorpyrifos masses to apply to systems, as well as time required for their hydraulic turnovers. Targeted concentrations following simulated rainfall dilution were 73, 147, and 733 µg/l chlorpyrifos for experimental wetland cells. The 147 µg/l chlorpyrifos concentration was repeated in a second experimental wetland cell, giving a total of four experimental cells in addition to an unamended control. Thirty min following each wetland's chlorpyrifos application (distributed evenly along the entire inflow edge of each wetland), a simulated rainfall with an intensity of 12.6 l/s was initiated. The simulated rainfall had a duration which provided three volume additions within each wetland cell. To appropriately simulate this event, a diffuser was constructed by drilling holes every 5 cm in a 6.1 m length of 7.6 cm PVC pipe. The diffuser was then connected to a 7.6 cm diameter hose which ran from a gas-powered 8-HP pump, located at one of the three water source wetland cells.

2.1.3. Sample collection

Each experimental wetland (including control) was divided into four equal longitudinal transects, designated as inflow, #2, #3, and outflow. Composite water, sediment, and plant samples were collected for pesticide analysis across these transects one week prior to chlorpyrifos application, as well as every seven days, for approximately 84 days following chlorpyrifos application. Aqueous samples were collected in acid/acetone-rinsed 100 ml amber glass bottles. Sediment samples were collected from the top 6 cm of wetland sediment using a stainless steel scoop. Samples were wrapped in aluminum foil and stored on ice (<2 h) until they could be placed in a freezer (−4 °C) for storage pending analysis. Plant samples collected consisted of only that portion of the plant exposed in the water column (i.e., above the sediment, but not exposed to atmosphere). Samples were likewise wrapped in aluminum foil and stored on ice (<2 h) until being placed in a freezer pending analysis.

2.1.4. Chlorpyrifos analysis

Ethyl acetate extracts of water, sediment, and plant samples were analyzed for chlorpyrifos at the USDA-ARS National Sedimentation Laboratory using gas chromatographic procedures (Smith et al., 1995). Gas chromatographs used were Tracor model 540, equipped with Dynatech Precision GC-411V autosamplers. A PE Nelson 2700 chromatography data system, consisting of three model 970 interfaces, Turbochrom^{TM} 4.11 software, and microcomputer was used for automated quantification and reporting of pesticide peak data including gas chromatograms. A multi-level calibration procedure was used with standards and samples injected in triplicate. Calibration curves were updated every tenth sample. The main analytical column was a 15 m × 0.53 mm i.d. J and W Scientific DB 210 (1.0 µm film thickness) Megabore^{TM} column. The carrier gas was

ultra-high purity helium at 12.3 cc/min, whereas both the column makeup gas and detector purge gas were ultra-high purity nitrogen at 60 and 10 cc/min, respectively. Column oven, inlet, and electron-capture detector temperatures were 140, 240, and 350 °C, respectively. Under these conditions, chlorpyrifos had a retention time of 3.04 min. The lower limit of quantitative detection for chlorpyrifos was 0.01 μg/l. Mean extraction efficiencies, based on fortified samples, were >90% from water, sediment, and plant material. Chlorpyrifos residues were confirmed with a second analytical column of intermediate polarity (DB 17) and/or with a nitrogen–phosphorus detector.

Observed half-lives in aqueous, sediment and plant compartments of each wetland were determined by performing an exponential regression on measured concentrations across each entire wetland. By substituting K into the following equation, observed half-lives were determined.

$$T_{1/2} = 0.693/K,$$

where $T_{1/2}$ is the half-life (days), K is the partition coefficient (days).

2.2. Lourens River wetland

2.2.1. Study region and climate conditions

The Lourens River originates at an altitude of 1080 m in a naturally vegetated fynbos area and flows in a southwesterly direction for approximately 20 km before discharging into False Bay at Strand, Western Cape, South Africa. The catchment region is characterized by intensive farming, with orchards and vineyards in its middle reaches. The Lourens River has a total catchment area of approximately 92 km^2 and receives an annual mean rainfall of 91.5 cm. Approximately 87% of its 35×10^6 m^3 mean annual discharge occurs during the winter months between April and October (Tharme et al., 1997), as is characteristic of the region's Mediterranean climate. The main soil type is silty loam.

The 400 ha orchard area consists mainly of pears, plums, and apples. Pesticide application period within the study area's orchards proceeds from early August and continues until the end of March. Organophosphate insecticides such as azinphos-methyl and chlorpyrifos are applied between October and February quite frequently to pears and plums.

The constructed wetland studied is located along one of the tributaries shortly before its entry into the Lourens River. This tributary has an average width and depth of 0.89 m × 0.30 m and a current velocity of approximately 0.1 m/s. It has a total length of 1.8 km and flows from a dam through a forest area for 800 m and then into pasture land for 400 m before flowing through the orchard area for a further 600 m. Average discharge

in the tributary is 0.03 m^3/s in January and 0.32 m^3/s in July.

The study period lasted from the beginning of August to the end of September 1998. An application of chlorpyrifos (720 g active ingredient/ha) on pears in the catchment of the constructed wetland had taken place on August 11. On August 13 and 14, a 2.36 cm rainfall event occurred, allowing for runoff samples to be collected.

2.2.2. Wetland description

Built in 1991 along one of the Lourens River tributaries, the wetland was specifically constructed to prevent nonpoint source pollution with suspended particles from entering into the Lourens River. It is situated 15 m before the tributary discharges into the Lourens River. The inlet and outlet of the tributary are formed by concrete tubes with a diameter of 0.7 and 0.6 m. Approximately 15 ha of orchard, 10 ha of pasture land, and 18 ha of forest make up the wetland catchment area. The tributary flows in a longitudinal direction through the wetland. The wetland (36 m wide × 134 m length) has a total area of 0.44 ha. Water depth varies between 0.3–1 m, which is much lower than the initial depth of approximately 1.5 m at construction. The first 30 m of the wetland are free of vegetation, while the remaining area is covered mainly with *Typha capensis* Rohrb. (60% coverage), *Juncus kraussii* Hochst (10% coverage) and *Cyperus dives* Delile (5% coverage).

2.2.3. Sampling procedure and analysis

Two main sampling stations were used: inlet sampling was carried out in the tributary approximately 5 m before its entry into the wetland, while outlet sampling took place in the tributary approximately 7 m below the wetland. Standard sampling procedure included measurement of discharge, several physicochemical water quality parameters, as well as collection of water and suspended sediment samples for pesticide analysis. Discharge was calculated from velocity measurement along cross-sectional profiles. Total suspended solids were measured using a turbidity meter (Dr. Lange, Duessseldorf, Germany). Turbidity readings were calibrated as described by Gippel (1995).

Samples of water for pesticide analysis were collected at the inlet and outlet site in 3 l glass jars at 1 h composite samples (150 ml every 10 min) during the rainfall even on August 13, 1998. Water samples (500–900 ml) were solid-phase extracted within 10 h after sampling, using C18 columns (Chromabond). The columns were air dried for 30 min and kept at −18 °C until analysis (Liess et al., 1999).

Suspended sediments were obtained from continuously operating suspended-particle samples (Liess et al., 1996) installed in the stream bottom. Suspended-particle samplers were emptied approximately every two weeks

between July 29, 1998 and September 29, 1998 and were analyzed for pesticide content.

Analysis was performed by the Forensic Chemistry Laboratory of the Department of National Health, Cape Town. Pesticides from suspended sediment samples were extracted with methanol and concentrated using C18 columns. Measurements were done using gas chromatographs (Hewlett-Packard 5890) fitted with standard electron-capture, nitrogen–phosphorus and flame-photometric detectors (Liess et al., 1996). Concentrations for sediments were expressed as µg/kg dry weight. The following detection limits were obtained for water and suspended sediments: 0.01 µg/l and 0.1 µg/kg dry weight. Spiked recovery efficiencies were between 79–106%.

2.2.4. In situ exposure bioassays

Midges (*Chironomus* sp.) were used as a test organism. Animals were obtained from a clean water pond at Somerset West Water Treatment Plant. The organisms were collected 1 h before the exposure began. At each site, four replicate exposure beakers containing 20 4th instar larvae were placed in the stream. Mortality was measured after a 24 h exposure period. Two trials were performed, one during a day without any rainfall beginning at 10 a.m., August 9, and one during the rainfall-related runoff event (from 10 a.m., August 13 to 10 a.m., August 14). Another set of four exposure beakers was employed during the second trial at a site in the tributary flowing through the wetland approximately 300 m upstream of the orchard area, to serve as a control without pesticide contamination but with increased total suspended solids (TSS) levels. The in situ exposure methodology is outlined in detail in Schulz and Liess (1999).

3. Results

3.1. Mississippi experimental wetlands

No detectable concentrations of chlorpyrifos were measured in water, sediment, or plant tissue samples collected one week prior to chlorpyrifos application in any of the exposure wetlands. Likewise there were no detectable concentrations of chlorpyrifos measured in the control wetland throughout the duration of this experiment. Samples (water, sediment, and plant) collected in each wetland, immediately following the conclusion of the simulated runoff event (day 0), indicated 25–34% of measured chlorpyrifos (as percent mass) was in wetland inflow transects (transect lengths of wetland inflows ranged from 15–18 m). Between 47% and 65% of the total measured chlorpyrifos was within the first 30–36 m of the wetlands on day 0 (Table 3).

Following the 84 d exposure period, transfer/transformation of chlorpyrifos was determined for each wetland component (water, sediment, and plant). In both wetlands with targeted chlorpyrifos concentration of 147 µg/l (wetlands 147A and 147B), 99% of the aqueous chlorpyrifos was transferred/transformed. Wetland 147A had 44% and 84% transfer or transformation of chlorpyrifos in sediment and plant material, respectively, while wetland 147B had 89% and 97% transfer/transformation of chlorpyrifos in sediment and plant material, respectively. The wetland treated with targeted concentration of 73 µg/l demonstrated greatest transfer/transformation efficiency with over 99% of aqueous chlorpyrifos, 94% of sediment-associated chlorpyrifos and 97% of plant-associated chlorpyrifos transferred/transformed. In the 733 µg/l wetland, 99% of aqueous chlorpyrifos, 50% of sediment-associated chlorpyrifos, and 94% of plant-associated chlorpyrifos was observed to have been transferred/transformed. Likewise, after 84 d from initial chlorpyrifos exposure, an average of 84–91% of measured chlorpyrifos was present in the first three transects (inflow, transect 2, and transect 3) of each wetland. With the exception of the 73 µg/l wetland, approximately one-half of the total chlorpyrifos was measured in inflows of each wetland (Table 4).

Based on total measured concentrations combining water, sediment, and plants within each wetland, all wetlands had an overall chlorpyrifos transfer/transformation efficiency of $\geq 83\%$. The 73 µg/l wetland had the greatest overall chlorpyrifos transfer/transformation efficiency of approximately 98% (Fig. 1).

Observed half-lives in aqueous portions of these wetlands ranged from 4.6 d (73 µg/l wetland) to 13 d (wetland 147B) (Table 5). Observed half-lives were

Table 3
Percentage of total chlorpyrifos in individual transects within Mississippi wetlands at the end of the simulated rainfall event (day 0)

Targeted concentration (µg/l)	Percent (%) chlorpyrifos (as total mass)				Transect length (m)
	Inflow	Transect 2	Transect 3	Outflow	
73	25	22	22	31	15
147A	30	35	17	18	16
147B	34	25	21	20	18
733	30	21	11	38	18

Table 4
Transport of chlorpyrifos within Mississippi wetland mesocosms 84 d post-chlorpyrifos exposure

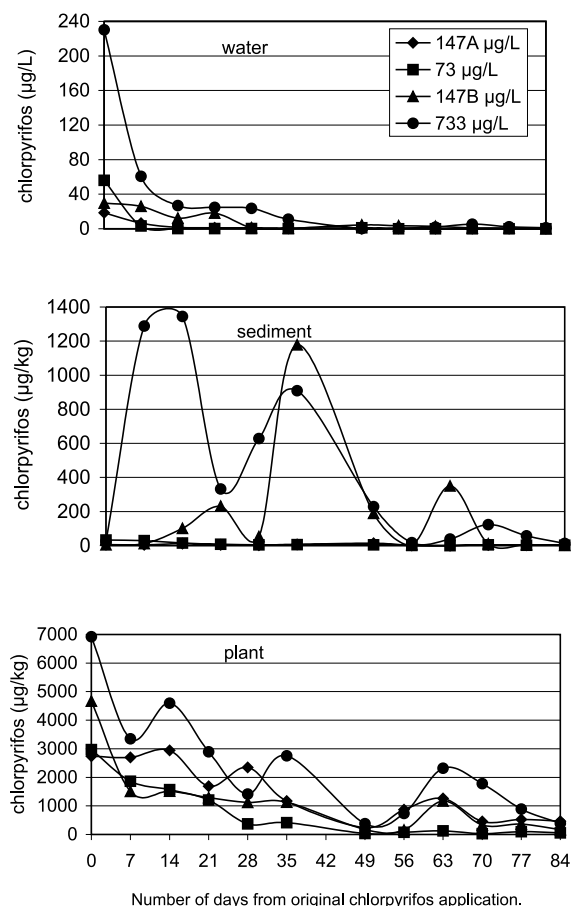| Targeted concentration (µg/l)	Percent chlorpyrifos mass (±S.D.)				Transect length (m)
	Inflow	Transect 2	Transect 3	Outflow	
73	21 (14)	27 (14)	36 (26)	16 (13)	15
147A	49 (16)	25 (10)	17 (9)	9 (5)	16
147B	47 (25)	24 (10)	18 (14)	11 (7)	18
733	59 (17)	23 (12)	7 (4)	11 (10)	18

Fig. 1. Mean concentrations of chlorpyrifos in water, sediment, and plants of each Mississippi wetland mesocosm.

determined for both sediment and plants according to preceding equations. Half-lives observed in sediments ranged from 16 (73 µg/l wetland) to 53 d (wetland 147A). For plants, observed half-lives ranged from 12.4 (73 µg/l wetland) to 31 d (wetland 147A) (Table 5).

Sorption by plants and sediment is an important aspect of pesticide fate studies. In the current study, sorption coefficients for plant material (K_p) (µg/kg) and sediment (K_d) (µg/kg) were determined throughout the 84 d exposure period. In wetland 147A, observed plant partitioning (K_p) increased more than an order of mag-

nitude from 148 (day 0) to 7350 (day 49), before slowly decreasing to 3531 (day 84). Sediment partitioning (K_d) increased three orders of magnitude from day 0 (0.33) to day 49 (446), while slowly decreasing until day 84 (27). Wetland 147B had observed K_p of 157 (day 0) which increased more than an order of magnitude to 3000 by day 84. Sediment partitioning for wetland 147B increased four orders of magnitude from day 0 (0.18) to day 35 (2963) before decreasing by day 84 (11). Observed plant partitioning for the 73 µg/l wetland increased two orders of magnitude from day 0 (53) to day 56 (7750). Similarly, sediment partitioning increased two orders of magnitude from day 0 (0.59) to day 56 (73). Observed plant partitioning for the 733 µg/l wetland increased two orders of magnitude from day 0 (30) to day 49 (1931) before decreasing by day 84 (337). Conversely, sediment partitioning increased four orders of magnitude from day 0 (0.11) to day 49 (1159), before decreasing by day 84 (11).

3.2. Lourens River wetland

3.2.1. Chlorpyrifos levels in water

A heavy rainfall event (2.36 cm) followed by edge-of-field runoff commenced at 4 p.m. on August 13, 1998 and continued until 3 a.m. on August 14, 1998. Discharge, TSS, and pesticide concentrations in water samples increased during the rainfall event (Table 6). An increase in TSS was initially detected from 5 p.m. and was still detectable at 8 p.m., August 13, 1998. A maximum TSS value of 236 mg/l in the inlet was measured approximately 2 h after the commencement of the rainfall. All outlet levels measured remained constantly below 20 mg/l. Chlorpyrifos was detected in the inlet samples between 5 and 8 p.m. and attained a maximum of 1.3 µg/l between 5 and 6 p.m. A maximum of 0.03 µg/l of chlorpyrifos was detected in the outlet between 5 and 6 p.m.

3.2.2. Chlorpyrifos levels in suspended particles

Concentrations of chlorpyrifos in suspended particles sampled over the 2-month period including the rainfall-induced runoff event in the middle of August are summarized in Table 7. Several strong rainfall events had occurred during this period. The two events in the be-

Table 5
Observed chlorpyrifos half-lives of water, sediment, and plants in Mississippi wetland mesocosms following 84 d study

Targeted concentration (μg/l)	Half-life (d)			Overall removal (%)
	Water	Sediment	Plants	
73	4.6	16	12	98
147A	9.4	53	31	83
147B	13	29	17	96
733	9.1	36	22	94

Table 6
Discharge, TSS and chlorpyrifos concentration in inlet and outlet of Lourens River wetland during a rainfall event on August 13, 1998

Sampling interval	Discharge (m³/s)		TSS (mg/l)		Chlorpyrifos (μg/l)	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
4–5 p.m.	0.08	0.07	23	10	nd	nd
5–6 p.m.	0.32	0.30	165	11	1.3	0.03
6–7 p.m.	0.30	0.31	236	17	0.4	0.01
7–8 p.m.	0.11	0.12	77	14	0.08	nd

nd indicates concentrations below detection limit of 0.01 μg/l.

Table 7
Occurrence of strong rainfall events and concentrations of chlorpyrifos in suspended particles continuously sampled above and below the Lourens River wetland. Chlorpyrifos was applied on August 11, 1998

Sampling interval	Days with rainfall >1 cm/d	Chlorpyrifos (μg/kg)	
		Inlet	Outlet
July 29–August 12, 1998	August 3, August 6	nd	nd
August 12–August 28, 1998	August 13, August 14	89.4	nd
August 28–September 13, 1998	–	21.8	nd
September 13–September 29, 1998	September 23	2.6	nd

nd indicates concentrations below detection limit of 0.01 μg/l.

ginning of August, before application of chlorpyrifos, caused no increase in the chlorpyrifos levels. Chlorpyrifos concentrations in the inlet samples increased considerably during the first strong rainfall after chlorpyrifos application on August 13 to 89.4 μg/kg and declined afterwards to 2.6 μg/kg within a 1.5 month period. Suspended particles at the outlet station never contained detectable levels of chlopyrifos.

3.2.3. Toxicological evaluations

Mortality of midges exposed for 24 h in situ in the inlet and outlet of the wetland is illustrated in Table 8. During periods without runoff (TSS < 20 mg/l), the average mortality was 2%. In the 24 h period beginning at 10 a.m. August 13, 1998, the average mortality of exposed midges was 46% at the inlet station, in comparison to 6% at the outlet. Mortality at a control site in the same tributary upstream of the orchard area was $3.7 \pm 1.2\%$. This site revealed no detectable pesticide contamination, but had increased levels of TSS (maximum 197 mg/l).

Table 8
Mortality ($\pm$SE; $n = 4$) of *Chironomus* sp. exposed for 24 h in both the inlet and outlet of the Lourens River wetland during a period without any edge-of-field runoff and during the runoff event on August 13, 1998

	Mortality (%)	
	Before runoff	During runoff
Inlet	2.5 ± 1.4	46.2 ± 4.3
Outlet	1.2 ± 1.2	6.2 ± 3.1
Turbidity control[a]	–	3.7 ± 1.2

[a] Turbidity control refers to an exposure setup carried out during the August 13 runoff event at a site upstream of the orchard growing area without pesticide contamination, but attaining high turbidity levels.

4. Discussion

In agriculture, BMPs have arisen as a means of risk aversion for both terrestrial and aquatic systems. From an agricultural perspective, BMPs decrease risk

to receiving systems as well as save potential profits in the form of decreased soil erosion, pesticide loss, etc. Previous research on BMPs has been conducted, with a great majority focusing on grass buffer (filter) strips and tillage practices (conventional vs no-till). Likewise, research of riparian buffer effects on agricultural runoff has shown significant reduction in nutrients in both surface and shallow ground water (Dillaha et al., 1989; Christensen et al., 1993). Less research has intently focused on the potential use of constructed wetlands as buffers between agricultural fields and downstream receiving systems. The premise of this research is that by replacing or constructing wetlands between agricultural fields and the receiving aquatic system, mitigation (decrease in risk) of pesticide-associated agricultural runoff can potentially be achieved.

In order to decrease risk to aquatic receiving systems, exposure must decrease as well. To decrease exposure, one must decrease concentration, frequency of exposure, duration, or alter the form of exposure (e.g., metals). Similarly, exposure has three constituencies including concentration, duration/pattern, and form (bioavailable vs bound).

An important question to address concerns the concentration of exposure which will not adversely affect organisms in aquatic receiving systems. More simply stated, what margin of safety should be available if constructed wetlands are implemented as BMPs for pesticide mitigation? Intensive mesocosm field studies provide background data on initial sorption and chlorpyrifos partitioning which can then be used to determine constructed wetland design parameters.

At the Mississippi wetland research site, the wetland with the least overall chlorpyrifos transfer/transformation efficiency (wetland 147A – 83%) had the longest sediment and plant-associated chlorpyrifos half-lives of 53 and 31 d, respectively. There were no observed relationships between targeted concentrations and overall removal, except that the wetland with the lowest targeted concentration (73 µg/l) had the greatest overall removal with 98%. This same wetland had the shortest observed aqueous-, sediment-, and plant-associated chlorpyrifos half-lives of 4.6, 16, and 12 d, respectively.

The 73 µg/l wetland had a targeted concentration of one order of magnitude less than that of the 733 µg/l wetland, yet all observed half-lives in the 73 µg/l wetland were approximately one-half those of the 733 µg/l wetland. However, the overall percent chlorpyrifos removal was similar (98% for 73 µg/l wetland and 94% for 733 µg/l wetland).

When examining results of chlorpyrifos fate in aqueous phases of Mississippi wetland mesocosms, declining trends are readily evident. Decreases in chlorpyrifos concentrations in water generally fit a first-order decay model with coefficients of determination 0.95 or higher (Giddings et al., 1997). While concentrations examined in that study were orders of magnitude less than those examined in the current study (0.3–3 µg/l vs 73–733 µg/l), fate of chlorpyrifos in water apparently behaved similarly. This was most pronounced when averaging decreases for mean chlorpyrifos concentrations across the entire wetland, rather than focusing on individual transects. Although half-lives for chlorpyrifos and water previously reported in literature were slightly lower than those observed in this study, well over one-half of the chlorpyrifos initially measured in the water column (day 0) was transferred prior to collection of samples on day 7 (next sampling date) (Kersting and van Wijngaarden, 1992; Knuth and Heinis, 1992). Some researchers have suggested that because most studies do not include measurements of pesticide losses within the first 24 h, longer half-lives are observed (Knuth and Heinis, 1992). Data from the current study suggest that the majority of chlorpyrifos transfer occurred from day 0 to day 7, while much less transfer occurred from day 7 through 84. Two separate studies agreed that transfer/transformation of chlorpyrifos is rapid during the first few days following application (Knuth and Heinis, 1992; Racke, 1993). This transfer/transformation is generally attributed to potential volatilization, which may reduce the pesticide's efficacy in the field (Meikle and Youngson, 1978). However, Racke (1993) pointed out that, although chlorpyrifos has a "moderate" volatilization coefficient (Table 1), actual field volatilization itself is a function of how chlorpyrifos is applied and other partitioning processes.

Transfer of chlorpyrifos from sediment was not as easily distinguished as was water transfer. When examining sediment concentrations in individual transects, variability is apparent; however, when wetlands are viewed as an independent entity (mean wetland concentrations rather than individual transects), definite declines in concentration are evident. Obviously with a low water solubility, chlorpyrifos will partition out of the water column to some form of organic carbon (e.g., sediments, plants). Observed sediment partition coefficients generally are within ranges of those reported by Racke (1993) (1.34–2000). Results from the current study suggest that sediment sorption plays an important role, with generally >50% of measured chlorpyrifos-associated with sediment over time.

While fate of chlorpyrifos in plant tissue was similar in variability to that of sediment, definite trends of transfer over time were observed. Crum and Brock (1994) reported that macrophytes initially sorbed approximately 40% of chlorpyrifos. In wetland 147A, macrophytes were responsible for sorption of approximately half of the measured chlorpyrifos; however, in remaining wetlands, sorption only amounted to approximately 20% of measured chlorpyrifos. This is, however, not to underscore the potential importance of macrophytes in sorption of chlorpyrifos.

As evidenced by the Lourens River wetland, if sufficient size and design are integrated into the construction, mitigation of chlorpyrifos-associated runoff is possible. Another example of the wetland efficiency was seen through results of in situ *Chironomus* bioassays. Toxicity (due to chlorpyrifos) was significantly decreased. Constructed wetlands are not panaceas for environmental problems, but can in agricultural settings, in combination with other BMPs, be beneficial (De Laney, 1995). Given proper situations, they can greatly enhance "water quality" in a variety of settings – municipal, industrial, and agricultural. Current research has offered valuable data concerning effectiveness for using constructed wetlands as buffers for pesticide-associated stormwater runoff.

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