



Mitigation of two pyrethroid insecticides in a Mississippi Delta constructed wetland[☆]

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A wetland length of 215 m × 30 m mitigated pyrethroid runoff from a 14 ha field.

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ABSTRACT

Constructed wetlands are a suggested best management practice to help mitigate agricultural runoff before entering receiving aquatic ecosystems. A constructed wetland system (180 m × 30 m), comprising a sediment retention basin and two treatment cells, was used to determine the fate and transport of simulated runoff containing the pyrethroid insecticides lambda-cyhalothrin and cyfluthrin, as well as suspended sediment. Wetland water, sediment, and plant samples were collected spatially and temporally over 55 d. Results showed 49 and 76% of the study's measured lambda-cyhalothrin and cyfluthrin masses were associated with vegetation, respectively. Based on conservative effects concentrations for invertebrates and regression analyses of maximum observed wetland aqueous concentrations, a wetland length of 215 m × 30 m width would be required to adequately mitigate 1% pesticide runoff from a 14 ha contributing area. Results of this experiment can be used to model future design specifications for constructed wetland mitigation of pyrethroid insecticides.

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1. Introduction

In 2001, the world market for pesticides was nearly \$32 billion, with insecticides making up 28% of those expenditures (Kiely et al., 2004). Over 340 million kg of conventional pesticide active ingredient were used in US agricultural applications that same year (USEPA, 2004). Lambda-cyhalothrin [λ -cyano-3-phenoxybenzyl-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropanecarboxylate] is a fourth generation pyrethroid insecticide sold under such trade names as Karate[®], Matador[®], Grenade[®], and Sentinel[®] (EXTOXNET, 1996) (Table 1). In 2002, it was the third most commonly applied pyrethroid insecticide in the US with over 117,000 kg active ingredient used (Gianessi and Reigner, 2006). From 1991 to 2000, over 58,000 kg of active ingredient were applied to corn (*Zea mays*), cotton (*Gossypium hirsutum*), soybeans (*Glycine max*), rice (*Oryza sativa*), and wheat (*Triticum aestivum* L.) (USDA, 2004). Cyfluthrin [cyano (4-fluoror-3-phenoxy-phenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] is

also a fourth generation pyrethroid insecticide (Table 1). Sold under the trade name Baythroid[®], over 67,000 kg of active ingredient were applied in the US in 2002 (Gianessi and Reigner, 2006). Primarily used on cotton and corn, over 43,000 kg of active ingredient cyfluthrin were used in the US between 1991 and 2000 (USDA, 2004).

Although pesticides have been used for centuries, dating back to at least ancient Rome, little public concern over potential non-target effects existed until the 1962 publication of Rachel Carson's *Silent Spring* (Delaplane, 2000). Since that time, intense scrutiny has been placed not only on the pesticide industry, but also on the impacts of pesticide usage upon water quality of the US. Organochlorine insecticides, credited for many problems highlighted by Carson were eventually phased out, replaced by organophosphates. Although still in use, organophosphates are being replaced by the more efficient pyrethroid class of insecticides (Amweg et al., 2006). Even with advancements in pesticide chemical properties, USEPA (2007) data reported over 1300 water bodies in the US were listed as impaired due to pesticides.

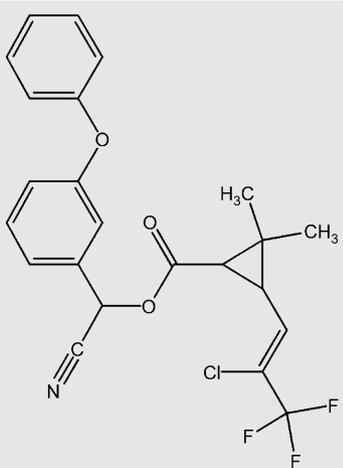
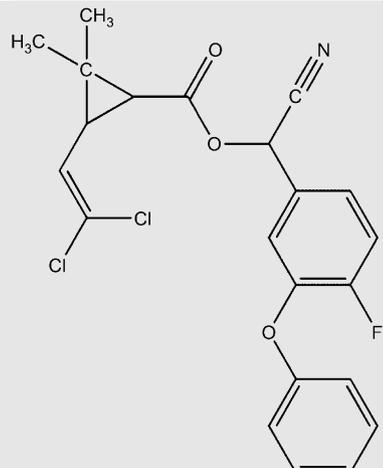
While some have advocated elimination of pesticides across the board, studies have indicated the dire consequences of such action. Oerke et al. (1994) estimated declines in crop yields by as much as 50% without the use of pesticides. Knutson et al. (1990) suggested the significant decline in crop production may result in increased acreage to compensate for production, increased food expenditures, and increased inflation. Such a need for increased

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Table 1
Physical and chemical properties of lambda-cyhalothrin and cyfluthrin

	Lambda-cyhalothrin	Cyfluthrin
Structure ^{a,b}		
Molecular weight ^{a,b}	449.9	434.29
Water solubility (mg/L) ^{a,b}	0.005	0.002
Vapor pressure (mm Hg at 25°) ^{b,d}	1.5×10^{-9}	3.24×10^{-8}
K_{OW} ^{c,d}	10,000,000	4.58×10^5 – 6.4×10^5
K_{OC} ^{b,c}	180,000	62,400
Hydrolysis ($t_{1/2}$) (d) ^{a,b}	233.1	193 (25 °C at pH 7)

^a Casjens (2002).

^b EXTOXNET (1996).

^c Schroer et al. (2004).

^d Hand et al. (2001).

crop acreage would put a strain on the intensively cultivated Mississippi Delta's agricultural ecosystem. To balance the value of pesticide usage yet maximize environmental safety, management practices targeting mitigation of pesticide runoff have been developed.

Constructed and natural wetlands have been successful in mitigating runoff associated with agricultural pesticides (Wolverton and Harrison, 1973; Higgins et al., 1993; Rodgers et al., 1999; Moore et al., 2002; Schulz et al., 2003a,b; Schulz, 2004). One of the three critical aspects of constructed mitigation wetlands is the presence of vegetation. Benefits of plants include physical filtration, surface area for microbial attachment, and stabilization of bed sediments (Brix, 1994). Wetland plant organic matter may also aid in mitigation by increasing the potential transfer of pesticides from the water column to plant material (Moore et al., 2007). The objective of this research was to evaluate the use of a constructed wetland system in the Mississippi Delta, USA, for mitigating lambda-cyhalothrin and cyfluthrin concentrations associated with a simulated storm runoff event.

2. Methods

2.1. Study site description

Beasley Lake (Sunflower County, Mississippi, USA) is a 25 ha oxbow lake surrounded by 850 ha of land within the watershed (Locke, 2004). In 2003, a constructed wetland system (180 m × 30 m), comprised a sediment retention pond and two individual cells, was established adjacent to the lake (Weaver et al., 2004; see Moore et al. (2007) for schematic diagram). Dominant vegetation included *Cyprus iria* (rice field flatsedge), *Sorghum halepense* (johnsongrass), *Digitaria ischaemum* (small crabgrass), *Polygonum lapathifolium* (pale smartweed), and *Alternanthera philoxeroides* (alligatorweed) (Weaver and Zablotowicz, 2004). To facilitate collection of water, sediment, and plant samples, 10 stations at distances from inflow of 1 (site 1), 10 (site 2), 15 (site 3), 30 (site 4), 60 (site 5), 85 (site 6), 90 (site 7), 120 (site 8), 150 (site 9), and 170 m (site 10) were established within the constructed wetland system (Moore et al., 2007).

2.2. Simulated storm runoff event

Simulated storm runoff was introduced to the constructed wetland system in July 2003. Karate™ (19 g lambda-cyhalothrin active ingredient total), Baythroid™ (79.5 g cyfluthrin active ingredient total), 568 L of suspended sediment slurry (inflow suspended sediment concentration of 403 mg/L), and surface water from Beasley Lake (Table 2) were mixed together in a 7570 L chamber for 1 h prior to actual amendment into the sediment retention pond of the wetland system for four consecutive hours. During the 4-h amendment, lake water was also constantly added to the wetland system via the sediment retention pond. Amount of pesticides used was based on the recommended application rates (0.12 kg lambda-cyhalothrin/ha; 0.57 kg cyfluthrin/ha); wetland contributing acreage (14 ha); and assumed 1% pesticide runoff (Wauchope, 1978). Simulated rainfall contributions to the storm event were based on a 1.3 cm event, with assumed rainfall runoff of 50% (~917,000 L). Source water from Beasley Lake was transported via pump into the wetland system at a rate of approximately 3800 L/min for 4 h in order to complete the simulated runoff event.

2.3. Collection of water, sediment, and plant samples

Grab samples of wetland water were collected in 1-L amber glass bottles at 15 min intervals for the first hour, then again at 0.06, 0.08, 0.13, 0.17, 0.38, 1, and 2 d

Table 2
Pesticide concentrations (µg/L) in Beasley Lake source water (from Moore et al., 2007)

Sample collected	Pesticide 5/19/03
Atrazine	0.227
Methyl parathion	0.015
Metolachlor	0.011
Chlorpyrifos	0.000
Cyanazine	0.002
Fipronil	0.011
Fipronil sulfone	0.001
pp'-DDE	0.002
pp'-DDD	0.003
pp'-DDT	0.014
Chlorfenapyr	0.004
Bifenthrin	0.006
Lambda-cyhalothrin	0.002

at individual sampling sites according to Moore et al. (2007). When water was available, collections were also made on 7, 13, 27, 41, and 55 d post-application. With no inflow after the 4-h event and little natural rainfall throughout the experiment, certain wetland sampling stations were dry after 7 d. Collected samples were stored on ice immediately and returned to the laboratory for extraction within 24 h of collection. Sediment and plant material (10 g wet weight) were collected at 0.04, 0.13, 0.38, 1, 2, 7, 13, 27, 41, and 55 d. Sediment samples, collected with a shovel, were limited to the top 3 cm, and only leaves and shoots exposed in the water column (from sediment surface to water surface) were collected as plant samples. Samples were wrapped in foil, stored on ice, and transported to the laboratory. Upon arrival, samples were stored in a freezer (-20°C) until being dried for analysis.

2.4. Pesticide extraction and analysis

Lambda-cyhalothrin and cyfluthrin analyses were conducted on unfiltered water, sediment, and plants to determine pesticide concentrations in the three environmental matrices. Extraction methods used were similar to those of Bennett et al. (2000). Briefly, water samples were extracted by liquid–liquid extraction using ethyl acetate. Individual water sample volumes were recorded (500–800 mL) prior to addition of 200 mL of ethyl acetate and 100 mg of potassium chloride for a single extraction. Prior to extraction, sediment and plant samples were air-dried and ground to pass through a 2 mm sieve. Both sediment and plant samples were extracted by ultrasonication using ethyl acetate. Extracts were also subjected to silica gel cleanup before analysis.

Lambda-cyhalothrin and cyfluthrin were analyzed using an HP 6890 gas chromatograph equipped with a 30 m HP-1MS column. A multi-level calibration procedure was used with standards (AccuStandard, New Haven, CT; 99% purity) and updated every ninth sample. Limits of detection (LOD) for both lambda-cyhalothrin and cyfluthrin in water were 1 ng/L. Limits of quantification for both insecticides were 10 ng/L. For both sediments and plants, lambda-cyhalothrin and cyfluthrin LOD were 10 ng/kg. LOC for both insecticides in sediments and plants were 100 ng/kg. Mean extraction efficiencies, based on fortified samples, were >90% for water, sediment, and plants.

2.5. Data analysis

Mass balances were determined using a model previously developed by Bennett et al. (2005) and Moore et al. (2006, 2007). Data on water, plant, and sediments collected along transects of the sediment detention pond, vegetated wetland cell 1 and vegetated cell 2 at each sample time point (0.04, 0.13, 0.38, 1, 2, 7 and 13 d) were used to calculate mass balances. Because of dry conditions 13 d after experiment initiation, water data were unavailable at some locations. Hence, no further mass balances were derived for comparisons of the three environmental matrices (water, plant, and sediment).

3. Results

3.1. Lambda-cyhalothrin concentrations

Thirty minutes following exposure initiation, mean lambda-cyhalothrin concentrations were restricted to the sediment detention pond ($8.75 \pm 5.8 \mu\text{g/L}$) and wetland cell 1 ($28.5 \pm 12.5 \mu\text{g/L}$).

Concentrations in wetland cell 2 were below detection limits (Table 3). Four hours following exposure initiation, lambda-cyhalothrin had migrated into wetland cell 2 (mean aqueous concentration of $5.03 \pm 3.2 \mu\text{g/L}$). Outflow (190 m) aqueous concentrations were below detection with the exception of the samples collected at 6 (0.36 $\mu\text{g/L}$), 9 (0.62 $\mu\text{g/L}$), 24 (0.43 $\mu\text{g/L}$), and 48 h (0.77 $\mu\text{g/L}$). From 7 to 55 d, aqueous concentrations were again below detection limits. By plotting maximum observed aqueous concentrations versus sample distance from inflow, trends of decreasing concentration with distance were noted (Fig. 1). When comparing concentrations of lambda-cyhalothrin in the entire wetland system throughout the 55 d experiment, the mean concentrations were $4.17 \pm 0.48 \mu\text{g/L}$, $121 \pm 59 \mu\text{g/kg}$ (dry weight), and $65.9 \pm 21 \mu\text{g/kg}$ (dry weight) in water, sediment, and plant compartments, respectively. Overall, water and sediment were responsible for 3 and 63%, respectively, of the measured lambda-cyhalothrin concentrations, while wetland plants were associated with 34% of measured lambda-cyhalothrin concentrations. The sediment detention pond retained $30 \pm 7\%$ of lambda-cyhalothrin aqueous concentrations, while the majority ($52 \pm 6\%$) was retained in wetland cell 1.

3.2. Lambda-cyhalothrin mass

The total nominal mass of lambda-cyhalothrin (as active ingredient) added to the wetland system was 19 g. In comparison, the total calculated mass of lambda-cyhalothrin for the entire wetland system ($m_{\text{total}} (\text{detention} + \text{wetland } 1 + \text{wetland } 2)$) at the 3 h sampling point was 29.5 g. Mass balance assumptions of wetland water volume and sediment and plant biomass can lead to over-estimates of actual pesticide mass present in the system. The mass balance model used for this study has been used in similar wetland studies with success (Bennett et al., 2005; Moore et al., 2006, 2007). Within the sediment detention pond, overall measured lambda-cyhalothrin percent mass was 43 ± 19 , 28 ± 18 , and $30 \pm 14\%$, respectively, for water, sediments, and plants. Sediment-associated lambda-cyhalothrin measured mass in wetland cells 1 and 2 was 50 ± 17 and $39 \pm 18\%$, respectively. Plant-associated lambda-cyhalothrin measured mass were 33 ± 17 and $55 \pm 19\%$, respectively, for wetland cells 1 and 2. When calculating overall measured mass percentages for the 55-d experiment (Table 4), 6.3 ± 3.4 , 47 ± 14 , and $49 \pm 15\%$ was associated with water, sediments, and plants, respectively, indicating the importance of both sediments and plants in transferring lambda-cyhalothrin from the water column. Throughout the study, mass data indicated the initial cell (sediment

Table 3
Mean (\pm standard error) insecticide concentrations ($\mu\text{g/L}$) in wetland water

Time (d)	Sediment					
	Detention pond (sites 1–2)		Wetland 1 (sites 3–6)		Wetland 2 (sites 7–10)	
	LC	CYF	LC	CYF	LC	CYF
0.01	17.4 ± 0.22	64.3 ± 11	11.4 ± 4.2	34.4 ± 11.8	ns	ns
0.02	8.75 ± 5.8	20.6 ± 15	10.1 ± 4.3	28.5 ± 12.5	bd	0.29 ± 0.0
0.03	4.65 ± 0.4	11.5 ± 3.5	13.2 ± 1.9	44.0 ± 5.20	bd	0.29 ± 0.05
0.04	4.58 ± 3.8	9.17 ± 7.0	17.8 ± 3.0	48.6 ± 7.5	0.81 ± 0.8	10.92 ± 0.68
0.06	21.4 ± 2.4	52.6 ± 15	13.7 ± 2.4	30.9 ± 6.9	0.53 ± 0.53	2.16 ± 1.8
0.08	2.21 ± 2.2	6.06 ± 5.1	13.4 ± 2.2	30.0 ± 5.2	3.02 ± 3.0	6.86 ± 6.6
0.13	1.57 ± 0.12	4.47 ± 0.78	5.83 ± 0.70	12.4 ± 1.4	3.2 ± 1.7	6.74 ± 3.5
0.17	14.1 ± 9.9	40.2 ± 31	2.87 ± 0.56	7.66 ± 1.3	5.03 ± 3.2	13.2 ± 8.3
0.25	0.13 ± 0.13	1.35 ± 0.47	0.79 ± 0.31	2.97 ± 0.86	1.05 ± 0.79	3.94 ± 2.4
0.38	0.45 ± 0	3.01 ± 0	1.24 ± 0.93	3.99 ± 1.9	0.26 ± 0.08	2.32 ± 0.56
1	1.37 ± 0	3.2 ± 0	0.42 ± 0.26	1.29 ± 0.47	0.8 ± 0.48	2.35 ± 0.87
2	bd	0.77 ± 0	0.33 ± 0.15	0.98 ± 0.14	0.24 ± 0.12	1.09 ± 0.34
7	bd	0.22 ± 0	0.04 ± 0.04	0.46 ± 0.12	0.01 ± 0.01	0.34 ± 0.11
13	ns	ns	ns	ns	0.04 ± 0.04	5.20 ± 5.1
27	ns	ns	ns	ns	bd	0.21 ± 0.09
41	ns	ns	ns	ns	bd	0.12 ± 0.03
55	ns	ns	ns	ns	bd	0.14 ± 0.05

ns = No sample; bd = below detection; LC = lambda-cyhalothrin; CYF = cyfluthrin.

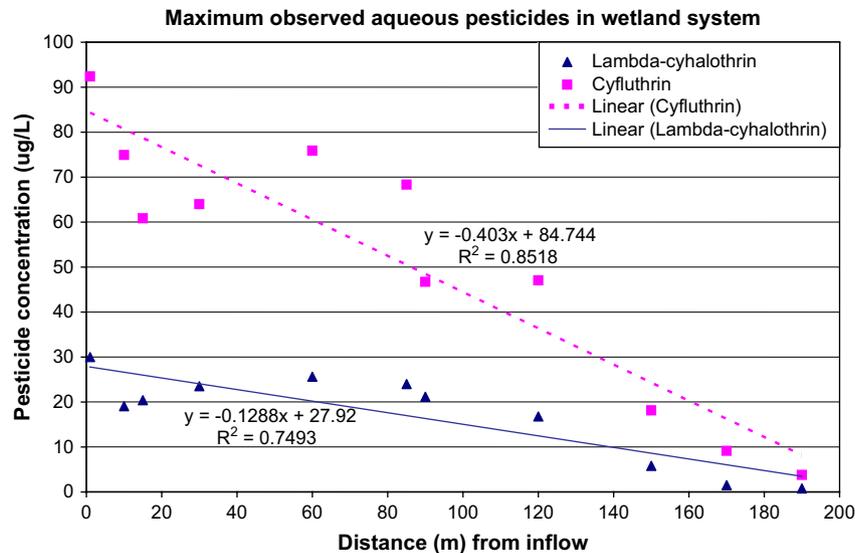


Fig. 1. Maximum observed aqueous concentrations in Beasley Lake wetland system.

detention pond) played an extremely limited role in overall pesticide retention. Less than 1% of the overall measured lambda-cyhalothrin mass was retained in the sediment detention pond, while 53 and 47% were in cells 1 and 2, respectively.

3.3. Cyfluthrin concentrations

Unlike lambda-cyhalothrin, cyfluthrin was measured entering wetland cell 2, some 30 min following exposure initiation (0.29 µg/L) (Table 3). At the end of the simulated event (4 h), cyfluthrin had a mean aqueous concentration of 13.2 ± 8.3 µg/L in wetland cell 2. Cyfluthrin was measured in collected outflow (190 m) aqueous samples beginning at 0.03 d (0.15 µg/L) and continuing for the duration of the 55 d experiment, peaking at 12 h (3.77 µg/L) before declining to 0.05 µg/L (55 d). When comparing concentrations of cyfluthrin in the entire wetland system throughout the 55 d experiment, the mean concentrations were 11.4 ± 1.3 µg/L, 8.03 ± 1.8 µg/kg (dry weight), and 284 ± 55 µg/kg (dry weight) in the water, sediment, and plant compartments, respectively. In contrast to lambda-cyhalothrin, wetland plants were associated with 94% of the overall measured cyfluthrin concentrations, while water and sediment were responsible for 4 and 2%, respectively.

3.4. Cyfluthrin mass

The total nominal mass of cyfluthrin added to the wetland system was 79.5 g, four times more than the 19 g of lambda-cyhalothrin. At the 3 h sample collection, just 1 h prior to the end of the simulated storm input, the total calculated mass of cyfluthrin for the entire wetland system ($m_{\text{total}}(\text{detention} + \text{wetland 1} + \text{wetland 2})$) was 13.2 g. Total measured cyfluthrin mass had increased to 49 g by the 9 h sample collection. Within the sediment detention pond, overall measured cyfluthrin percent mass for the study was 44 ± 15 , 0.5 ± 0.5 , and $56 \pm 15\%$, respectively, for water, sediment, and plants. Sediment-associated cyfluthrin measured mass in wetland cells 1 and 2 was below 10% (8 ± 6 and $5 \pm 2\%$, respectively). Plant-associated cyfluthrin measured mass was 73 ± 10 and $75 \pm 11\%$, respectively, for wetland cells 1 and 2. Evaluating the entire 55 d experiment (Table 5), the overall measured mass percentages for water, sediment, and plants were 18 ± 9 , 7 ± 3 , and $75 \pm 8\%$, respectively, signifying the crucial role of vegetation in transferring

cyfluthrin from the water column. As with lambda-cyhalothrin, mass data indicated the limited role of the sediment detention pond in overall pesticide retention. Only 1% of the overall measured cyfluthrin mass was retained in the sediment detention pond, while 21 and 78% were in cells 1 and 2, respectively.

Table 4

Lambda-cyhalothrin mass for Beasley Lake constructed wetland system

Time	Cell	Water (%)	Sediment (%)	Plants (%)	Mass (g)	Total mass (g)
1 h	DP	100	0	0	0.07	17.2
	W1	92	8	0	2.60	
	W2	10	90	0	14.5	
3 h	DP	44	0	56	0.05	29.5
	W1	8	92	0	10.4	
	W2	17	83	0	19.0	
9 h	DP	100	0	0	4.00E-03	106.6
	W1	0	100	0	89.5	
	W2	2	0	98	17.1	
24 h	DP	13	0	87	0.09	31.3
	W1	3	57	40	1.50	
	W2	1	95	4	29.7	
48 h	DP	0	77	23	0.05	2.52
	W1	4	56	40	0.60	
	W2	7	87	6	1.87	
7 d	DP	0	89	11	0.75	8.40
	W1	0	0	100	0.46	
	W2	0	1	99	7.19	
13 d	DP	0	100	0	3.00E-03	3.29
	W1	0	100	0	0.03	
	W2	0	1	99	3.26	
27 d	DP	nd	100	0	1.00E-03	1.00E-03
	W1	nd	nd	nd	nd	
	W2	nd	nd	nd	nd	
41 d	DP	nd	nd	nd	nd	0.75
	W1	nd	nd	nd	nd	
	W2	nd	3	97	0.75	
55 d	DP	nd	nd	nd	nd	3.22
	W1	nd	0	100	1.95	
	W2	nd	0	100	1.27	

DP = detention pond; W1 = wetland 1; W2 = wetland 2; nd = pesticide not detected.

Table 5
Cyfluthrin mass data for Beasley Lake constructed wetland system

Time	Cell	Water (%)	Sediment (%)	Plants (%)	Mass (g)	Total mass (g)
1 h	DP	89	0	11	0.16	10.5
	W1	72	3	25	8.80	
	W2	91	9	0	1.56	
3 h	DP	74	0	26	0.10	13.2
	W1	43	0	57	4.02	
	W2	73	2	25	9.08	
9 h	DP	62	3	35	0.04	49.0
	W1	15	1	84	3.96	
	W2	5	0	95	45.0	
24 h	DP	11	0	89	0.23	22.1
	W1	2	2	96	9.45	
	W2	9	2	89	12.4	
48 h	DP	7	0	93	0.09	12.7
	W1	2	0	98	3.72	
	W2	6	3	91	8.88	
7 d	DP	20	0	80	5.00E-03	67.3
	W1	0	5	95	7.62	
	W2	0	3	97	59.7	
13 d	DP	nd	46	54	0.18	21.6
	W1	nd	39	61	2.90	
	W2	17	5	78	18.5	
27 d	DP	nd	22	78	0.12	10.1
	W1	nd	20	80	2.47	
	W2	1	6	93	7.51	
41 d	DP	nd	74	26	0.03	5.95
	W1	nd	48	52	1.89	
	W2	1	20	79	4.03	
55 d	DP	nd	0	100	5.00E-03	3.22
	W1	0	43	57	1.14	
	W2	2	0	98	2.07	

DP = detention pond; W1 = wetland 1; W2 = wetland 2; nd = pesticide not detected.

4. Discussion

Water solubility (5 and 2 µg/L) and K_{oc} values (180,000 and 62,400) for lambda-cyhalothrin and cyfluthrin, respectively, indicate these pyrethroids' tendency to partition out of the water column. Accidental spills, spray drift, or storm runoff following a recent pyrethroid application may result in introduction into aquatic receiving systems, causing harm to fish, invertebrates, and other associated fauna. While no USEPA-approved acute or chronic freshwater ambient water quality criteria exist for either lambda-cyhalothrin or cyfluthrin, several toxicity assessments have been conducted on both pesticides (Hill, 1989; Mokry and Hoagland, 1990; Farmer et al., 1995; Heckmann and Friberg, 2005; Lauridsen and Friberg, 2005). Schroer et al. (2004) suggested 10 ng/L as a potential regulatory acceptable environmental concentration of lambda-cyhalothrin. Conducted in The Netherlands, this study provided 5th and 10th percentile hazard concentrations (HC_5 and HC_{10}) for both laboratory and field exposures. Laboratory and field HC_5 s for lambda-cyhalothrin were 2.7 and 4.1 ng/L, respectively, while HC_{10} s for both laboratory and field exposures were 5.1 ng/L (Schroer et al., 2004). Wetland cell 2 outflow data indicated aqueous lambda-cyhalothrin concentrations exiting the system between 6 and 48 h were above these levels (ranging from 360 to 777 ng/L). The potential for impairment to aquatic species would be present in water bodies with these inflow lambda-cyhalothrin concentrations. Fewer studies are available for cyfluthrin. Mokry and Hoagland (1990) reported a 48 h LC_{50} for *Daphnia magna* at

0.17 µg/L cyfluthrin, and Munn et al. (2006) reported a 48 h EC_{50} for *D. magna* and cyfluthrin of 0.083 µg/L. Wetland cell 2 outflow cyfluthrin concentrations were above the 48 h EC_{50} from 45 min post-amendment through 41 d.

Ecological effects of lambda-cyhalothrin on macroinvertebrate drift have been reported by Farmer et al. (1995), Lauridsen and Friberg (2005), and Heckmann and Friberg (2005). Farmer et al. (1995) reported several ecological effects of a 1.7 g a.i./ha (lambda-cyhalothrin) dose on aquatic ecosystems. Initial knockdown of surface-dwelling insects was followed by a period of recovery. Increased algal blooms and copepod abundance were noted as indirect effects, yet no adverse effects on algal chlorophyll content, productivity, or community metabolism were noted (Farmer et al., 1995). Heckmann and Friberg (2005) noted macroinvertebrate recovery 2 weeks following a 30 min pulse exposure of lambda-cyhalothrin. In a study conducted in Denmark, lambda-cyhalothrin pulse concentrations of 0.001, 0.01, 0.1, and 1.0 µg/L were applied to experimental channels, resulting in catastrophic drift (Lauridsen and Friberg, 2005). A drift response threshold of 0.01 µg/L lambda-cyhalothrin was reported for *Baetis rhodani* and *Leuctra fusca/digitata*, two insect species (Lauridsen and Friberg, 2005).

Because agriculture is often the target of non-point source contamination of aquatic receiving systems, the industry has invested significant resources into developing and refining various land management practices to alleviate potential water quality concerns. One such practice, constructed wetlands, has been successful at mitigating various pesticide concentrations exiting agricultural production acreage (Moore et al., 2000, 2002, 2007; Sherrard et al., 2004). Both biotic and abiotic functions within constructed wetlands work in conjunction to remediate pesticide runoff.

An important environmental characteristic in constructed wetland systems is pH. Cyfluthrin dissipates (half-life of 12.2 d) through aqueous photolysis at pH 7, and it also degrades abiotically through hydrolysis (Casjens, 2002). No hydrolysis was reported to have occurred with lambda-cyhalothrin in water of 5–7 pH (NPTN, 2001). Leistra et al. (2003) determined that lambda-cyhalothrin is relatively stable to aqueous hydrolysis in acid or neutral pH systems. With reported wetland water pH values of 4.85–5.21 (Weaver et al., 2004), pyrethroid degradation was likely not influenced by hydrolysis.

To further understand the fate of lambda-cyhalothrin and cyfluthrin within the vegetated wetland system, mass balance calculations were performed to determine partitioning between water, sediment and plant components. At the 3 h sample collection, lambda-cyhalothrin mass was primarily in sediment (Table 4). This contradicts Roessink et al. (2005) who reported no lambda-cyhalothrin from sediment samples collected after pesticide application to the water column. Cyfluthrin, at 3 h, was still predominantly in the aqueous phase (Table 5). Gupta and Gajbhiye (2005) examined cyfluthrin dissipation in water and water + sediment, noting that cyfluthrin water (only) dissipation was along the line of first-order kinetics with a half-life of 8.4–10.5 d. When examining cyfluthrin dissipation in water and sediment combined, two distinct trends were noted, where up to 10 d, the half-life ranged from 3 to 4.3 d, while after 10 d, cyfluthrin half-life increased to 13.5–13.9 d (Gupta and Gajbhiye, 2005). By 9 h after introduction during the current study, lambda-cyhalothrin mass was evenly distributed, percentage wise, among water, sediment, and plants. Cyfluthrin demonstrated a different distribution, with 71% of mass being associated with plants at 9 h within the overall system.

Lambda-cyhalothrin sorption to macrophytes has been previously reported (Hand et al., 2001; Moore et al., 2001). Different macrophyte densities have reportedly influenced the fate and bioavailability of lambda-cyhalothrin in wetland systems (Hand

et al., 2001; Leistra et al., 2003; Van Wijngaarden et al., 2006). In contrast to Moore et al. (2001), where 87% of measured lambda-cyhalothrin's concentrations were associated with plants, the current study revealed only 34% of measured lambda-cyhalothrin concentrations were sorbed to plant material. Lambda-cyhalothrin residue in plants within a high plant density ditch enclosure reached 50% of original dose after 24 h, while intermediate and low plant densities only had 3–11% pesticide residue after 1–2 d (Leistra et al., 2003). This study concluded that the lower percentage of lambda-cyhalothrin in ditch sediment was a result of higher plant densities (Leistra et al., 2003). In evaluating the fate of both lambda-cyhalothrin and cyfluthrin, it appears the majority of lambda-cyhalothrin sorbed to sediment material, while cyfluthrin mainly partitioned to plant organic material. Earlier studies on cyfluthrin's sorption to plants reported a low tendency to actually penetrate plant tissues for minimal pesticide translocation (Tomlin, 1997; Casjens, 2002). Hand et al. (2001) determined that macrophytes have considerable impact on fate of adsorptive pesticides such as lambda-cyhalothrin.

In the current study, estimates of constructed wetland length needed for sufficient mitigation of both lambda-cyhalothrin and cyfluthrin were determined by performing regression analyses on data from Fig. 1. Utilizing available conservative toxicity endpoints (lambda-cyhalothrin 21 d *D. magna* NOEC = 0.003 µg/L; cyfluthrin 48 h *D. magna* EC₅₀ = 0.083 µg/L), wetland lengths of 217 and 210 m would be needed for mitigation inflow concentrations of lambda-cyhalothrin and cyfluthrin, respectively. While these regression equations are only rough estimates, they do provide initial data for further wetland design parameters, as well as an efficient starting point for those interested in implementing such management practices. Constructed wetlands should be considered one potential management tool available to farmers, landowners, and conservationists. As with other practices, when used as part of a suite of management opportunities, one can expect improved water quality for receiving aquatic ecosystems.

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References

- Amweg, E.L., Weston, D.P., You, J., Lydy, M.J., 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environmental Science and Technology* 40, 1700–1706.
- Bennett, E.R., Moore, M.T., Cooper, C.M., Smith Jr., S., 2000. Method for the simultaneous extraction and analysis of two current use pesticides, atrazine and lambda-cyhalothrin, in sediment and aquatic plants. *Bulletin of Environmental Contamination and Toxicology* 64, 825–833.
- Bennett, E.R., Moore, M.T., Cooper, C.M., Smith Jr., S., Shields Jr., F.D., Drouillard, K., Schulz, R., 2005. Vegetated agricultural ditches for the mitigation of pyrethroid associated runoff. *Environmental Toxicology & Chemistry* 24, 2121–2127.
- Brix, H., 1994. Functions of macrophytes in constructed wetlands. *Water Science and Technology* 4, 71–78.
- Casjens, H., 2002. Environmental Fate of Cyfluthrin. California Department of Pesticide Regulation, Sacramento, California. Available from: <www.cdpr.ca.gov/docs/emppm/pubs/fatememo/cyfluthrn.pdf>.
- Delaplane, K.S., 2000. Pesticide usage in the United States: history, benefits, risks, and trends. University of Georgia Cooperative Extension Service, Bulletin 1121, 7 pp.
- Extension Toxicology Network (EXTOXNET), 1996. Pesticide information profiles. Available from: <<http://extoxnet.orst.edu/pips/lambdacy.htm>>.
- Farmer, D., Hill, I.R., Maund, S.J., 1995. A comparison of the fate and effects of two pyrethroid insecticides (lambda-cyhalothrin and cypermethrin) in pond mesocosms. *Ecotoxicology* 4, 219–244.
- Gianessi, L., Reigner, N., 2006. Pesticide use in US crop production: 2002. Insecticides and other pesticides. CropLife Foundation Report, Washington, DC.
- Gupta, S., Gajbhiye, V.T., 2005. Dissipation of beta-cyfluthrin in water as affected by sediment, pH, and temperature. *Bulletin of Environmental Contamination and Toxicology* 74, 40–47.
- Hand, L.H., Kuet, S.F., Lane, M.C.G., Maund, S.J., Warinton, J.S., Hill, I.R., 2001. Influences of aquatic plants on the fate of the pyrethroid insecticide lambda-cyhalothrin in aquatic environments. *Environmental Toxicology & Chemistry* 20, 1740–1745.
- Heckmann, L.-H., Friberg, N., 2005. Macroinvertebrate community response to pulse exposure with the insecticide lambda-cyhalothrin using in-stream mesocosms. *Environmental Toxicology & Chemistry* 24, 582–590.
- Higgins, M.J., Rock, C.A., Bouchard, R., Wengrezynek, B., 1993. Controlling agricultural runoff by use of constructed wetlands. In: Moshiri, G.A. (Ed.), *Constructed Wetlands for Water Quality Improvement*. CRC Press, Boca Raton, Florida, pp. 359–367.
- Hill, I.R., 1989. Aquatic organisms and pyrethroids. *Pesticide Science* 27, 429–457.
- Kiely, T., Donaldson, D., Grube, A., 2004. Pesticide industry sales and usage: 2000 and 2001 market estimates. EPA-733-R-040001. Washington, DC.
- Knutson, R.D., Taylor, C.R., Penson, J.B., Smith, E.G., 1990. Economic Impacts of Reduced Chemical Use. Knutson and Associates, College Station, Texas.
- Lauridsen, R.B., Friberg, N., 2005. Stream macroinvertebrate drift response to pulsed exposure of the synthetic pyrethroid lambda-cyhalothrin. *Environmental Toxicology* 20, 513–521.
- Leistra, M., Zweers, A.J., Warinton, J.S., Crum, S.J.H., Hand, L.H., Beltman, W.H.J., Maund, S.J., 2003. Fate of the insecticide lambda-cyhalothrin in ditch enclosures differing in vegetation density. *Pest Management Science* 60, 75–84.
- Locke, M.A., 2004. Mississippi Delta management systems evaluation area: overview of water quality issues on a watershed scale. In: Nett, M.T., Locke, M.A., Pennington, D.A. (Eds.), *Water Quality Assessments in the Mississippi Delta: Regional Solutions, National Scope*, ACS Symposium Series, Washington, DC 877, pp. 1–15.
- Mokry, L.E., Hoagland, K.D., 1990. Acute toxicities of five synthetic pyrethroid insecticides to *Daphnia magna* and *Ceriodaphnia dubia*. *Environmental Toxicology & Chemistry* 9, 1045–1051.
- Moore, M.T., Rodgers Jr., J.H., Cooper, C.M., Smith Jr., S., 2000. Constructed wetlands for mitigation of atrazine-associated agricultural runoff. *Environmental Pollution* 110, 393–399.
- Moore, M.T., Bennett, E.R., Cooper, C.M., Smith Jr., S., Shields Jr., F.D., Milam, C.D., Farris, J.L., 2001. Transport and fate of atrazine and lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi Delta, USA. *Agriculture, Ecosystems & Environment* 87, 309–314.
- Moore, M.T., Schulz, R., Cooper, C.M., Smith Jr., S., Rodgers Jr., J.H., 2002. Mitigation of chlorpyrifos runoff using constructed wetlands. *Chemosphere* 46, 827–835.
- Moore, M.T., Bennett, E.R., Cooper, C.M., Smith Jr., S., Farris, J.L., Drouillard, K., Schulz, R., 2006. Influence of vegetation in mitigation of methyl parathion. *Environmental Pollution* 142, 288–294.
- Moore, M.T., Cooper, C.M., Smith Jr., S., Cullum, R.F., Knight, S.S., Locke, M.A., Bennett, E.R., 2007. Diazinon mitigation in constructed wetlands: influence of vegetation. *Water, Air and Soil Pollution* 184, 313–321.
- Munn, M.D., Gilliom, R.J., Moran, P.W., Nowell, L.H., 2006. Pesticide Toxicity Index for Freshwater Aquatic Organisms, second ed. U.S. Geological Survey Scientific Investigations Report 2006-5148, 81 pp.
- NPTN (National Pesticide Telecommunications Network), 2001. Lambda-Cyhalothrin Technical Fact Sheet. Corvallis, Oregon.
- Oerke, E.C., Dehne, H.W., Schonbeck, F., Weber, A., 1994. Crop Production and Crop Protection: Estimated Losses in Major Food and Cash Crops. Elsevier, Amsterdam, The Netherlands.
- Rodgers Jr., J.H., Dickson, G.W., Dillon, T., Dorn, P.B., Farmer, J.E., Gearheart, R.A., Hall, J.F., McFarland, B., Nelson, M.K., Nix, P., Richardson, C.J., Tierney, D.P., 1999. Workgroup V synopsis: constructed wetlands as a risk mitigation alternative. In: Lewis, M.A., Mayer, F.L., Powell, R.L., Nelson, M.K., Klaine, S.J., Henry, M.G., Dickson, G.W. (Eds.), *Ecotoxicology and Risk Assessment for Wetlands*. SETAC, Pensacola, Florida.
- Roessink, I., Arts, G.H.P., Belgers, D.M., Bransen, F., Maund, S.J., Brock, T.C.M., 2005. Effects of lambda-cyhalothrin in two ditch microcosm systems of different trophic status. *Environmental Toxicology & Chemistry* 24, 1684–1696.
- Schroer, A.F.W., Belgers, J.D.M., Brock, T.C.M., Matser, A.M., Maund, S.J., Van den Brink, P.J., 2004. Comparison of laboratory single species and field population-level effects of the pyrethroid insecticide lambda-cyhalothrin on freshwater invertebrates. *Archives of Environmental Contamination and Toxicology* 46, 324–335.
- Schulz, R., Moore, M.T., Bennett, E.R., Farris, J.L., Smith Jr., S., Cooper, C.M., 2003a. Methyl parathion toxicity in vegetated and non-vegetated wetland mesocosms. *Environmental Toxicology & Chemistry* 22, 1262–1268.
- Schulz, R., Moore, M.T., Bennett, E.R., Milam, C.D., Bouldin, J.L., Farris, J.L., Smith Jr., S., Cooper, C.M., 2003b. Acute toxicity of methyl parathion in wetland mesocosms: assessing the influence of aquatic plants using laboratory testing with *Hyalella azteca*. *Archives of Environmental Contamination and Toxicology* 45, 331–336.
- Schulz, R., 2004. Field studies on exposure, effects, and risk mitigation of aquatic non-point source insecticide pollution: a review. *Journal of Environmental Quality* 33, 419–448.
- Sherrard, R.M., Berr, J.S., Murray-Gulde, C.L., Rodgers Jr., J.H., Shah, Y.T., 2004. Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures. *Environmental Pollution* 127, 385–394.
- Tomlin, C. (Ed.), 1997. *The Pesticide Manual*, 11th ed. British Crop Protection Council.

- USDA, 2004. National Agricultural Statistics Service (NASS) usage search. Available from: <http://www.pestmanagement.info/nass/app_usage.cfm>.
- USEPA, 2004. 2000–2001 Pesticide sales and usage report. Available from: <<http://www.epa.gov/oppbead1/pesticidesales/01pestsales/usage2001.html>>.
- USEPA, 2007. Available from: <http://iaspub.epa.gov/waters/national_rept_control>.
- Van Wijngaarden, R.P.A., Brock, T.C.M., van den Brink, P.J., Gylstra, R., Maund, S.J., 2006. Ecological effects of spring and late summer applications of lambda-cyhalothrin on freshwater microcosms. *Archives of Environmental Contamination and Toxicology* 50, 220–239.
- Wauchope, R.D., 1978. The pesticide content of surface water draining from agricultural fields: a review. *Journal of Environmental Quality* 7, 459–472.
- Weaver, M.A., Zablotowicz, R.M., 2004. Microbial indicators of wetland succession. In: *Agronomy Society of America Annual Meeting Abstracts*, Seattle, WA.
- Weaver, M.A., Zablotowicz, R.M., Locke, M.A., 2004. Laboratory assessment of atrazine and fluometuron degradation in soils from a constructed wetland. *Chemosphere* 57, 853–862.
- Wolverton, B.C., Harrison, D.D., 1973. Aquatic plants for the removal of mevinphos for the aquatic environment. *Journal of the Mississippi Academy of Sciences* 19, 84–88.