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Influence of Selected Water Quality Characteristics on the Toxicity of λ-Cyhalothrin and γ-Cyhalothrin to *Hyalella azteca*

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Abstract This study was conducted to assess the influence of suspended solids, dissolved organic carbon, and phytoplankton (as chlorophyll *a*) water quality characteristics on λ-cyhalothrin and γ-cyhalothrin aqueous toxicity to *Hyalella azteca* using natural water from 12 ponds and lakes in Mississippi, USA with varying water quality characteristics. *H. azteca* 48-h immobilization EC50 values ranged from 1.4 to 15.7 ng/L and 0.6 to 13.4 ng/L for λ-cyhalothrin and γ-cyhalothrin, respectively. For both pyrethroids, EC50 values linearly increased as turbidity, suspended solids, dissolved organic carbon and chlorophyll *a* concentrations increased.

Keywords λ-Cyhalothrin · γ-Cyhalothrin · Toxicity · Phytoplankton

Synthetic pyrethroid insecticides, such as λ-cyhalothrin, and the recently resolved active isomer, γ-cyhalothrin, are used to control insect pests of agricultural crops such as cotton, a major agricultural crop in Mississippi. These compounds' chemical and physical properties include relatively rapid degradation rates, low water solubility, and low vapor pressure allowing ready sorption to soil, sediment, plant, algae, detritus, suspended particulate matter and dissolved organic matter (Day 1991; Maund et al. 1998; Leistra et al. 2003; Liu et al. 2004). While several laboratory studies have described the influence of suspended sediment in mitigating pyrethroid toxicity to non-target organisms in receiving waters (Maund et al. 1998, 2002; Yang et al. 2006a), fewer studies have described how non-sediment materials, such as dissolved organic carbon (DOC) and sestonic phytoplankton, may influence pyrethroid toxicity (Day 1991; Barry et al. 1995; Yang et al. 2006b). In addition, while laboratory aqueous λ-cyhalothrin toxicity has been extensively studied (Mokry and Hoagland 1990; Day 1991; Maund et al. 1998; Schroer et al. 2004), γ-cyhalothrin aqueous toxicity has not been as well assessed (Frederiksen et al. 2003).

The purpose of the current study was to examine the influence of four selected water quality characteristics: turbidity, suspended solids, DOC, and chlorophyll *a*, measured in field samples of natural Mississippi pond and lake water on the acute aqueous toxicity of two pyrethroids, λ-cyhalothrin and γ-cyhalothrin, to the freshwater amphipod, *Hyalella azteca*.

Materials and Methods

Unfiltered dilution water for all toxicity bioassays was collected from 12 ponds and lakes in northern Mississippi, USA from October to December 2006. Water samples were collected from ten ponds, varying from oligotrophic to hypertrophic according to Dodds (2002), located at the University of Mississippi Field Station (UMFS) in Lafayette County, Mississippi, USA (Table 1). One water sample was collected from Beasley Lake (eutrophic) in Sunflower County, Mississippi, USA, and one sample was collected from a Coldwater River Bendway (hypertrophic ephemeral oxbow lake) in Tunica County, Mississippi, USA (Table 1). Due to the extremely soft nature of the dilution water, all water samples were hardness adjusted to between 80 and 100 mg/L as $CaCO_3$ with sodium bicarbonate and calcium chloride. Selected water quality

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Table 1 Mean (SD) values of selected water quality characteristics from 12 northern Mississippi water bodies

Water body	Turbidity[a]	TSS (mg/L)	Chlorophyll *a* (μg/L)	DOC (mg/L)
UMFS pond 1	7.0 (0.3)	10 (6)	3.8 (2.5)	10.6 (2.4)
UMFS pond S-2	3.1 (0.2)	2 (1)	2.9 (1.7)	1.4 (0.2)
UMFS pond S-4	0.7 (0.2)	4 (3)	5.3 (2.5)	1.0 (0.2)
UMFS pond 92	6.6 (0.5)	13 (4)	35.9 (3.7)	16.7 (5.8)
UMFS pond 97	1.2 (0.5)	4 (2)	1.7 (1.7)	1.9 (0.2)
UMFS pond 98	16.0 (0.5	15 (5)	76.1 (2.3)	11.4 (3.7)
UMFS pond 146	3.5 (0.2)	5 (3)	3.0 (1.8)	2.7 (0.2)
UMFS pond 167	1.9 (0.2)	1 (1)	1.7 (1.2)	2.8 (0.4)
UMFS pond 179	2.0 (0.2)	6 (3)	1.2 (1.3)	5.3 (1.0)
UMFS Bramlett pond	1.4 (0.1)	2 (1)	5.6 (3.2)	1.7 (0.3)
Beasley lake	19.9 (0.6)	14 (7)	36.2 (2.1)	11.4 (1.8)
Coldwater bendway	67.2 (2.0)	79 (5)	102.0 (5.8)	32.9 (10.2)

TSS Total suspended solids, *DOC* dissolved organic carbon

[a] NTU

Table 2 Nominal and measured unfiltered stock concentrations, and percent (%) recoveries of λ-cyhalothrin (λ) and γ-cyhalothrin (γ)

Water body	Nominal (μg/L)		Measured (μg/L)		Recovery (%)	
	λ	γ	λ	γ	λ	γ
UMFS pond 1	6.0	6.0	2.4	2.0	40.8	34.1
UMFS pond S-2	3.0	1.5	1.4	0.8	47.9	50.4
UMFS pond S-4	3.0	0.75	0.9	0.2	31.1	30.8
UMFS pond 92	6.0	6.0	2.3	4.5	37.8	75.5
UMFS pond 97	6.0	6.0	2.4	2.0	40.8	34.1
UMFS pond 98	6.0	6.0	2.3	4.5	37.8	75.5
UMFS pond 146	6.0	6.0	4.5	3.9	75.8	65.6
UMFS pond 167	3.0	1.5	0.9	1.0	31.1	66.5
UMFS pond 179	6.0	6.0	4.5	3.9	75.8	65.6
UMFS Bramlett pond	3.0	1.5	1.4	0.8	47.9	50.4
Beasley lake	6.0	6.0	3.6	4.6	59.6	76.0
Coldwater bendway	6.0	6.0	3.6	4.6	59.6	76.0

parameters of turbidity, total suspended solids, dissolved organic carbon, and chlorophyll *a* were measured according to APHA (1998).

Technical grade emulsifiable concentrated pyrethroid insecticide stock solutions for toxicity bioassays were prepared by diluting KARATE^{TM} ZEON^{TM} (22.8% active ingredient λ-cyhalothrin) and GF317^{TM} (registered in USA as PROAXIS^{TM}; 5.9% active ingredient γ-cyhalothrin) in 0.8 L of unfiltered dilution water ranging from 0.75 to 6 μg/L. Aqueous nominal exposure concentrations ranged from 0.9 to 60 ng/L and 0.4 to 30 ng/L for λ-cyhalothrin and γ-cyhalothrin, respectively. All solutions were allowed to equilibrate for 24 h in darkness after pyrethroid amendment to allow sorption to suspended and dissolved constituents. Analysis was conducted on 13 0.8 L stock concentrations (six λ-cyhalothrin and seven γ-cyhalothrin samples) via a method similar to that of Bennett et al. (2000) and modified by Smith and Cooper (2004). A Hewlett-Packard 6890 gas chromatograph equipped with dual HP 7683 ALS autoinjectors was used. Upon collection, 0.8 L aliquot of aqueous samples were extracted by sonification with reagent-grade KCl and 80 mL pesticide-grade ethyl acetate, dried over anhydrous sodium sulfate, subjected to cleanup by silica gel column chromatography, and concentrated to 1 mL for analysis. Level of quantification for aqueous analysis was 0.01 μg/L. Mean extraction efficiencies based on fortified samples were >90%.

Standard laboratory 48-h static aqueous toxicity bioassays using *H. azteca* were conducted in a Powers Scientific Inc. incubator at 23 ± 1°C with a photoperiod of 16:8 light:dark (USEPA 1994) at the USDA-ARS National Sedimentation Laboratory (NSL), Oxford, Mississippi, USA. Animals passing through a 600 μm stainless steel mesh sieve but retained by a 425 μm stainless steel mesh sieve (approximately 1–2 weeks old) were collected for the experiment. Five *H. azteca* were placed in each of six replicate 87 mL polyethylene plastic test chambers per concentration with one 2 cm × 2 cm square sterile cotton gauze as substrate. After 48 h, immobilization was determined by the number of organisms floating at the water surface or not responding when gently prodded with forceps. Standard toxicity bioassay water quality parameters of water temperature, pH, conductivity, dissolved oxygen, alkalinity, and hardness were measured according to APHA (1998). All animals were cultured at the USDA-ARS NSL culturing facility following the methods and procedures of de March (1981).

H. azteca 48-h immobilization EC50 values were calculated using Probit analysis when data met parametric assumptions and trimmed Spearman–Karber analysis was used for non-parametric data (APHA 1998). Linear regression analysis was performed on pyrethroid EC50 values versus each of the four selected water quality characteristics (Steel et al. 1997).

Results and Discussion

Average percent recoveries of unfiltered stock solutions for λ-cyhalothrin and γ-cyhalothrin were 48.8% ± 16.4% and 57.0% ± 18.8%, respectively and ranged from 31.1% to 75.8% and 30.8% to 76.0%, respectively (Table 2). Although values appear low, solutions were held for 24 h prior within glass containers to initiation of bioassays to maximize sorption of the test chemicals to available

Table 3 Measured aqueous 48 h *Hyalella azteca* immobilization EC50 values (95% confidence intervals) of pyrethroid amended water

Water body	λ-Cyhalothrin (ng/L)	γ-Cyhalothrin (ng/L)
UMFS pond 1	2.8 (2.0–3.8)	1.5 (1.1–1.9)
UMFS pond S-2	1.7 (1.3–2.2)	1.2 (0.9–1.5)
UMFS pond S-4	2.4 (1.8–3.1)	1.1 (0.8–1.4)
UMFS pond 92	10.4 (8.3–13.6)	5.4 (4.4–6.6)
UMFS pond 97	1.5 (1.1–1.9)	0.6 (0.4–0.9)
UMFS pond 98	7.4 (5.9–9.2)	5.7 (4.4–7.4)
UMFS pond 146	3.9 (3.0–4.9)	2.0 (1.5–2.6)
UMFS pond 167	1.4 (1.1–1.8)	1.0 (0.7–1.3)
UMFS pond 179	3.6 (2.8–4.5)	1.1 (0.9–1.5)
UMFS Bramlett pond	2.2 (1.7–2.8)	1.1 (0.9–1.4)
Beasley lake	11.1 (8.7–14.3)	6.0 (4.7–7.6)
Coldwater bendway	15.7 (12.5–19.7)	13.4 (10.1–17.8)

aqueous matrix components. Maund et al. (1998) described both the rapid rate of λ-cyhalothrin degradation, approximately 50% within 24 h, and the rapid rate of sorption to hydrophobic and organic compounds, approximately 90% within 12–24 h. In addition, Wheelock et al. (2005) reported how pyrethroids readily sorb to walls of glass containers.

Mean standard water quality parameters assessed during all bioassays were within accepted limits for hardness-adjusted water (dissolved oxygen 7.7 mg/L; pH 8.0; conductivity 360 μmhos/cm; hardness 93 mg/L as $CaCO_3$; alkalinity 55 mg/L as $CaCO_3$) according to USEPA acute reference toxicity tests for *H. azteca* (USEPA 1994). Average 48-h *H. azteca* dilution water control survival/mobility was 99% ± 1% for both λ-cyhalothrin and γ-cyhalothrin bioassays. *H. azteca* measured EC50 values ranged from 1.4 to 15.7 ng/L and 0.6 to 13.4 ng/L for λ-cyhalothrin and γ-cyhalothrin, respectively (Table 3). Based on these data, γ-cyhalothrin was found to be about 1.9 times more toxic to *H. azteca* than λ-cyhalothrin. Amphipods, such as *H. azteca*, are among the most sensitive species to pyrethroids and are about 100 fold more sensitive to λ-cyhalothrin than the more commonly tested crustacean, *Daphnia magna* (Maund et al. 1998). Significant λ-cyhalothrin toxicity data exists for a wide diversity of aquatic invertebrates (Maund et al. 1998; Schroer et al. 2004) and Schroer et al. (2004) lowest reported 48-h EC50 value was 2.3 (1.8–4.1) ng/L for *H. azteca*. This study reports a lowest 48-h λ-cyhalothrin measured EC50 of 1.4 (1.1–1.8) ng/L for the same species, however, several measured EC50 values ranging from 1.7 to 3.9 ng/L are similar to those reported by Schroer et al. (2004). Much less literature exists on toxicity of γ-cyhalothrin to aquatic organisms. Frederiksen et al. (2003) reported an emusifiable concentrate formulation 48-h EC50 of 100 ng γ-cyhalothrin/L for *D. magna*. Our study reported *H. azteca* 48-h γ-cyhalothrin measured EC50 values from 0.6 to 13.4 ng/L with most values around 1 ng/L. This agrees with Maund et al. (1998) assertion that *H. azteca* is about 100-fold more sensitive to cyhalothrin than *D. magna*.

Dilution water quality had a significant influence on pyrethroid toxicity. Linear regression analyses for λ-cyhalothrin showed significant relationships between EC50 values and measured water parameters, turbidity

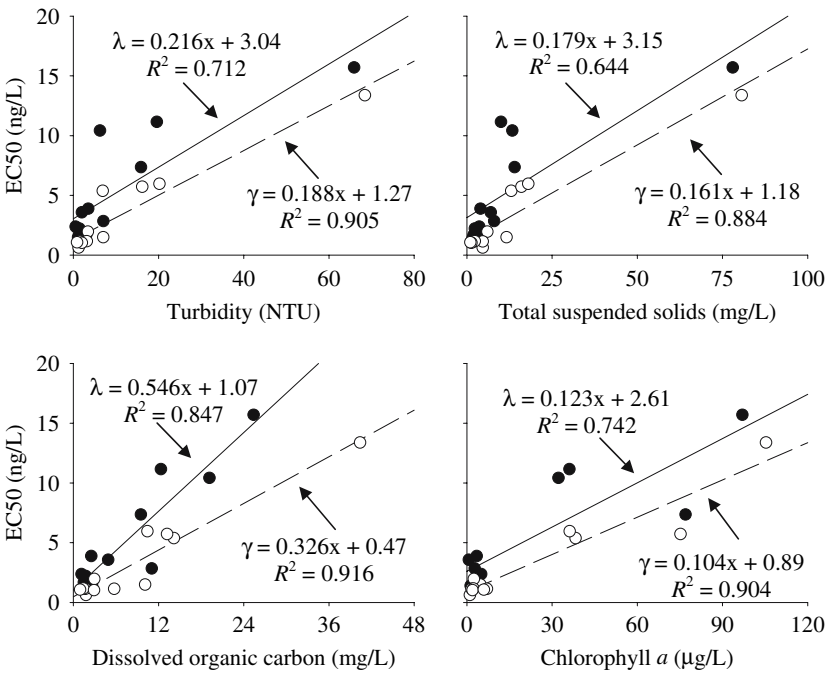

Fig. 1 Relationships between λ-cyhalothrin (λ, *closed circle*) and γ-cyhalothrin (γ, *open circle*) aqueous 48-h *Hyalella azteca* measured EC50 values versus four selected water quality characteristics measured from 12 Mississippi water bodies

($R^2 = 0.712$, $F = 24.7$, $p = 0.0006$), suspended solids ($R^2 = 0.644$, $F = 18.1$, $p = 0.0017$), DOC ($R^2 = 0.847$, $F = 55.3$, $p < 0.0001$), and chlorophyll *a* ($R^2 = 0.742$, $F = 28.7$, $p = 0.0003$) as shown in Fig. 1. For γ-cyhalothrin, significant relationships between EC50 values and turbidity ($R^2 = 0.905$, $F = 95.5$, $p < 0.0001$), suspended solids ($R^2 = 0.884$, $F = 76.4$, $p < 0.0001$), DOC ($R^2 = 0.916$, $F = 109.3$, $p < 0.0001$), and chlorophyll *a* ($R^2 = 0.904$, $F = 94.3$, $p < 0.0001$) were also observed (Fig. 1). In this study, turbidity and suspended solids are associated with phytoplankton density and not sediment due to regional climate conditions (Smith and Cooper 2004). DOC was observed by Day (1991) to decrease λ-cyhalothrin toxicity to *D. magna* by almost 2-fold. The current study, controlling for phytoplankton (chlorophyll *a*), showed DOC to similarly decrease both λ-cyhalothrin and γ-cyhalothrin toxicity to *H. azteca* by 2–2.5-fold, respectively. Influence of phytoplankton (as chlorophyll *a*) on pyrethroid toxicity was apparent. Barry et al. (1995) reported a decrease in pyrethroid (esfenvalerate) toxicity to *Daphnia carinata* with an increase in algal density. The present study, controlling for DOC, showed phytoplankton (chlorophyll *a*) to similarly decrease both λ-cyhalothrin and γ-cyhalothrin toxicity to *H. azteca* by 4-fold.

Under current study conditions, turbidity, suspended sediment, DOC and chlorophyll *a* concentrations can be used to determine the toxicity of both λ-cyhalothrin and γ-cyhalothrin to *H. azteca*. In addition, this study shows that interaction of increased DOC and phytoplankton (as chlorophyll *a*) decreases toxicity of both pyrethroids to *H. azteca* by more than 10-fold. Such results emphasize the importance of measuring these components when assessing pyrethroid toxicity to aquatic organisms.

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