

Chemical Residence Time and Hydrological Conditions Influence Treatment of Fipronil in Vegetated Aquatic Mesocosms

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Fipronil, a phenyl-pyrazole insecticide, is often used in rice (*Oryza sativa* L.) production agriculture, with elevated runoff concentrations and loads having potential toxicological effects on downstream aquatic environments. This study evaluated two species of aquatic plants—broadleaf cattail (*Typha latifolia* L.) and powdery alligator-flag (*Thalia dealbata* Fraser ex Roscoe)—placed in series against a nonvegetated mesocosm in reducing concentrations and loads of fipronil, and associated metabolites. Vegetation type and hydrological condition (inundated vs. dry) were treatment effects used for comparison. The vegetated mesocosms significantly reduced higher loads and concentrations of fipronil, fipronil sulfone, and sulfide in both inundated and dry hydrological conditions over nonvegetated mesocosms. Under inundation conditions, vegetated mesocosms reduced >50% of influent fipronil concentrations and between 60 and 70% of fipronil loads, which was significantly higher than the dry conditions (10–32% concentration and load). These results show that agricultural management strategies using ephemeral aquatic zones, such as drainage ditches, can be optimized to couple chemical applications with vegetation presence and hydrology to facilitate the reduction in chemical waste loads entering downstream aquatic ecosystems. Such reduction is critical for use with fipronil, where negative impacts have been demonstrated with several nontarget species.

FIPRONIL, a phenyl-pyrazole insecticide, is gaining increased popularity in effective insect control as a result of enforced cancellations by USEPA of many organophosphate insecticides (Overmyer et al., 2005). Fipronil, with its specificity in γ -aminobutyric acid receptor inhibition, is considered a safer option than traditional organophosphates because of higher target specificity, its unique action mechanism, and low mammalian toxicity (Gant et al., 1998). Fipronil is the active ingredient in typical commercial products such as Icon (coated rice seed), Frontline Topspot (flea treatment), Over'n Out (fire ant control), Chipco Topchoice (mole cricket control on golf courses), and Termidor (termite treatment).

Surface water contamination in areas where fipronil is actively used has the potential to significantly impact nontarget aquatic organisms. Examples of toxicity to nontarget organisms include grass shrimp (Wirth et al., 2004), estuarine copepods (Cary et al., 2004; Chandler et al., 2004), crayfish (Schlenk et al., 2001), and common cladocerans (Stark and Vargas, 2005).

In production agriculture, fipronil is typically associated with Icon-coated rice seeds, which is often aerially seeded. Fipronil is usually used to reduce the impact of rice pests, such as rice water weevil, rice stinkbug, and fall army worms. Typically, double cropping of crawfish and rice (*Oryza sativa* L.) (harvest separated temporally) leads to potential toxicological effects of fipronil to crawfish (Lutz, 2000). Another environmental concern, however, is that often rice fields are drained with effluents moving through drainage ditches into downstream aquatic environments. Depending on timing and seed applications, fipronil concentrations and loads can vary in runoff effluent. Biever et al. (2003) showed an average of $8 \mu\text{g L}^{-1}$ fipronil residue in drainage ditches below fipronil-treated rice fields in southern Louisiana. This concentration is important, as it is significantly higher than the LC_{50} concentrations for estuarine copepods ($0.7 \mu\text{g L}^{-1}$, Cary et al., 2004; $3.5\text{--}6.8 \mu\text{g L}^{-1}$, Chandler et al., 2004) and falls in the lower limit of acute LC_{50} concentrations for common cladoceran *Daphnia pulex* ($8.8 \mu\text{g L}^{-1}$).

Kröger and Moore (2008) examined the potential of using obligate wetland vegetation to mitigate the impact of fipronil, with no differences in load or concentration reductions occurring among species. Reductions were not significant among

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Abbreviations: CRT, chemical retention time; DO, dissolved oxygen; G–G, Greenhouse–Geisser; H–F, Huyn–Feldt; NV, nonvegetated; UHP, ultrahigh pure; V, vegetated.

monoculture communities of all species studied by Kröger and Moore (2008). However, percent in situ reductions between two species varied enough to spark additional study. Specifically, we wanted to determine if stand-alone and mixed broadleaf cattail (*Typha latifolia* L.) and powdery alligator-flag (*Thalia dealbata* Fraser ex Roscoe) communities can reduce higher fipronil concentrations if water residence times are increased from 3 to 6 h, as suggested by management entities. The primary objective of this study was to determine if there was a difference between how vegetated (*T. latifolia* and *T. dealbata*) and nonvegetated mesocosms under increased residence times reduce fipronil and associated degradate metabolites (sulfone, sulfide, and desulfinyl) from a simulated agricultural runoff solution. A secondary objective was to assess the effects of hydrological condition (inundated vs. dry) on vegetated fipronil and metabolite reductions.

Materials and Methods

Study Setup

Plants

Two experiments were performed, 2 wk apart, in June 2008, to determine the effects of hydrological conditions (inundated vs. dry) on mitigation of fipronil and associated degradate metabolites between vegetated and nonvegetated mesocosms. Each experiment had identical experimental designs. There were six vegetated and two nonvegetated units (Fig. 1) per experiment. The vegetated unit consisted of an upper mesocosm planted monospecifically in *Typha latifolia* L., connected to a lower mesocosm planted monospecifically with *Thalia dealbata* Fraser ex Roscoe (Fig. 1). *Typha latifolia* and *T. dealbata* are classified as obligate wetland species in the southeast region of the United States (USEPA region IV) and are common in constructed wetlands and agricultural drainage ditches. The nonvegetated units consisted of upper and lower mesocosms devoid of vegetation.

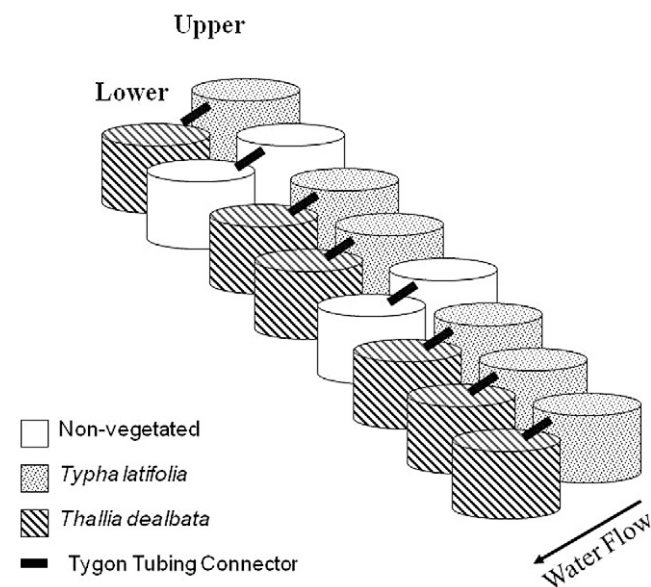


Fig. 1. The connected experimental design with two sets (upper and lower) of halved, 209-L mesocosms. Upper units were planted with *Typha latifolia*, whereas lower units were planted with *Thalia dealbata*. Blank units represent the nonvegetated mesocosms.

All upper mesocosm outflows were 15 cm above the lower mesocosms. For both vegetated and nonvegetated units, the mixing chamber, upper mesocosm, and lower mesocosm were independently plumbed and connected with clear, Tygon plastic tubing (Saint-Gobain Performance Plastics, Garden Grove, CA).

Mesocosms

Halved, 209-L polycarbonate storage drums were used to house both vegetated and nonvegetated mesocosms. Mesocosm containers had an average height of 46.0 ± 0.3 cm, an average internal diameter of 56.3 ± 0.4 cm, and were spaced approximately 20 cm apart. Each mesocosm was filled with a sand-base substrate and overlaid with 5 to 10 cm of wetland soils from the University of Mississippi Field Station, Abbeville, MS. Plant stands were grown for 2 yr to achieve field replicate density levels. Average plant stem densities per square meter for *T. latifolia* and *T. dealbata* were 49 ± 5 (19 ± 5 alive) and 38 ± 2 (24 ± 2 alive) m^{-2} , respectively. Units were grown outside and exposed to natural light cycles and typical temperature conditions for the southern regions of the United States.

Fipronil Application

Fipronil (Regent 4SC, BASF, Research Triangle Park, NC) concentrations were delivered at $5 \mu g L^{-1}$ per treatment replicate. This application represented a typical stormwater runoff scenario of 0.1% of the total insecticide application for a hypothetical rice farm of 32 ha. Each unit pair was amended according to a calculated 6-h chemical retention time (CRT) (3 h upper and 3 h lower). The application, however, was delivered for 8 h to simulate overloading of the CRT. The CRT was increased based on a previous study by Kröger and Moore (2008), as well as on the aqueous half-life of fipronil when exposed to light (3.6 h) (Tingle et al., 2003). The fipronil application was premixed in large, 209-L polycarbonate storage drums (termed, mixing chambers) and delivered to each upper mesocosm using Fluid Metering Inc. (Syosset, NY) laboratory pumps, model QD-1 (flow range of $0-552 mL min^{-1}$) and QD-2 (flow range of $0-1242 mL min^{-1}$), at a calculated rate specific to each mesocosm (range of $254-654 mL min^{-1}$). Although unknown, the influence of tubing, mixing chambers, and 209-L drums on fipronil adherence was assumed consistent among all replicates. Future efforts are working toward quantifying rate of dose loss due to adherence.

Sampling Strategy

Preapplication samples of water were taken from the outflows of each mesocosm. The inundated tubs were at maximum retention capacity as the application was initiated. For the dry experiment, all water was removed from the mesocosms; therefore, there were no effluent background samples. Water samples were taken from each mixing chamber before the application to assess baseline fipronil and metabolite concentrations entering each treatment replicate. Water samples were collected in 1-L amber glass jars with Teflon-lined screw caps every hour for 8 h from the lower outflow in the inundated experiment. For the dry experiment, water samples were taken from the upper outflows from 3 through 8 h and taken out of the lower outflows at 6, 7, and 8 h. Water quality characteristics of pH, dissolved oxygen (DO), and water temperature were taken within every unit, at each sampling time, for upper and lower mesocosms,

for both inundated and dry experiments. The pH was measured with a pH Testr 2 (Oakton Instruments, Vernon Hills, IL), whereas DO and water temperature were recorded using a YSI-85 conductivity meter (Yellow Springs Instruments, Yellow Springs, OH).

Pesticide Analysis

Water samples (500 mL), once collected, were immediately fixed onsite in the pesticide analysis laboratory with approximately 2 g reagent-grade KCl and 100 mL distilled reagent-grade ethyl acetate. Pesticide extraction involved sonification (1 min/pulse mode/80% duty cycle), partitioning in a separatory funnel, silica gel column chromatography cleanup, and concentration of the sample to 1 mL under ultrahigh pure (UHP) nitrogen (Bennett et al., 2000; Smith and Cooper, 2004; Kröger and Moore, 2008). Recoveries of fortified pesticide samples were >95% for fipronil and its metabolites.

Pesticide analysis was conducted on an Agilent Technologies (Santa Clara, CA) model 7890A gas chromatograph, equipped with Agilent 7683B ALS autoinjector, dual-capillary columns, equipped with an Agilent Chemstation fitted with two Agilent microelectron capture detectors (μ ECD) for fipronil, and its three dominant degradative metabolites—fipronil desulfinyl, fipronil sulfide, and fipronil sulfone. The main analytical column was a HP 5MS (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness), with a μ ECD temperature of 325°C and a UHP nitrogen makeup gas flow of 40 mL min⁻¹. The carrier gas was UHP helium at 28 cm s⁻¹ average velocity at 250°C (Smith et al., 2006). The autoinjector furnished 1.0 μ L into the capillary column for each sample. Retention times on the gas chromatographs were as follows: 20.139 min fipronil desulfinyl, 27.756 min fipronil sulfide, 28.222 min fipronil, and 31.242 min fipronil sulfone. All samples were analyzed against a multilevel standard calibration (0.1 and 1 μ g mL⁻¹), updated every 10th sample.

Statistics

Each hydrological experiment (dry and inundated) was analyzed independently. Fipronil concentrations multiplied by water volume provided load estimates for each application for each system. Shapiro–Wilks W test was used to test for normality in the datasets. If the data distributions were non-normal, percent data were arcsine transformed to fit the normality assumption of repeated measures ANOVA. Repeated measures ANOVA described significant differences between vegetated and nonvegetated mesocosms through time for each hydrological circumstance. In JMP 8.1 (SAS Institute, 2008), a MANOVA Model was fit using time and treatments (vegetated and nonvegetated) as effects. The univariate repeated measures ANOVA ($\alpha = 0.05$) output generated differences among time and time \times treatment interactions among treatments. Within the univariate repeated measures output, the Mauchly's sphericity or compound symmetry result was examined. The conditions established a priori for sphericity were that the variances of the response variable (i.e., percentage reductions) were the same at each time point, and second, the correlation between repeated measurements are equal, regardless of the time interval between measurements. If conditions for compound symmetry were not met (i.e., $P \leq 0.05$), then

both the Greenhouse–Geisser (G–G) Epsilon and Huyn–Feldt (H–F) Epsilon methods were used to adjust for lack of sphericity. Only the G–G Epsilon values are reported as probability results were similar between G–G and H–F.

Results

Physicochemical Characteristics

Temperature (°C) (Fig. 2A), DO (mg L⁻¹) (Fig. 2B), and pH (Fig. 2C) varied with hydrological circumstance and temporally within vegetated and nonvegetated mesocosms. The DO concentrations typically increased as the experiment progressed throughout the day when mesocosms were completely inundated but not when dry (Fig. 2B). Interestingly,

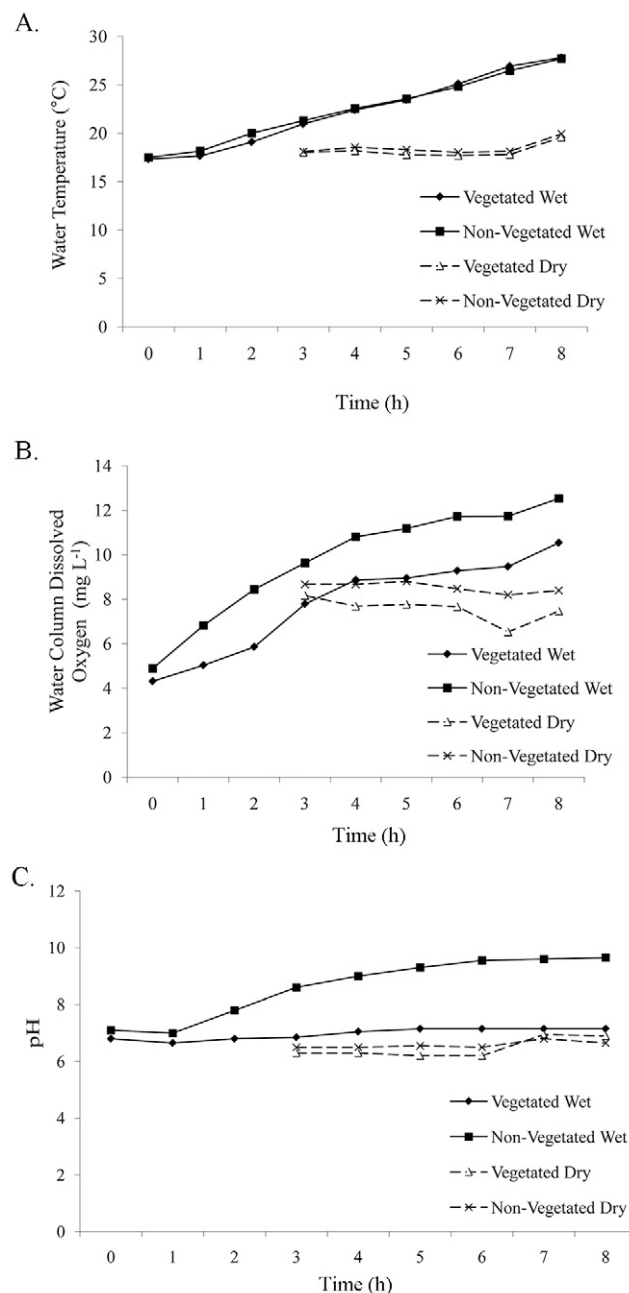


Fig. 2. Temporal changes in (A) water temperature, (B) dissolved oxygen, and (C) pH among vegetated and nonvegetated mesocosms for both inundated and dry experiments.

the nonvegetated mesocosms in both inundated and dry experiments had significantly higher DO concentrations throughout the experiment's duration than vegetated mesocosms. Similarly, pH was also significantly higher in nonvegetated mesocosms (pooled data between both hydrological experiments; ANOVA, $F_{3,38} = 28.8$; $P \leq 0.001$). Overall, the nonvegetated inundated treatment had significantly higher pH over the duration of the experiment than either vegetated inundated and dry, and nonvegetated dry.

Fipronil and Metabolite Reduction—Inundated

Both vegetated (V) and nonvegetated (NV) mesocosms had >50% reduction in concentration ($\mu\text{g L}^{-1}$) and load (μg) for fipronil, fipronil sulfone, and fipronil sulfide. The vegetated mesocosms had higher mean (\pm standard deviation) reductions of fipronil sulfide (V: $66\% \pm 3$; NV: $54\% \pm 5$; MANOVA G-G $\epsilon = 0.393$; $P = 0.14$), fipronil (V: $61\% \pm 2$; NV: $51\% \pm 4$; G-G time $\epsilon = 0.376$; $P < 0.001$; time \times treatment $P = 0.03$), and fipronil sulfone (V: $61\% \pm 3$; NV: $42\% \pm 8$; G-G $\epsilon = 0.419$; time $P \leq 0.001$; time \times treatment $P = 0.04$) concentrations. Load reductions had similar reduction capacities. Through unforeseen circumstances, hydrological fluxes occurred in one replicate (Tub 8), skewing load output. A Mahalanobis Outlier distance plot confirmed Tub 8 (V) as an outlier and thus was removed from the load analyses. The *Typha/Thalia* vegetated-connected combination reduced a significantly larger percent of fipronil sulfone (Fig. 3A) (V: $67\% \pm 5$; NV: $52\% \pm 9$; $P = 0.04$) than nonvegetated mesocosms. Similarly, for the parent compound fipronil, the vegetated mesocosms reduced loads by $70\% \pm 2$, which was significantly greater (MANOVA G-G $\epsilon = 0.248$; time $P = 0.005$; time \times treatment $P = 0.02$) than $60\% \pm 5$ of nonvegetated mesocosms (Fig. 3B). There was no difference in fipronil sulfide (V: $73\% \pm 4.1$; NV: $66\% \pm 9.3$; $P = 0.499$) load reductions between vegetated and nonvegetated mesocosms (Fig. 3C).

Fipronil and Metabolite Reduction—Dry

In all samples analyzed, the vegetated mesocosm (both *Typha* upper and *Thalia* lower components) reduced a higher percent of fipronil and associated metabolite concentrations than nonvegetated mesocosms (Table 1). Overall, the vegetated mesocosms reduced significantly higher concentrations of fipronil sulfide (V: $22\% \pm 10$; NV: $-7\% \pm 12$; MANOVA G-G $\epsilon = 0.421$; time $P = 0.03$; time \times treatment $P = 0.0017$), fipronil sulfone (V: $18\% \pm 7$; NV: $-25\% \pm 9$; G-G $\epsilon = 0.408$; time $P = 0.01$; time \times treatment $P = 0.007$), and fipronil (V: $32\% \pm 5$; NV: $18\% \pm 8$; G-G $\epsilon = 0.52$; time and time \times treatment $P \leq 0.05$) (Table 1).

Figures 4A, B, and C describe the differences in inflow and outflow loads among the respective upper and lower vegetated and nonvegetated mesocosms. Percent differences for the respective upper and lower mesocosm treatments were summed over time for comparison. Fipronil sulfone outflow loads (Fig. 4A) were reduced in a similar capacity from inflow loads for both *Typha*-upper ($51\% \pm 2$) and *Thalia*-lower ($52\% \pm 2$). Fipronil sulfone load reduction was lower in the upper nonveg-

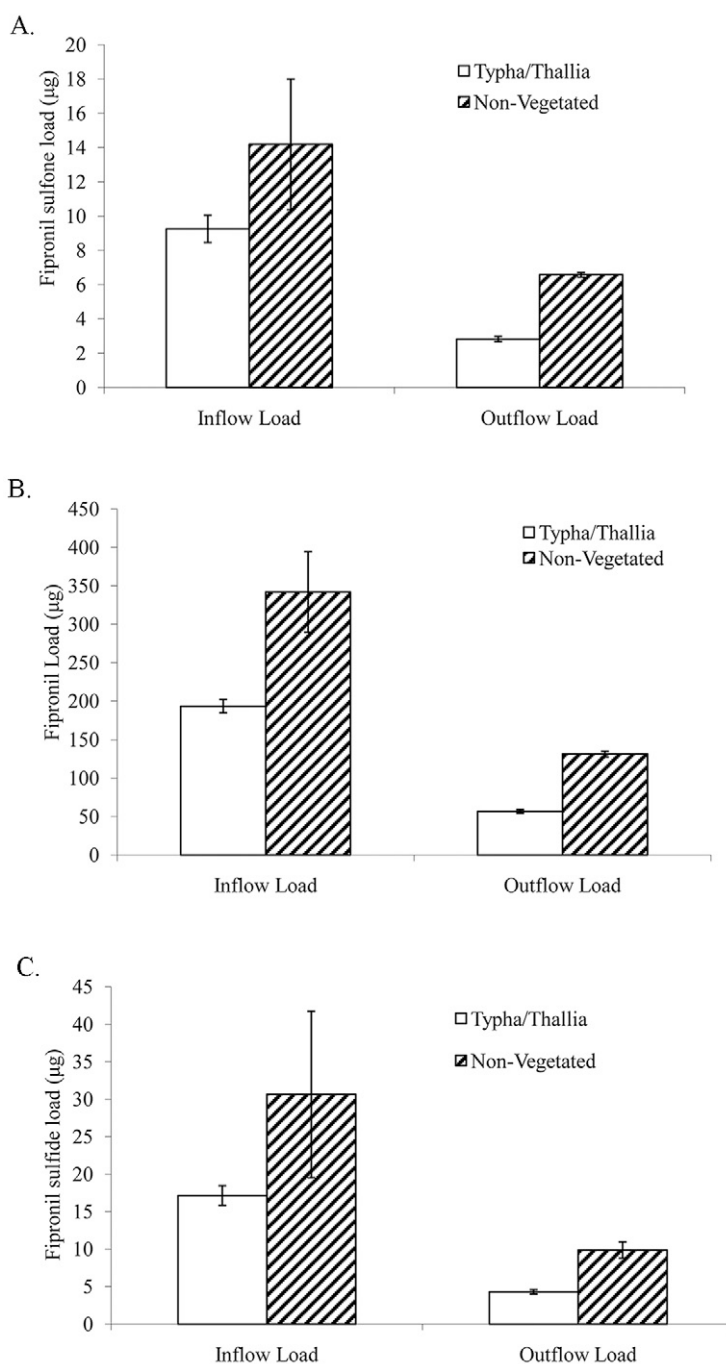


Fig. 3. Changes in inflow and outflow loads of (A) fipronil sulfone, (B) fipronil, and (C) fipronil sulfide for both vegetated and nonvegetated mesocosms for the inundated experiment. Fipronil desulfinyl concentrations and loads were negligible for all replicates.

etated ($26\% \pm 5.1$) than in the lower nonvegetated counterpart ($61\% \pm 1.9$). For fipronil (Fig. 4B) and fipronil sulfide (Fig. 4C), the lower vegetated mesocosm had greater percent reductions in both fipronil (64% *Thalia* vs. 53% *Typha*) and fipronil sulfide (67% *Thalia* vs. 43% *Typha*) than the upper. The upper vegetated mesocosm demonstrated higher fipronil (53% *Typha* vs. 42% Upper NV) and fipronil sulfide (43% *Typha* vs. 37% Upper NV) load reductions. *Thalia* and lower nonvegetated mesocosms had very similar percent reductions for fipronil (64 and 68% , respectively) (Fig. 4B) and fipronil sulfide (67 and 66% , respectively) (Fig. 4C) loads.

Fipronil desulfinyl, a metabolite known to be more toxic than the parent fipronil compound, was not detected in the mixing chambers for either inundated or dry experiments. The only detection of fipronil desulfinyl was post the 8-h amendment at 48 and 168 h. Even then, the concentrations never were $>0.04 \mu\text{g L}^{-1}$. There were no significant differences among outflow concentrations and loads for fipronil desulfinyl between vegetated and nonvegetated mesocosms, and between inundated and dry experiments as desulfinyl metabolite generation was extremely low. For the majority (noted exception was the nonvegetated fipronil sulfone and fipronil loads in the inundated experiment where significant decreases in reduction occurred), all concentration and load reductions for fipronil and generated metabolites were stable and did not significantly increase or decrease post the 6-h CRT (i.e., 6–8 h) as analyzed by Pearson correlations for reduction by time for each treatment ($0.00015 < r^2 < 0.449$; 0.106 ± 0.132). Interestingly, there were no significant differences in line slopes between experiment initiation and 6-h CRT, and post the 6-h CRT in the dry experiment ($r^2 = 0.05$; $P = 0.75$), whereas there were significant differences in pre- and post-6-hr CRT in the inundated experiment.

Discussion

The use of aquatic systems to reduce pollutant concentrations and loads is well known (Perry and Kleinmann, 1991; Greenway and Woolley, 1999; Casey and Klaine, 2001; Coleman et al., 2001; Maltais-Landry et al., 2009). Less is known about using aquatic systems associated with agriculture, namely drainage ditches, as nonpoint source remediation tools (Moore et al., 2001a; Moore et al., 2001b; Moore et al., 2005; Kröger et al., 2007a, 2008b). Fipronil concentrations and loads are of concern leaving agricultural landscapes. Fipronil (and thus, degrade metabolites sulfone, sulfide, and desulfinyl) is often used in or near aquatic environments, and typically in agriculture associated with rice production (Stehr et al., 2006). Cary et al. (2004) demonstrated small concentrations ($<2 \mu\text{g L}^{-1}$) of fipronil had significant effects on reproductive traits of copepods, with the study measuring fipronil concentrations as high as $5.8 \mu\text{g L}^{-1}$ leaving fipronil-treated rice fields in southern Louisiana. Fipronil use against larval culicine and chironomid midge species has also been suggested to have toxic effects on nontarget organisms in adjacent aquatic environments (Key et al., 2003; Shan et al., 2003; Wirth et al., 2004; Stark and Vargas, 2005). Earlier efforts by Kröger and Moore (2008) described the ability of various species of emergent wetland plant species in fipronil and fipronil sulfone concentration, and load reductions in aquatic systems. Results for that study highlighted no

trends or differences in fipronil reduction for all plant species and a nonvegetated control.

The results between vegetated and nonvegetated units in the current study highlighted, irrespective of hydrological circumstance, that a doubling of CRT (from 3 to 6 h) resulted in vegetated, multispecies mesocosms having statistically significantly higher reductions ($P \leq 0.05$) in fipronil, fipronil sulfone, and fipronil sulfide than a nonvegetated mesocosm. *Typha latifolia* and *T. dealbata* were investigated in series to begin to mimic a natural drainage ditch community. Drainage ditches are often dominated by several emergent wetland plant species occurring randomly and longitudinally within the ditch. This experiment provides a greater ecological dimension to reduction/mitigation process than single monospecific type experiments undertaken to date.

If the treatments were evaluated by hydrological circumstance, inundated and dry effects resulted in higher and lower reduction potentials, respectively, for the vegetated and nonvegetated mesocosms. When evaluated as a dry experiment, the vegetated and nonvegetated mesocosms reduced fipronil and metabolites between 18 and 32%. The lack of dilution is hypothesized to have played a role in lower than expected reductions of fipronil, as noted by differences in the slopes of linear regressions from pre- and post-6-h CRT. Interestingly, in the inundated experiment, when the chemical residence time was doubled from 3 to 6 h, the vegetated treatments showed significantly higher ($>50\%$ in concentration, and between 60 and 70% in load) reductions in fipronil. The increased chemical residence time was hypothesized and suggested by Kröger and Moore (2008) to increase biological degradation and improve the oxidizing hydrosphere for fipronil degradation. Such an increase in residence time, however, has very applied consequences. Research in agricultural management has moved to investigate innovative controlled drainage management practices for improving water residence in drainage ditches and thus, potentially, optimizing nonpoint source mitigation. Kröger, Cooper, and Moore (2008a) published data on the use of low-grade weirs as a new management practice for improved residence times in drainage ditches. By incorporating these weirs into drainage ditches actively receiving fipronil runoff, the chemical residence time of the system can increase and improve the ability of the aquatic system to reduce fipronil concentrations and loads.

Destructive vegetation management of drainage ditches (i.e., clear scraping, herbicide applications) often occurs by farmers in lieu of improving drainage function and maintaining neat agricultural landscapes. The results from the current study showed that the occurrence and presence of vegetation

Table 1. Percent concentration ($\mu\text{g L}^{-1}$) reduction between vegetated and nonvegetated mesocosms for the dry experiment for fipronil, fipronil sulfone, and fipronil sulfide.

	Upper mesocosm				Lower mesocosm			
	<i>Typha latifolia</i>		Nonvegetated		<i>Thalia dealbata</i>		Nonvegetated	
	Mean	SE†	Mean	SE	Mean	SE	Mean	SE
	%		%		%		%	
Fipronil	21.2	3.13	8.6	6.12	14.9	3.85	14.7	1.15
Fipronil sulfone	17.5	4.96	−14.2	8.87	−2.4	5.60	−4.5	3.60
Fipronil sulfide	5.1	9.34	−2.8	4.00	15.9	11.91	3.4	10.12

† SE, standard error.

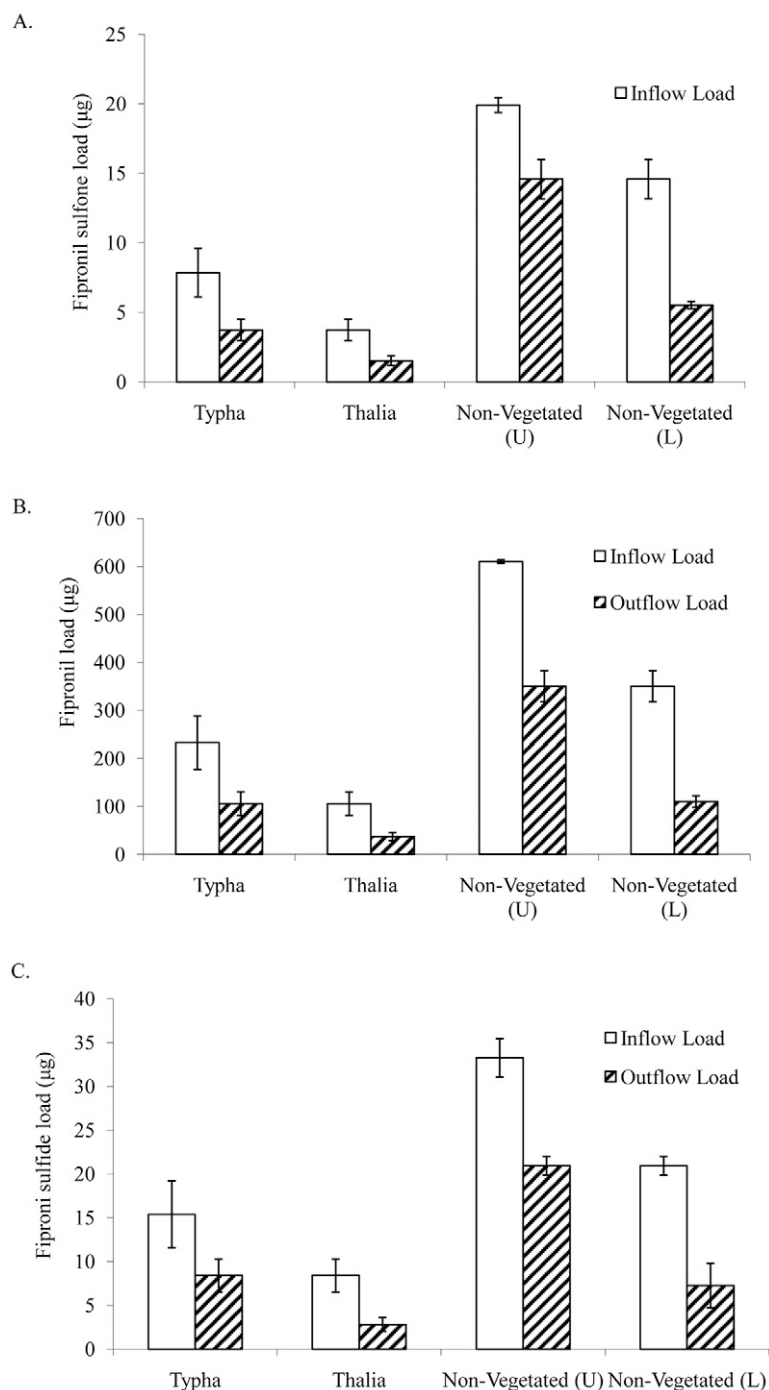


Fig. 4. Changes in inflow and outflow loads for (A) fipronil sulfone, (B) fipronil, and (C) fipronil sulfide for each vegetation type (*Typha* and *Thalia*), as well as both upper and lower nonvegetated mesocosms for the dry experiment. Fipronil desulfinyl concentrations and loads were negligible for all replicates.

within the drainage system, as well as the increase in chemical residence time (i.e., behind weirs in ditches), improved fipronil and degradate metabolite mitigation. Effectiveness of vegetation in mitigation of contaminants is not limited to organic compounds. Inorganic compounds, specifically nutrients, have shown the capability of being phytoremediated via aquatic vegetation (Gottschall et al., 2007; Iamchaturapatr et al., 2007; Kröger et al., 2007b).

The added pollutant remediation benefit from the presence of aquatic vegetation and increased CRT is hypothesized

as twofold: (i) increased surface area attachment for pesticide molecules, and (ii) improved degradation and incorporation of the pesticide by aquatic plants, algae, and associated biofilms. Fipronil in soil pore water and below the soil surface, however, undergoes either oxidation or reduction, depending on the soil redox potential, as well as dissipates through soil binding and breakdown through microbial actions (Bobe et al., 1997; Bobe et al., 1998; Connelly, 2001; Mize et al., 2007). Interestingly, Ying and Kookana (2001) found that fipronil sorption coefficients were correlated with soil organic C. Though the soil organic C was not tested through loss of ignition, it can be hypothesized as being greater in the vegetated treatments. The vegetated and non-vegetated treatments had identical initial clay/loam substrates, but the vegetated component had been established for nearly 2 yr before the initiation of the dry and inundated experiments. The slow addition of microbes, biofilms, sloughed, and decaying vegetative matter over time would have added to the soil organic C pool in the vegetated mesocosms and conversely the lack thereof in the nonvegetated mesocosms. The increased chemical residence time would have improved contact time with soil organic C and significantly improved exchange between soil pore water and the overlying water column. Tingle et al. (2003) indicated that major fipronil dissipation pathways on and below the soil surface included soil binding (clays and organic C), followed by slower biotic processes but also suggested that half-lives of fipronil were longer on bare soils as compared with turfed soils. The authors concluded that microbial (biotic) processes may have been responsible for this difference between vegetated and nonvegetated treatments (Tingle et al., 2003).

Conclusions

Results suggest that innovative management strategies in aquatic systems associated with agriculture that increase chemical or water residence time, as well as maintain a multiple species vegetation assemblage, will significantly improve fipronil concentration and load reductions to sensitive downstream aquatic ecosystems. Future research needs to focus on field circumstances, whereby naturally vegetated systems can be manipulated pre- and post-hydrologic management to evaluate aquatic system capacity for pollutant mitigation.

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References

- Bennett, E.R., M.T. Moore, C.M. Cooper, and S.J. Smith. 2000. Method for simultaneous extraction and analysis of two current use pesticides, atrazine and lambda-cyhalothrin, in sediment and aquatic plants. *Bull. Environ. Contam. Tox.* 64:825–833.
- Biever, R.C., J.R. Hoberg, B. Jacobsen, E. Dionne, M. Sulaiman, and P. McCahon. 2003. Icon rice seed treatment toxicity to crayfish (*Procambarus clarkii*) in experimental rice paddies. *Environ. Toxicol. Chem.* 22:167–174.
- Bobe, A., C.M. Coste, and J. Cooper. 1997. Factors influencing the adsorption of fipronil on soils. *J. Agric. Food Chem.* 45:4861–4865.
- Bobe, A., P. Meallier, J.-F. Cooper, and C.M. Coste. 1998. Kinetics and mechanisms of abiotic degradation of fipronil (hydrolysis and photolysis). *J. Agric. Food Chem.* 46:2834–2839.
- Cary, T.L., G.T. Chandler, D.C. Volz, S.S. Walse, and J.L. Ferry. 2004. Phenylpyrazole insecticide Fipronil induces male infertility in the estuarine meiobenthic crustacean *Amphiascus tenuiremis*. *Environ. Sci. Technol.* 38:522–528.
- Casey, R.E., and S.J. Klaine. 2001. Nutrient attenuation by a riparian wetland during natural and artificial runoff events. *J. Environ. Qual.* 30:1720–1731.
- Chandler, G.T., T.L. Cary, D.C. Volz, S.S. Walse, J.L. Ferry, and S.L. Klosterhaus. 2004. Fipronil effects on estuarine copepod (*Amphiascus tenuiremis*) development, fertility, and reproduction: A rapid life-cycle assay in 96-well microplate format. *Environ. Toxicol. Chem.* 23:117–124.
- Coleman, J., K. Hench, K. Garbutt, A. Sexstone, G. Bissonnette, and J. Skousen. 2001. Treatment of domestic wastewater by three plant species in constructed wetlands. *Water Air Soil Pollut.* 128:283–295.
- Connelly, P. 2001. Environmental fate of fipronil. p. 1–17. Environmental Monitoring Branch, Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA.
- Gant, D.B., A.E. Chalmers, M.A. Wolff, H.B. Hoffman, and D.F. Bushey. 1998. Fipronil: Action at the GABA receptor. *Rev. Toxicol.* 2:147–156.
- Gottschall, N., C. Boutin, A. Crolla, C. Kinsley, and P. Champagne. 2007. The role of plants in the removal of nutrients at a constructed wetland treating agricultural (dairy) wastewater, Ontario, Canada. *Ecol. Eng.* 29:154–163.
- Greenway, M., and A. Woolley. 1999. Constructed wetlands in Queensland: Performance efficiency and nutrient bioaccumulation. *Ecol. Eng.* 12:39–55.
- Iamchaturapatt, J., S.W. Yi, and J.S. Rhee. 2007. Nutrient removals by 21 aquatic plants for vertical free surface-flow (VFS) constructed wetland. *Ecol. Eng.* 29:287–293.
- Key, P.B., K.W. Chung, A.D. Opatkiewicz, E.F. Wirth, and M.H. Fulton. 2003. Toxicity of the insecticides fipronil and endosulfan to selected life stages of the grass shrimp (*Palaemonetes pugio*). *Bull. Environ. Contam. Toxicol.* 70:533–540.
- Kröger, R., C.M. Cooper, and M.T. Moore. 2008a. A preliminary study of an alternative controlled drainage strategy in surface drainage ditches: Low-grade weirs. *Agric. Water Manage.* 95:678–684.
- Kröger, R., M.M. Holland, M.T. Moore, and C.M. Cooper. 2007a. Hydrological variability and agricultural drainage ditch inorganic nitrogen reduction capacity. *J. Environ. Qual.* 36:1646–1652.
- Kröger, R., M.M. Holland, M.T. Moore, and C.M. Cooper. 2007b. Plant senescence: A mechanism for nutrient release in temperate agricultural wetlands. *Environ. Pollut.* 146:114–119.
- Kröger, R., M.M. Holland, M.T. Moore, and C.M. Cooper. 2008b. Agricultural drainage ditches mitigate phosphorus loads as a function of hydrological variability. *J. Environ. Qual.* 37:107–113.
- Kröger, R., and M.T. Moore. 2008. Utilization of common ditch vegetation in the reduction of fipronil and its sulfone metabolite. *Pest Manage. Sci.* 64:1212–1217.
- Lutz, C.G. 2000. The suffering Louisiana crawfish industry. *Aquacult. Mag.* 26:48–54.
- Maltais-Landry, G., R. Maranger, J. Brisson, and F. Chazarenc. 2009. Nitrogen transformations and retention in planted and artificially aerated constructed wetlands. *Water Res.* 43:535–545.
- Mize, S.V., S.D. Porter, and D.K. Demcheck. 2007. Influence of fipronil compounds and rice-cultivation land-use intensity on macroinvertebrate communities in streams of southwestern Louisiana, USA. *Environ. Pollut.* 152:491–503.
- Moore, M.T., E.R. Bennett, C.M. Cooper, S. Smith, Jr., F.D. Shields, Jr., C.D. Milam, and J.L. Farris. 2001a. Transport and fate of atrazine and lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi Delta, USA. *Agric. Ecosyst. Environ.* 87:309–314.
- Moore, M.T., C.M. Cooper, and J.L. Farris. 2005. Drainage ditches. *In* J. Lehr, J. Keeley, J. Lehr and T. B. Kingery (ed.) *Water encyclopedia*. John Wiley & Sons, New York.
- Moore, M.T., C.M. Cooper, S.J. Smith, E.R. Bennett, and J.L. Farris. 2001b. Drainage ditches: New conceptual BMPs for non-point source pollution and TMDL development. p. V 65–71. *In* Proc. of the Seventh Federal Interagency Sedimentation Conf., Reno, NV. 25–29 Mar. 2001. USGS, Reston, VA.
- Overmyer, J.P., B.N. Mason, and K.L. Armbrust. 2005. Acute toxicity of imidacloprid and fipronil to a nontarget aquatic insect, *Simulium vittatum* Zetterstedt cytospecies IS-7. *Bull. Environ. Contam. Toxicol.* 74:872–879.
- Perry, A., and R.L.P. Kleinmann. 1991. The use of constructed wetlands in the treatment of acid mine drainage. *Nat. Resour. Forum* 15:178–184.
- SAS Institute. 2008. JMP 8 introductory guide. SAS Inst., Cary, NC.
- Schlenk, D., D.B. Huggett, J. Allgood, E.R. Bennett, J. Rimoldi, A.B. Beeler, D. Block, A.W. Holder, R. Hovinga, and P. Bedient. 2001. Toxicity of fipronil and its degradation products to *Procambarus* sp.: Field and laboratory studies. *Arch. Environ. Contam. Toxicol.* 41:325–332.
- Shan, Z., L. Wang, D. Cai, R. Gong, Z. Zhu, and F. Yu. 2003. Impact of fipronil on crustacean aquatic organisms in a paddy field-fishpond ecosystem. *Bull. Environ. Contam. Toxicol.* 70:746–752.
- Smith, S.J., and C.M. Cooper. 2004. Pesticides in shallow groundwater and lake water in the Mississippi Delta MSEA. p. 91–103. *In* M. Nett, M. Locke, and D. Pennington (ed.) *Water quality assessments in the Mississippi Delta, regional solutions, national scope*. ACS Symposium Series 877. Am. Chemical Soc., Oxford University Press, Chicago, IL.
- Smith, S., Jr., C.M. Cooper, R.E. Lizotte, Jr., and F.D. Shields, Jr. 2006. Storm pesticide concentrations in Little Toposhaw Creek, USA. *Int. J. of Ecol. and Environ. Sci.*, 32:173–182.
- Stark, J.D., and R.I. Vargas. 2005. Toxicity and hazard assessment of fipronil to *Daphnia pulex*. *Ecotoxicol. Environ. Safety* 62:11–16.
- Stehr, C.M., T.L. Linbo, J.P. Incardona, and N.L. Scholz. 2006. The developmental neurotoxicity of fipronil: Notochord degeneration and locomotor defects in zebrafish embryos and larvae. *Toxicol. Sci.* 92:270–278.
- Tingle, C.C.D., A.R. Joachim, C.F. Dewhurst, S. Lauer, and W.J. King. 2003. Fipronil: Environmental fate, ecotoxicology and human health concerns. *Rev. Environ. Contam. Toxicol.* 176:1–66.
- Wirth, E.F., P.L. Pennington, J.C. Lawton, M.E. DeLorenzo, D. Bearden, B. Shaddix, S. Sivertsen, and M.H. Fulton. 2004. The effects of the contemporary-use insecticide (fipronil) in an estuarine mesocosm. *Environ. Pollut.* 131:365–371.
- Ying, G.G., and R.S. Kookana. 2001. Sorption of fipronil and its metabolites on soils from south Australia. *J. Environ. Sci. Health B* 36:545–558.