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Transformation and Sorption of Fipronil in Urban Stream Sediments

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Fipronil is an urban-use insecticide, and the increased use has led to its frequent detections in urban streams. Most studies on the environmental fate of fipronil so far have focused on soils, and little is known about its behavior in sediment−water systems. In this study, we investigated the transformation and sorption of fipronil in urban stream sediments from California, incubated under facultative and anaerobic conditions. Degradation of fipronil in sediments generally followed exponential decay kinetics, and the first-order half-lives of fipronil were only 4.6−18.5 days in anaerobic sediments. The persistence of fipronil under facultative conditions was considerably longer, with half-lives from 25 to 91 days. Sterilization generally decreased the dissipation of fipronil, indicating that microbial activity was an important factor in fipronil transformations in sediments. Under facultative conditions, fipronil sulfide and sulfone were observed, while only fipronil sulfide was detected in anaerobic samples. The sorption coefficient K_d consistently increased with organic carbon contents of sediments. In the same sediment, K_d usually also increased with contact time, suggesting decreased availability for aged residues. Results from this study showed that the stability of fipronil in sediments depends closely on the oxygen status and that due to the readily conversion of fipronil to the sulfone and sulfide metabolites, the overall risk assessment of fipronil in surface aquatic systems should take into consideration fipronil as well as its metabolites.

KEYWORDS: Fipronil; sediment toxicity; biodegradation; urban pesticides; runoff

INTRODUCTION

Fipronil (**Figure 1**) is a broad spectrum phenylpyrazole insecticide that was first discovered in 1987 and introduced into the market in 1993 (*1*). Its registration in California was granted exclusively for structural pest control in urban areas in the late 1990s. The binding affinity of fipronil to γ-aminobutyric acid receptor in invertebrates is about 500-fold that in mammals, offering a high degree of species selectivity and relative human health safety (*2*). Also, because of the restrictions of other urban insecticides such as diazinon and chlorpyrifos, the annual use of fipronil in California has increased rapidly since its registration, from 300 kg (as active ingredient) in 2000 to 44803 kg in 2006 (*3*).

The widespread use of fipronil has apparently caused the increasing occurrence of its residue in surface aquatic environments. The U.S. Geological Survey monitoring studies showed that most urban streams from 10 states surveyed in the United States contained sub-parts per billion levels of fipronil (*4*). For example, the concentrations of fipronil in urban creeks feeding into the Sacramento and San Joaquin Rivers in California were 4.0−8.0 ng/L. The fipronil concentration in surface water from a small bayou in the Mermentau River Basin, Louisiana, was as high as 5.3 μg/L (*5*). The same survey also showed that fipronil was ubiquitously present in urban streams from states where fipronil was not registered for agricultural use, convincingly suggesting that fipronil applied in urban areas can transport

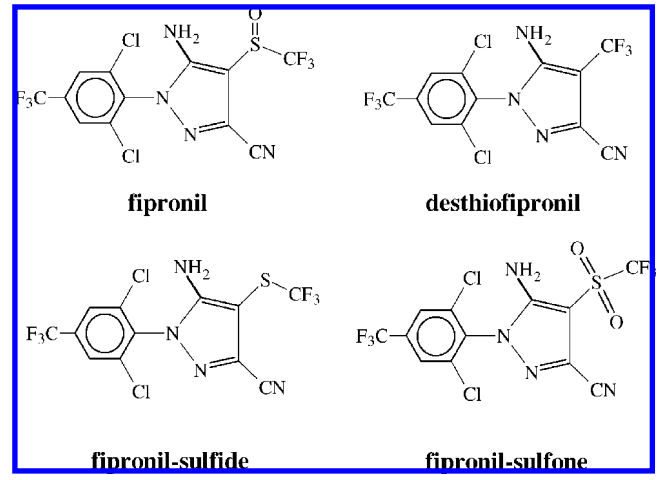

Figure 1. Chemical structures of fipronil and its major metabolites.

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to urban streams. In an ongoing monitoring study, we have detected fipronil and its metabolites in almost all runoff water samples collected directly from eight neighborhoods in Sacramento County and Orange County in California over more than 18 months (unpublished data).

Although the transformation of fipronil in agricultural soils has been well-studied (*6*−*10*), knowledge on the fate of fipronil in stream sediments is scarce. It is known that after application to plants or soils, fipronil can be transformed to a number of metabolites (**Figure 1**), including desthiofipronil, fipronil sulfide, and fipronil sulfone, and that the potential for the formation of each metabolite closely depends on the environmental conditions (*11*). Moreover, from a limited number of studies, desthiofipronil, fipronil sulfide, and fipronil sulfone have demonstrated comparable or greater toxicities to certain aquatic organisms than fipronil itself (*12*). For instance, the 96 h measured median lethal concentrations to *Procambarus clarkii* for fipronil, desthiofipronil, fipronil sulfide, and fipronil sulfone were 14.3, 68.6, 15.5, and 11.2 μg/L, respectively (*12*). In another study, the 21 day median effective concentrations to *Daphnia magna* for fipronil, desthiofipronil, fipronil sulfide, and fipronil sulfone were 190, 230, 27, and 4.5 μg/L, respectively (*1*). As compared to fipronil, desthiofipronil and fipronil sulfone were about 8.1 and 6.4 times more toxic, respectively, to rainbow trout (*1*). Therefore, the increasing occurrence, along with the demonstrated acute toxicities of fipronil and its metabolites to aquatic organisms, dictates the need for understanding its fate and ecological risks in urban streams. The objectives of this study were to evaluate fipronil persistence and transformation in sediments under facultative and anaerobic conditions and to characterize fipronil sorption as a function of sediment type and contact time.

MATERIALS AND METHODS

Chemicals. Standards of fipronil (5-amino-1-[2,6-chloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile, 98.9%) and its corresponding derivatives desthio (98.7%), sulfide (98.8%), and sulfone (99.7%) were obtained from Environmental Protection Agency's National Pesticide Standard Repository in Fort Meade, MD. Solvents (methylene chloride, petroleum ether, and acetone) and other chemicals (copper powder, anhydrous sodium sulfate) were of high-performance liquid chromatography or analytic grade. Before use, the copper powder was treated with dilute nitric acid to remove oxides and rinsed with deionized water and acetone. Sodium sulfate was heated at 400 °C for 4 h prior to use. The other chemicals were used as received.

Sediments. Three sediment samples were collected from San Diego Creek (SDC) in Orange County (CA), Santa Ana River (SAR) in Riverside County (CA), and Miles Creek (MC) in San Joaquin County (CA). After collection, the sediment samples were drained of free water, sieved through 2 mm, mixed thoroughly, and stored at 4 °C until use. The moisture contents were kept the same as the gravity-drained samples to preserve the original microbial activity. Sterile sediments were prepared by autoclaving sediments at 121 °C for 45 min over three consecutive days. Textural and chemical properties of the sediments are listed in **Table 1**. No detectable fipronil or any of its metabolites was found at detectable levels in the sediments.

Degradation Experiments. For facultative degradation incubation, 10 g aliquots (dry weight equivalent) of sediment were weighed into glass jars (5.4 cm diameter × 4.6 cm height), and 5.0 mL of deionized water was added to each jar to submerge the sediment. The sediment samples were then spiked with 10 μL of acetone solution containing 10.0 μg of fipronil to generate the initial nominal concentration of 1.0 mg/kg dry weight sediment. The treated samples were incubated in a dark and airy cabinet at room temperature (21 ± 2 °C). The slurry samples were undisturbed, and the aeration of the microcosm was achieved only by the spontaneous oxygen exchange between the overlaying water and the atmosphere. The samples were checked daily for water loss by weighing, and deionized water was added to compensate for water loss when necessary. The slurry samples were kept undisturbed, and the aeration of the microcosm was achieved only by the spontaneous oxygen exchange between the overlaying water and the atmosphere. Redox potentials (*Eh*) of incubated samples were measured with an Ionalyzer 701 digital pH meter (Orion Research Incorporated, Cambridge, MA). The measured *Eh* was expressed as the relative potential between the platinum electrode and an Ag/AgCl reference electrode connected to a saturated KCl salt bridge. Redox potentials of the samples during incubation are given in **Table 1**, suggesting that the sediments were slightly reduced under the facultative conditions.

Table 1. Textural and Chemical Properties of Sediments Used in This Study and Redox Potentials (*Eh*) during Facultative and Anaerobic Incubations

sediment[a]	clay (%)	sand (%)	silt (%)	OC[b] (%)	OM[c] (%)	CEC[d] (mequiv/100 g)	pH	*Eh* (mv) facultative	*Eh* (mv) anaerobic
MC	9.0	74.0	17.0	0.98	1.68	9.2	6.7	−46 to −25	−341 to −387
SDC	4.0	92.0	4.0	0.18	0.32	3.1	8.0	−75 to −70	−365 to −393
SAR	3.0	85.0	12.0	0.45	0.77	4.8	7.6	−71 to −55	−351 to −385

[a] MC, SDC, and SAR sediments were collected from MC in San Joaquin County (CA), SDC in Orange County (CA), and SAR in Riverside County (CA), respectively. [b] OC, organic carbon content (%). [c] OM, organic matter content (%). [d] CEC, cation exchange capacity.

For anaerobic degradation, 10 g aliquots (dw equivalent) of sediment were weighed into 40 mL glass vials (2.8 cm diameter × 9.5 cm height), and 5 mL of deionized water was added to each sample to submerge the sediment. The sample vials were transferred into a gastight inflatable plastic glove chamber (Cole Parmer, Vermon Hill, IL) inflated with nitrogen (99.99%). The sample vials were flushed with nitrogen by alternately inflating and deflating the glove chamber. The sample vials were equilibrated in the inflated glove chamber for 1 day and then sealed with screw caps with Teflon-lined butyl rubber septa. The sediment samples were taken out of the glove chamber and spiked with 10 μL of acetone solution containing 10.0 μg of fipronil with a 10 -μL microsyringe (Hamilton, Reno, NV). The treated samples were votexed on a Genie 2 Fisher Votex (Fisher Scientific, Bohemia, NY) for 30 s and transferred back into the nitrogen-filled chamber and incubated at room temperature (21 ± 2 °C). The anaerobic conditions inside the vials were maintained by inflating nitrogen into the plastic glove when noticeable deflation occurred. Nonspiked samples of each sediment type were incubated for the measurement of *Eh*. The incubated samples in 40 mL vials were poured to a 50 mL beaker, and redox potentials were measured immediately using the same procedure as given above. Redox potentials of the anaerobic samples are given in **Table 1**, suggesting that the sediment samples incubated in N_2 were much more strongly reduced as compared to the facultative samples.

For the facultative samples, triplicate samples were removed on 0, 7, 14, 28, 56, 112, and 168 days after pesticide treatment, and the samples were analyzed immediately. For anaerobic samples, because of rapid transformation observed in preliminary experiments, triplicate samples were removed on 0, 2, 4, 8, 12, and 16 days after pesticide treatment for SDC and MC sediments. For SAR sediment samples, triplicate samples were withdrawn on 0, 7, 14, 28, 42, and 56 days after pesticide treatment. The removed sediment samples were immediately stored at −22 °C until analysis.

Sorption Experiments. The facultative degradation samples were also used to investigate the partition of fipronil between water and sediment phases over time. To obtain the aqueous phase concentration C_w (mg/L) and sediment phase concentration C_s [mg/kg (dw)], the sediment slurry was transferred to 200 mL glass centrifuge bottles, and 0.01 M $CaCl_2$ solution was added to each sample to form a slurry of water:sediment 4:1 (w/w). The slurry samples were shaken on a mechanic shaker at low speed for 30 min and then centrifuged at 1250 rpm for 30 min. The separated aqueous phase was removed to determine C_w of fipronil, while the residue sediment phase was analyzed to determine C_s, using procedures as described below.

Chemical Analysis. The separated aqueous phase was extracted with 25 mL of methylene chloride for three consecutive times. The combined solvent phase was dehydrated by passing through a filter paper filled with approximately 20 g of anhydrous sodium sulfate. The extract was concentrated to 1.0 mL on a vacuum ratorary evaporator, and an aliquot of the final sample was used to determine C_w of fipronil and metabolites by gas chromatography (GC) analysis.

The residue of fipronil and metabolites in the sediment phase was extracted by a sonication-assisted extraction. Briefly, the sediment was mixed with anhydrous sodium sulfate until dry, and 2.5 g of conditioned copper powder was added into the sample to remove elemental sulfur. A 1:1 (v/v) acetone−methylene chloride mixture (70 mL) was added to the sample, and the bottle was sonicated in an ultrasonic water bath (FS30H; Fisher Scientific, Fair Lawn, NJ) for 15 min. The extract was decanted and passed through a filter paper filled with approximate 30 g of anhydrous sodium sulfate. The remaining sediment was similarly extracted for two more times with fresh solvents. The combined extracts were concentrated to near dryness on a vacuum rotary evaporator at 35 °C, transferred to a 10 mL concentrator tube, and evaporated to dryness under a gentle stream of nitrogen. The residue was redissolved in 1.0 mL of petroleum ether−acetone mixture (70:30, v/v) and subjected to the following cleanup procedure. The sediment extract was cleaned using an Alltech silica solid-phase extraction cartridge (500 mg, 3 mL; Deerfield, IL). Before use, the cartridge was successively conditioned with 2 mL of petroleum ether−acetone mixture (70:30, v/v) and 2 mL of petroleum ether. The sediment extract (1.0 mL) was passed through the conditioned cartridge and eluted with 10 mL of petroleum ether−acetone mixture (70:30, v/v) at a flow rate of 0.5 mL/min. The eluate was evaporated to about 2 mL under a gentle nitrogen stream and reconstituted to 5.0 mL with a petroleum ether−acetone mixture (70:30, v/v). An aliquot of the final sample was used for analysis of C_s of fipronil and its metabolites.

The concentrations of fipronil and metabolites in the final extracts were analyzed using an Agilent 6890 series GC equipped with a Ni^{63} microelectron capture detector (ECD) (Agilent Technologies, Wilmington, DE). A HP-5MS column (30 m × 0.25 mm × 0.25 μm; Agilent Technologies) was employed for separation and analysis of fipronil and metabolites. The inlet temperature was 260 °C, and the detector temperature was 320 °C. The oven temperature was initiated at 80 °C, then increased to 160 at 20 °C/min, and further increased to 240 at 5 °C/min, and finally increased to 300 at 30 °C/min and held for 20 min. The flow rates of the carrier gas (helium) and makeup gas (nitrogen) for ECD were 1.0 and 60 mL/min, respectively. The injection of 1 μL of sample was conducted by an Agilent 7683 autosampler (Agilent Technologies) in the pulsed splitless mode, and the split mode was turned on after 1.0 min. The typical retention times for desthiofipronil, fipronil sulfide, fipronil, and fipronil sulfone under these conditions were 14.6, 17.1, 17.4, and 19.6 min, respectively.

Metabolite characterization was performed on an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer (MS) (Agilent Technologies). The MS detector was operated in the electron impact mode with 70 eV of ionization energy, and the mass spectra were acquired in the full scan mode with m/z ranging from 60 to 500. The chromatographic parameters were the same as given above for the GC-ECD analysis. Metabolites in the sample extracts were identified by comparing the retention times and MS spectra with those of corresponding standards.

A preliminary experiment showed the method detection limit for the analytes was 5 μg/kg. The recoveries for the spiked sediments with 0.05 mg/kg analytes ranged from 89 to 106% with relative standard deviations <6.7%.

Data Analysis. For degradation experiments, concentrations of fipronil and metabolites were expressed as the ratio of the total amount in sediment and water phases to the dry weight of sediment. The sorption coefficient K_d (L/kg) was calculated as the ratio of C_s to C_w, from which the organic carbon-normalized coefficient K_{OC} was further estimated by dividing K_d by the sediment organic carbon content.

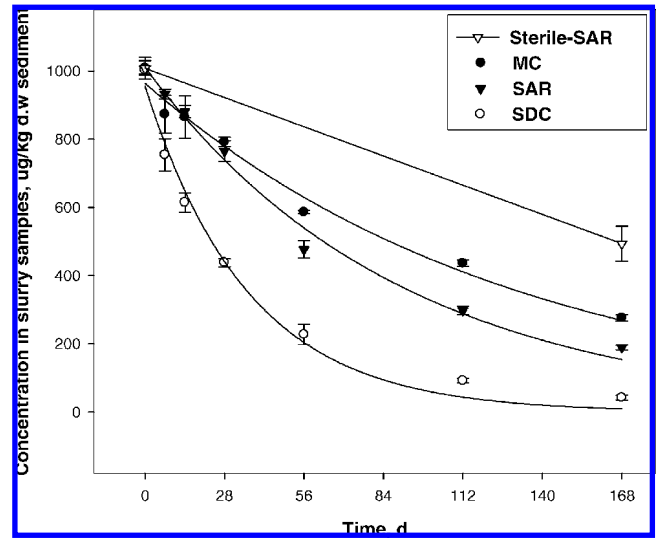

Figure 2. Degradation of fipronil in different sediments under facultative incubation conditions in the dark. Symbols are measured data (means ± standard errors), and curves are regressions using an exponential decay model (see text). MC, SDC, and SAR sediments were collected from MC in San Joaquin County (CA), SDC in Orange County (CA), and SAR in Riverside County (CA), respectively.

RESULTS AND DISCUSSION

Degradation of Fipronil in Sediments. The decline of fipronil concentration in the whole sediments (water and sediment phases combined) over time is plotted in **Figures 2** and **3** for facultative and anaerobic microcosms, respectively. Each of the disappearance curves was fitted to the following exponential decay model to estimate the degradation rate constant k ($days^{-1}$) and half-life $t_{1/2}$ (days) (**Table 2**):

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_0 (mg/kg) and C_t (mg/kg) are fipronil concentrations at time 0 and the elapsed time t, respectively. Most of the fits were excellent, with the correlation coefficients (R^2) being >0.98, suggesting that the degradation of fipronil in sediments closely followed the exponential decay model. Relatively poor fit (R^2 = 0.93) was found for SAR sediment under anaerobic conditions, where degradation appeared to abruptly accelerate after 14 days of incubation. The microbial degradation of fipronil in soils was also found to follow the exponential decay kinetics in most previous studies (*8*−*10*). However, Doran et al. (*7*) found that the dissipation of fipronil in two Australian rice soils followed a two-stage dissipation mode, with rapid transformation during the first 5 days followed by slower dissipation from 5 to 45 days.

Under the experimental conditions, fipronil displayed low to moderate persistence in the selected sediments (**Table 2**). The dissipation $t_{1/2}$ of fipronil ranged from 4.6 days in SDC sediment under anaerobic conditions to 91.2 days in the MC sediment under facultative conditions. The $t_{1/2}$ of fipronil was found to vary greatly in sediments or soils in other studies. Jones et al. (*6*) showed that in sulfidogenic or methanogenic sediments, fipronil displayed half-lives about 35 and 40 days, respectively. Under aerobic conditions, $t_{1/2}$ of fipronil was reported to be 122−128 days in a sandy loam soil and was as long as 308−342 days in a loamy sand soil (*13*). In the same study, fipronil was found to degrade slowly in water/sediment under anaerobic conditions, with $t_{1/2}$ of 116 days (*13*). The average $t_{1/2}$ of fipronil in two small plots at Roseworthy Farm and Terretfield in

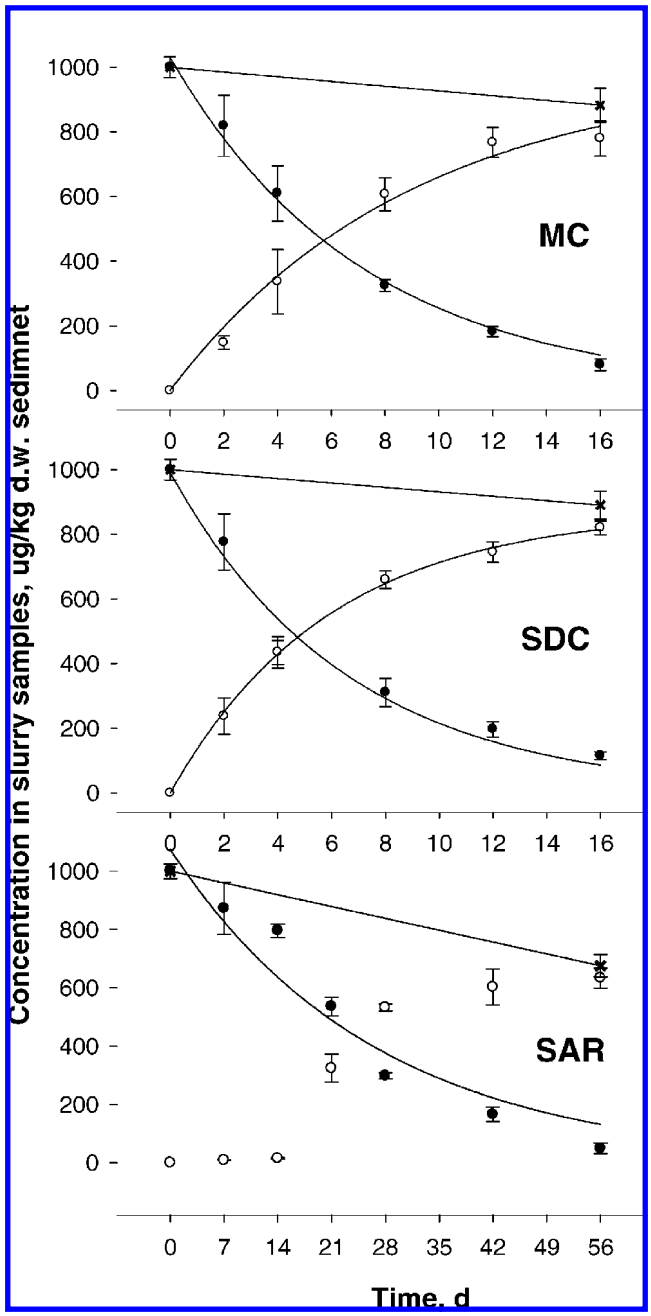

Figure 3. Degradation of fipronil in the sterile and nonsterile sediments under anaerobic conditions. Symbols are measured data (means ± standard errors), and curves are regressions using different models (see text). Symbols ×, ●, and ○ denote fipronil in sterile treatment, fipronil nonsterile treatment, and sulfide in nonsterile treatment, respectively. Sediment descriptions are the same as given in **Figure 2**.

Table 2. Estimated Degradation Rate Constants (k, days^{-1}) and Average Half-Life ($t_{1/2}$, days) of Fipronil in Sediments under Facultative and Anaerobic Conditions

	facultative conditions			anaerobic conditions		
sediment[a]	k	$t_{1/2}$	R^2	k	$t_{1/2}$	R^2
MC	0.0076 ± 0.0006	91.2	0.998	0.1398 ± 0.0081	5.0	0.997
SDC	0.0276 ± 0.0025	25.1	0.998	0.1524 ± 0.0180	4.6	0.988
SAR	0.0112 ± 0.0008	61.9	0.996	0.0375 ± 0.0059	18.5	0.925

[a] Sediment descriptions are the same as given in **Table 1**.

Adelaide, South Australia, Australia, under field conditions was 132 days (*9*). In contrast, fipronil in California, rice fields was found to be less persistent, with $t_{1/2}$ of 2−22 days (*10*). It is difficult to probe the causes for the great variations observed for fipronil persistence in soils and sediments, because the laboratory incubation conditions or field circumstances differed greatly among studies.

In this study, oxygen status appeared to be an important factor for influencing fipronil stability in the sediments. Degradation of fipronil under strongly reduced conditions (*Eh* ranging between −393 and −341 mv) was consistently much faster than that in the same sediment but incubated under less reduced conditions (*Eh* ranging between −75 and −25 mv) (**Table 1**). For example, $t_{1/2}$ values of fipronil in MC sediment under facultative and anaerobic conditions were 91.2 and 5.0 days, respectively, displaying about 18-fold difference. The dissipation rates of fipronil in SAR and SDC sediments under anaerobic conditions were, respectively, about 3.3 times and 5.5 times those under facultative conditions (**Table 2**). The dissipation rates of fipronil in anaerobic flooded or nonflooded rice soils were comparable or slightly faster than those in aerobic rice soils (*7*). Significant influence of oxygen status has also been observed for the persistence of other pesticides. For instance, DDT was found to degrade faster under anaerobic conditions than under aerobic conditions (*14*). However, transformation of herbicides phenoxic acid and mecoprop in a lake sediment decreased from 0.173 days^{-1} to less than 0.001 days^{-1} with decreasing oxygen concentration (*15*). The difference in fipronil persistence under different oxygen statuses was likely due to the effect of oxygen on microbial populations and activities that were responsible for fipronil transformations in the sediments.

Sediment properties also appeared to affect fipronil stability. Under facultative conditions, $t_{1/2}$ of fipronil varied from 91.2 days in MC sediment to 25.1 days in SDC sediment. Under anaerobic conditions, $t_{1/2}$ ranged from 18.5 days in SAR sediment to 4.6 days in SDC sediment (**Table 2**). The overall persistence of fipronil followed the order MC > SAR > SDC under facultative conditions and SAR > MC > SDC under anaerobic conditions (**Table 2**). In a previous study, degradation of carbaryl, diazinon, malathion, and chlorpyrifos, all urban-use insecticides, also varied between different sediments under similar incubation conditions (*16*). The different degradation rates of fipronil in the different sediments may be attributable to two causes. First, different sediments may have different indigenous microbial populations, as seasonal and spatial variations could influence the microbial populations and activities in sediments (*17, 18*). On the other hand, the physical and chemical properties of sediments may also have contributed to the difference in fipronil degradation. For instance, regression of the degradation rate constants under facultative conditions with sediment properties showed that fipronil degradation rates were correlated inversely with sediment organic matter content (OM) ($R^2 = 0.73$) but proportionally with sediment pH ($R^2 = 0.71$). Previous studies have shown that pesticide degradation in soil may be inhibited by soil OM (*19*), and the inhibition was attributable to the fact that soil organic matter could serve as an alternative source of C and N for the microorganisms involved in pesticide degradation (*20*). In addition, higher pH promoted the hydrolysis of fipronil (*21*). Therefore, the slower degradation of fipronil in MC sediment may be attributed to the lower pH and higher OM content of this sediment as compared with SAR and SDC sediments.

Microbial activities apparently played an important role in fipronil degradation in the selected sediments. In sterilized sediments, there was generally a decrease in fipronil degradation rate (**Figures 2** and **3**). For instance, after incubation for 168

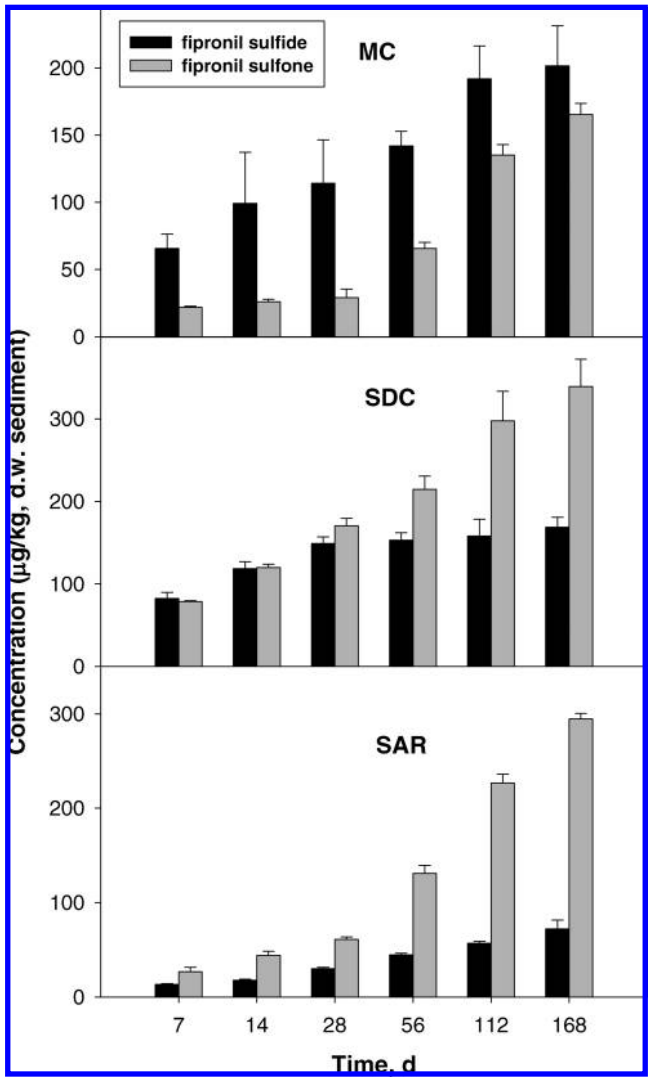

Figure 4. Formation of metabolites from fipronil degradation in nonsterile facultative incubation sediments. Bars are means ± standard errors. Sediment descriptions are the same as given in **Figure 2**.

days under facultative conditions, the fractions of fipronil transformed in the nonsterile and sterile SAR sediments were 81.1 and 50.7%, respectively (**Figure 2**). Fipronil degradation under anaerobic conditions showed even more pronounced differences between nonsterile and sterile treatments. For instance, after 56 days of incubation, 95.1 and 34.7% of fipronil were found to have degraded in the nonsterile and sterile SAR sediments, respectively (**Figure 3**). The percentages degraded in nonsterile and sterile treatments after 16 days were 99.2% as compared to 11.7% for MC sediment and 88.4% as compared to 10.5% for SDC sediment (**Figure 3**). The effect of sterilization treatment on fipronil degradation in sediments suggests that microorganisms were involved in fipronil transformations, and the role of microbial transformations appeared to be especially important for anaerobic conditions. Microbial transformation was also found to be important for fipronil disappearance in a sandy loam soil and a clay loam soil (*8, 9*). For example, $t_{1/2}$ of fipronil was 9.7 days in a nonsterile clay loam soil but increased to 33.5 days after sterilization (*8*).

Formation of Fipronil Metabolites. Under facultative conditions, fipronil sulfide and fipronil sulfone were detected in both sterile and nonsterile sediments (**Figure 4**). Both fipronil sulfide and sulfone concentrations increased over time. However, the ratios of fipronil sulfide to fipronil sulfone varied significantly among the sediments (P values <0.05). In SDC and SAR sediments, the concentrations of fipronil sulfone were higher than those of sulfide. However, in MC sediment, the concentrations of fipronil sulfide were consistently lower than those of sulfone. Under facultative incubation conditions, all ratios of fipronil sulfone to sulfide in the three sediments increased as the incubation time increased. For instance, in SAR sediment, the ratio of fipronil sulfone to sulfide increased from about 2:1 after 7 days to about 4:1 after 168 days of incubation.

Under the strongly reduced anaerobic conditions, fipronil sulfide was the only metabolite detected in all of sediment samples. Assuming that all fipronil was converted to sulfide and that the fipronil sulfide formation rate was much greater than its dissipation rate, the formation of sulfide could be expressed as

$$C_{\text{sulfide}} = C_{0,\text{fipronil}} - C_{t,\text{fipronil}} \quad (2)$$

From eq 1, fipronil sulfide C_{sulfide} can be expressed as

$$C_{\text{sulfide}} = C_{0,\text{fipronil}}(1 - e^{-kt}) \quad (3)$$

where $C_{0,\ \text{fipronil}}$ is the initial concentration of fipronil and k is the degradation rate constant for fipronil. The measured fipronil sulfide concentrations were used to fit eq 3 to estimate k values (days^{-1}) for fipronil. The fit was exceptionally good for MC (k = 0.1116 days^{-1}; R^2 = 0.99) and SDC (k = 0.1695 days^{-1}; R^2 = 0.99) sediments. The k values estimated from the formation of fipronil sulfide were in close agreement with the k values calculated directly from fipronil losses for these two sediments (**Table 2**), suggesting that fipronil was nearly completely converted to its sulfide analogue in these sediments under anaerobic conditions and that the further transformation of fipronil sulfide was much slower than its formation. However, the fit was relatively poor for SAR sediment (R^2 = 0.83), and the estimated k (0.0086 days^{-1}) differed substantially from that estimated from fipronil dissipation (k = 0.0375 days^{-1}; **Table 2**). This may be attributable to the fact that fipronil degraded slower in SAR sediment under anaerobic conditions. Furthermore, it is likely that the formed fipronil sulfide was concurrently further transformed to other metabolites.

It must be noted that no photodegradation product, desthiofipronil, was detected in any of the treatments in this study, which is likely due to the fact that all samples were shielded from direct sunlight during incubation. In natural environments, however, photodegradation of fipronil may not be neglected, especially for surface waters where direct sunlight is available. For instance, desthiofipronil was always concurrently detected with fipronil in surface waters (*4*). In addition, desthiofipronil was identified to be the major degradation product of fipronil in water from a rice paddy system (*10*).

Fipronil Sorption in Sediment. Partition of fipronil between water and sediment phases varied with sediment properties. As evident from the K_d values (**Table 3**), sorption of fipronil in sediments followed the order MC > SAR = SDC, showing a tendency that higher organic carbon content leads to greater sorption. After incubation for 2 days, the estimated K_{OC} values for MC, SDC, and SAR sediments were 1408, 1556, and 800, respectively. These values are in good agreement with the reported fipronil K_{OC} of 825 (*22*). The relatively weak sorption suggests that fipronil is transported mainly via the water phase in a water−sediment system. block

Sorption of fipronil in sediments increased with increasing incubation time (**Table 3**). For MC sediment, K_d reached a steady state after only 2 days of incubation. However, K_d values for SDC and SAR sediments increased continuously during the 168 day

Table 3. Sediment−Water Partition Coefficient (K_d, L/kg) of Fipronil in Studied Sediments (Data Are Given as Means ± Standard Deviations)[a]

time (days)	MC	SDC	SAR
0	7.8 ± 0.4	1.0 ± 0.1	1.6 ± 0.2
2	13.8 ± 0.2	2.8 ± 0.2	3.6 ± 0.2
7	11.7 ± 0.2	2.9 ± 0.2	5.5 ± 0.6
14	11.8 ± 0.9	2.9 ± 0.2	5.9 ± 0.3
28	11.3 ± 0.4	2.7 ± 0.5	6.4 ± 1.7
56	14.2 ± 0.7	4.5 ± 0.2	6.4 ± 1.0
112	14.3 ± 1.0	7.2 ± 0.6	8.4 ± 0.7
168	14.0 ± 1.5	10.0 ± 0.6	9.2 ± 0.8

[a] Sediment descriptions are the same as given in **Table 1**.

incubation. As compared with the time immediately after treatment, K_d at 168 days for SDC and SAR sediments increased from 1.0 to 10.0 L/kg and from 1.6 to 9.2 L/kg, respectively, representing about 6−10-fold increases. Time-dependent sorption was also observed for other pesticides in soils (*23*−*25*) and sediments (*16*). It is generally accepted that diffusion of pesticides to less accessible sorption sites, degradation of readily available chemical in aqueous and sorbed phases, and desorption-limited degradation might contribute to the increase of K_d over contact time (*24, 25*). The time dependence of K_d suggests that fipronil residue in sediments may become increasingly less available over time for transport or biological uptake.

Environmental Implications. Results from this study suggest that the persistence of fipronil in sediments closely depends on the sediment type and incubation conditions. Short persistence was observed for anaerobic conditions, likely due to the rapid conversion of fipronil to its sulfide derivative, but relatively long persistence occurred under facultative conditions. In most surface water bodies, water and the top-layer sediment mix constantly, preventing the persistence of anaerobic conditions. However, anaerobic conditions may occur in a lake or stream sediment under certain circumstances, such as in static systems where no water exchange occurs, for example, in salt marshes or wetlands (*26*). Furthermore, the top layer of sediment in a water course or lake can become anaerobic during summer months due to reduced dissolved oxygen (*27*). Even for the same system, oxygen status may vary with sediment depths. For instance, positive redox potentials are generally restricted to the top 5 mm of the sediment (*15*), while anaerobic conditions may be prevalent in deeper sediment layers in a lake or stream. This study further showed that sorption of fipronil in sediments may increase with contact time, which may affect its availability for transport or toxicity effects. The above observations together suggest that the overall fate and effects of fipronil under field conditions may be subject to significant temporal and spatial variations.

Two major transformation products, fipronil sulfide and fipronil sulfone, were found in the sediments incubated under facultative conditions, while only fipronil sulfide was detected in the sediments under anaerobic conditions. Given that both fipronil sulfone and sulfide were reported to have comparable or higher acute aquatic toxicities than fipronil (*12*), it is clearly important to understand the stability and further transformations of these metabolites in sediment−water systems. In addition, the occurrence of desthiofipronil, a photodegradation product of fipronil that also has enhanced aquatic toxicity, should be examined in sediments under outdoor conditions.

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