Sorption and Degradation of Fipronil in Flooded Anaerobic Rice Soils

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The fate of fipronil in flooded, reductive rice soils was modeled using a conceptual model. Rate constants for the various sorption and degradation processes were calculated from experimental studies involving intact soil cores, and the reductive degradation constant was used to calculate half-lives for fipronil on each soil. The data predicted that fipronil was subject to rapid, reductive degradation or immediate sorption to the soil and any sorbed fipronil desorbed was reductively degraded. The reductive metabolite, fipronil sulfide, accumulated over the 184 day duration of the experiment and sorbed rapidly to the soil, where it accumulated and did not appear to degrade. Neither fipronil nor fipronil sulfide was found beyond the top 1 cm of soil in Yanco soil, while a small amount of each chemical was found up to 4 cm deep in the Coleambally soil profile.

KEYWORDS: Fipronil; adsorption; sorption; degradation; diffusion; leaching; anaerobic; flooded; rice; pesticide

INTRODUCTION

Flooding of rice bays prior to the application of pesticides generates anaerobic, reducing conditions by consuming oxygen (*1*). Soil minerals may also be reduced, affecting the ability of the soil to retain introduced chemicals. For example, glyphosate sorption on soils has been shown to be dependent upon the iron hydroxide content (*2*), and their reduction under flooded conditions may decrease the ability of a soil to sorb glyphosate. Additionally, flooding soils can solubilize and mobilize some organic matter or previously sorbed material, while the anaerobic, reducing conditions may chemically alter the structure of insoluble or bound organic matter.

The mobility of applied organic chemicals in flooded soil may be slowed by sorption to the soil, which may in turn enhance chemical and microbial degradation of the chemicals. The sorption of hydrophobic organic chemicals, such as pesticides, is often influenced by soil organic carbon (OC) (*3−9*); however, other work has suggested char content may be a better predictor of sorbing potential (*10*). Once surface layers of soil are saturated, applied pesticides may leach beyond surface layers of soil, which are subject to different redox conditions (*11*) and, hence, potentially different environmental fates. This may be as a consequence of the type of microbial populations in the soil or as a result of a decrease in the soil redox. For example, rapid degradation of MCPA and mecoprop virtually terminated under anaerobic conditions (*12−15*), whereas DDT was shown to degrade slowly

under aerobic conditions but rapidly under anaerobic conditions (*16*).

Fipronil is an insecticide used by the Australian rice industry to combat blood worm, *Chironomus tepperi* (*17*), which can devastate rice crops. Because of its release in the early 1990s, the use of fipronil is in its infancy in the rice industry (*18*) but is becoming more widespread, mainly because of its lower application rate and toxicity when compared to chlorpyrifos (*19*). Additionally, fipronil has the ability to be used as a seed dressing to more effectively protect aerial sown rice crops. However, studies that indicate some mobility of fipronil indicate that, when used in flood-irrigated systems, there is potential for contamination of ground or surface water sources. Consequently, an understanding of its fate is essential in minimizing its risk as an environmental pollutant. Fipronil degradation occurs under both oxidative and reductive conditions, producing distinctly different metabolites. Fipronil sulfide is produced when the moisture content is at least 50% of the mean water holding capacity (MWHC) and reducing conditions prevail (*20*), whereas fipronil sulfone is produced under oxidative conditions. Additional fipronil metabolites may also result from hydrolysis and photodegradation, and while all fipronil metabolites may be present in commercial forms of fipronil, they are considered to be more toxic than fipronil (*21*).

The aim of the following work is to determine the extent of sorption and degradation of the commercial formulation of fipronil (Cosmos) when applied to flooded intact soil cores, in which reducing conditions were allowed to establish. A conceptual model was developed on the basis of the two-compartment model developed by Hamaker and Goring (*22*), to assist the interpretation of the data and predict the fate of fipronil and its main reductive metabolite.

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MATERIALS AND METHODS

Experimental Setup. Two rice growing soils used for experimentation were chosen from southwestern NSW, Australia: a Birganbigil clay loam from Yanco (34°36′S, 146°24′E) and a Wunnamurra self-mulching clay from Coleambally (34°47′S, 145°59′E), and were classified as a brown chromosol and a gray vertosol, respectively (*23*). Soil properties have been described elsewhere (*24*). Lengths of aluminum tubing (50 mm outer diameter × 25 cm long) were used to take soil cores to a depth of 10 cm at each of the sampling sites and returned to the glasshouse where their bases were sealed using PVC caps. The tubes were flooded to a depth of approximately 10 cm above the soil surface with untreated irrigation water from the Murrumbidgee River. After standing overnight, water levels were made up to a depth of 10 ± 0.5 cm above the soil surface and then covered with sheets of black plastic. Pesticides were applied to the floodwater after 5 weeks, as previous work indicated reducing conditions had sufficiently established after this period of time (*10*). Water levels were maintained at 10 ± 0.5 cm above the soil surface until the termination of the experiment using irrigation water, which had been deoxygenated with nitrogen.

Pesticide Application and Sampling. Cosmos (fipronil) concentrate was diluted in irrigation water 1:100 000 (v/v) with continual stirring. Aliquots of diluted pesticide solution (1.0 mL) were added to each flooded soil core, resulting in a theoretical fipronil concentration of 20 μg L^{-1}. Sampling was undertaken at 30 min and 1, 2, 4, 7, 14, 28, 63, 98, and 184 days after pesticide application. Ponded water (approximately 150 mL) was removed from flooded cores using a vacuum pump and a hooked-shaped Pasteur pipet to minimize disturbance of the sediment. The vacuum pump was used to draw the ponded water up the pipet and allow its collection in a Schott bottle (250 mL), which acted as a liquid trap. The Schott bottle was removed, the sampling line was flushed, and a new bottle was attached for each sample. The sampled water was extracted immediately for pesticide residues, while intact cores were placed vertically in a deep freeze (-20 °C) for subsequent extraction.

Extraction of Fipronil from Soil and Water. Fipronil and fipronil sulfide were extracted from water by SPE using the ascorbic acid stabilization method previously developed (*25*) and analyzed by GC–ECD. Fipronil was extracted from soils by slicing frozen cores transversely into 1 cm thick layers to depths of up to 5 cm from the soil surface. Subsamples (10–15 g) were taken from each fraction and placed in disposable centrifuge tubes (50 mL), which had been previously treated with Coatasil (dimethyl dichlorosilane). Soils were extracted using anhydrous sodium sulfate (5 g) and acetonitrile (20 mL) on a laboratory shaker (45 min, 400 oscillations min^{-1}) and centrifuged (10 min, 4000 rpm). Supernatant was removed from tubes and filtered (GF/F, 13 mm) into scintillation vials (20 mL). Samples were reduced to dryness under nitrogen (40 °C) and resuspended in ethyl acetate (200 μL) containing lindane internal standard (1 mg L^{-1}) for subsequent analysis by GC–ECD. Recoveries of fipronil and fipronil sulfide from soil and water, as well as detection limits, are shown in **Table 1**.

Interference of Emulsifiers on SPE. The extent of emulsifier influence on the efficiency of SPE of fipronil and fipronil sulfide from water over time was investigated in two separate experiments. The first involved a comparison of extraction between technical-grade fipronil (98%) and Cosmos. Solutions of known concentration were applied directly to SPE cartridges. Effluent exiting the SPE cartridge during extraction was collected and extracted for fipronil by SPME, and fipronil trapped on the cartridge was eluted with acetonitrile and concentrated as previously described. Both fractions were analyzed by GC–ECD. The second experiment involved repeating the main experiment reported in the Experimental Setup for a 28 day period. The fipronil and fipronil sulfide concentrations in water were determined by extraction with SPE cartridges, as previously described, and compared to results determined by SPME–GC–ECD using the methodology described in ref *10*.

Fate of Dissolved Organic Carbon (DOC). The potential interference of DOC on SPE was investigated by determining its initial concentration and persistence over time. Air-dried soil (500 g) from the 0–100 mm soil layer of each soil type was ground and sieved to < 1.5 mm and then stirred with instrument-grade water (500 mL) in a bottle for 1 h in the dark. Samples were taken from the stirring slurry and centrifuged

Table 1. Detection Limits for Fipronil and Fipronil Sulfide in Soil and Water, with Percentage Recoveries Shown in Parentheses ($n = 5 \pm$ SD)

pesticide	water (ng/mL)	soil (ng/g)
fipronil	0.5 (88 ± 2%)	5 (89 ± 3%)
fipronil sulfide	0.5 (90 ± 3%)	5 (92 ± 3%)

Table 2. Comparison of the Extraction Efficiency of SPE Cartridges for Commercial Blends and Technical-Grade Fipronil

pesticide	fraction	fipronil
Cosmos	cartridge	88 ± 2
	effluent	8 ± 2
	total recovered	96
technical	cartridge	98 ± 3
	effluent	0
	total recovered	98

(4000 rpm, 15 min). The supernatants were filtered through polycarbonate membranes (0.40 μm) for DOC analysis using the dichromate method, as previously described (*25*). The bottles were stored in an incubator (20 °C) in the dark, and samples were taken, analyzed for DOC routinely over a 92 day period.

Chromatographic Conditions. Fipronil was quantified using a Carlo Erba HRGC 5300 Mega Series gas chromatograph with ^{63}Ni electron capture detector (GC–ECD) and J&W Scientific DB-5 capillary column (30 m × 0.25 mm inner diameter with 0.25 μm film thickness). Injection was splitless with a 1 μL injection volume and injector port and detector temperatures of 280 and 290 °C, respectively. The carrier and makeup gases were high-purity nitrogen (2 mL min^{-1}) and argon containing 10% methane (20 mL min^{-1}), respectively. The temperature program began at 70 °C (held for 1 min), then increased to 260 °C (at 15 °C min^{-1}, held for 2 min), and then increased to 280 °C (at 20 °C min^{-1} for 3 min). Data were processed using Star Chromatography Workstation software (version 6.2).

Statistical Analysis. Logarithmic transformations of fipronil concentrations were analyzed using linear regression, and the gradient of each was compared using t tests for differences between two independent regression coefficients (*26*).

RESULTS AND DISCUSSION

Surfactant and DOC Influence on the Extraction of Fipronil from Water. The recovery of fipronil (applied as Cosmos) from the floodwater was lower than anticipated in the first 4 weeks of the main pesticide fate experiment, which may have been due to emulsifiers present in Cosmos or the presence of DOM influencing the extraction of fipronil from floodwater by SPE. More specifically, we speculated that (1) the emulsifiers present may have competed for the sorption sites in the SPE cartridge, (2) emulsifiers may have protected the fipronil molecules from the sorption sites in the SPE cartridges by forming micelles and allowing fipronil to pass through the SPE cartridge unretained, and (3) DOC resulting from the soil may have interfered with SPE. Consequently, three experiments were conducted to test these hypotheses.

In the first experiment, Cosmos and technical-grade fipronil were applied to SPE cartridges and their extraction efficiencies were compared (**Table 2**). Higher recoveries were obtained for technical-grade fipronil compared to Cosmos, and no fipronil was detected in the effluent exiting the base of SPE cartridges to which technical-grade fipronil was applied, when quantified with solid-phase microextraction (SPME). Conversely, approximately 8% of the fipronil applied to SPE cartridges escaped the cartridge when applied in the form of Cosmos. These findings agree with other studies in which poor recoveries of fipronil from water (*27*) were attributed to fipronil remaining associated with emulsifiers and requiring several days before release from the formulation.
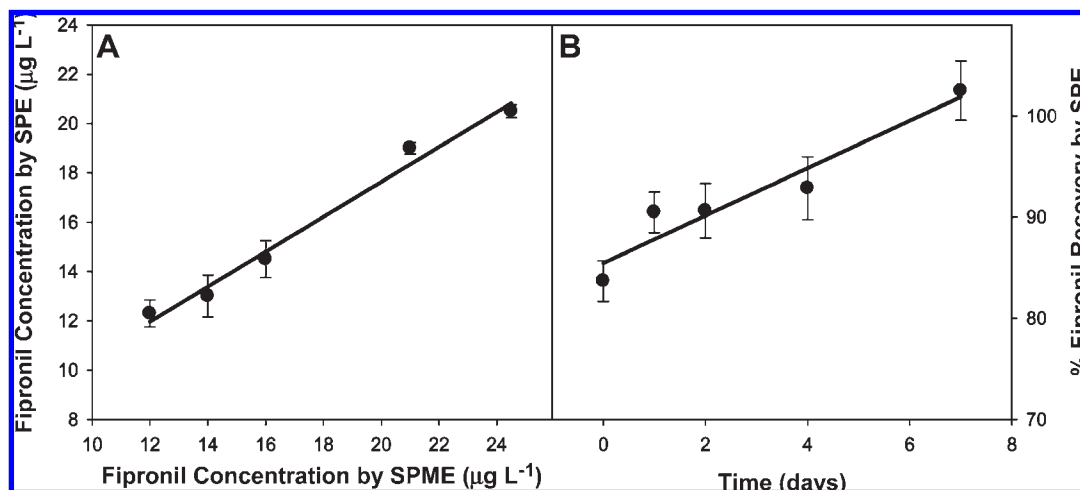
Figure 1. (A) SPE recovery versus fipronil concentration as determined by SPME and (B) percentage recovery of fipronil from the water column by SPE over time (mean $\pm$ SD; $n = 4$).

Work on other pesticides had a similar response. For example, less than two-thirds of thiobencarb, when applied as Saturn, and was trapped when extracted by SPE (*28*).

In the second experiment investigating the efficiency of fipronil extraction from floodwater by SPE, Cosmos was applied to water that had been ponded over soil. **Figure 1A** shows the linear relationship between the fipronil concentration in the water column when determined by SPE compared to analysis by SPME. While emulsifiers appear to have an effect on the efficiency of fipronil extraction by SPE, there did not appear to be any affect on SPME, despite the similarity of the two techniques. This was attributed to the addition of acetone containing an internal standard (50 μL) to water samples prior to SPME, resulting in micelle disruption or a change in the polarity of the solution. **Figure 1B** shows the percentage recovery of fipronil by SPE over a period of 7 days, which indicates that emulsifiers did not affect fipronil extraction from water by SPE after 7 days. A regression line was fitted to the data (**Figure 1A**), and the regression equation was used to correct the fipronil concentrations in water for the main fipronil sorption study (**Figures 2** and **3**).

Finally, the longevity of DOC in solution was investigated over a 3 month period as a potential interference for SPE. **Figure 4** shows that the initial DOC concentration at the time of flooding decreased by nearly 50% within 4 weeks and by a further 20% over the next 60 days. DOC-assisted leaching of organic chemicals [e.g., PAHs (*29*)] has been shown to occur because of the tendency of humic and fulvic acids to form micelles in water (*30*), in the same fashion as emulsifiers, which may also allow analytes to avoid retention by SPE cartridges. The results in the current experiment indicate that the persistence of DOC would have exerted the greatest influence on fipronil recovery by SPE over the first 4 weeks. How this occurs is a topic for further research.

Fate of Fipronil in Flooded Soils. The distribution of fipronil in water and soil in flooded soil cores from Yanco and Coleambally is shown in **Figures 2A** and **3A**, respectively. Because of differences in units of concentration between soil and water and differences in molecular masses of fipronil and fipronil sulfide, results are reported as "micrograms of fipronil equivalent" to allow for a direct comparison of the two chemicals recovered from the two different phases. This was calculated by dividing the mass of fipronil sulfide by its molecular weight and then multiplying by the molecular weight of fipronil. Error bars are shown only for the plot of "total material recovered" in each figure, which effectively shows the cumulative error for the experiment,
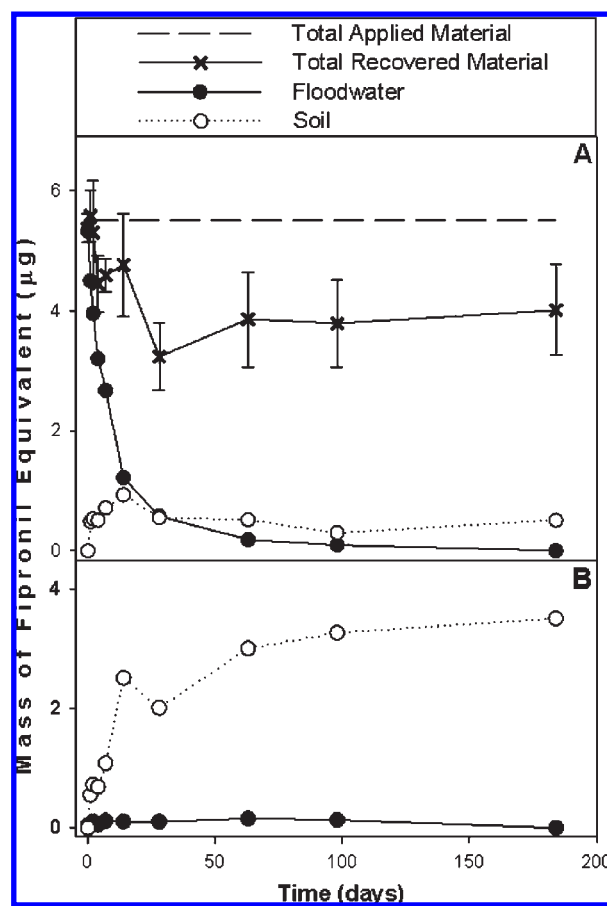

Figure 2. (A) Persistence of fipronil and (B) production of fipronil sulfide in flooded Yanco soil ($n = 4$).

because overlapping error bars between the plots decreased the overall clarity of the figures.

While fipronil and fipronil sulfide never moved beyond the top 0−1 cm layer of Yanco soil, fipronil was recovered from the 2−3 cm layer after 14 days and fipronil sulfide was recovered from the 3−4 cm in the soil layer after 28 days in the Coleambally soil. However, the majority (> 70%) of the two chemicals tended to remain in the 0−1 cm layer of soil. Because there was no leakage of water from the base of the cores, penetration of fipronil
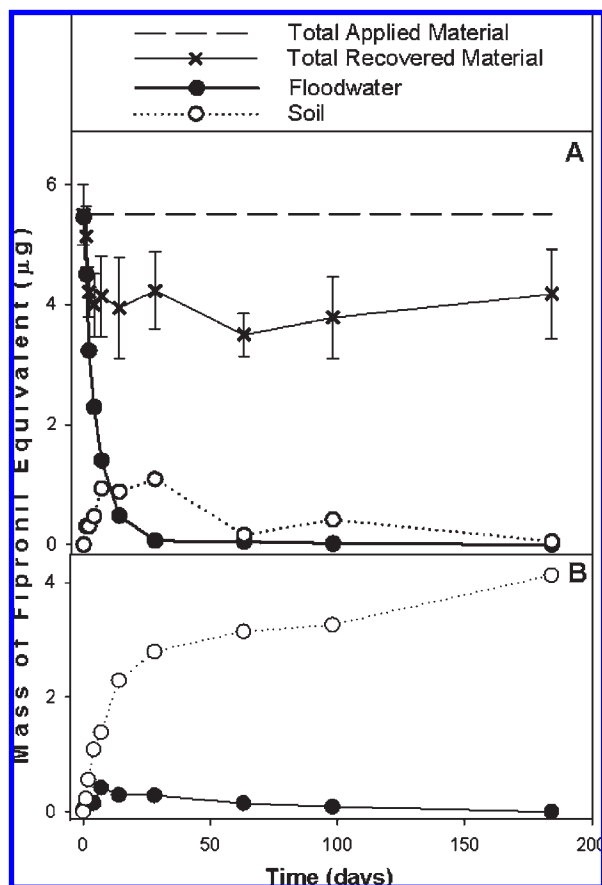
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Figure 3. (A) Persistence of fipronil and (B) production of fipronil sulfide in flooded Coleambally soil (*n* = 4).

Figure 4. Loss of DOC from the aqueous phase of flooded soils over time (mean ± SD; *n* = 4).

Figure 5. Conceptual model for the fate of fipronil and fipronil sulfide under flooded conditions.

and fipronil sulfide beyond the top 1 cm of soil was attributed to macropore-assisted diffusion via old root and worm holes present in the soil cores (*10*). For the sake of simplicity, only total fipronil and total fipronil sulfide from soil have been reported for the Coleambally soil in **Figure 3**.

Figures **2A** and **3A** show that fipronil in the water column decreased rapidly over the first 56 and 28 days for Yanco and Coleambally soils, respectively, because of sorption to the soil as well as degradation. Evidence in support of this can be clearly seen in both soils in **Figures 2A** and **3A**. After application of fipronil, the amount of fipronil sorbed onto the soil increased, as did the amount of fipronil sulfide present in soil and water. While the main mechanism for fipronil degradation in flooded soils is understood to be reduction, a small amount of oxidation and hydrolysis is presumed to have occurred because of the facultative conditions present in the water column (*31*). The peak fipronil concentration in soil resulting from sorption from the water column was approximately 15% of the applied fipronil (**Figures 2A** and **3A**), and occurred at 14 and 28 days for Yanco and Coleambally, respectively, after which the fipronil concentration declined in both soils. While present at trace levels in the applied Cosmos, fipronil sulfide was produced by reductive degradation of fipronil and appeared briefly in the water column for the first 7 days. Its concentration in water then decreased, presumably because of strong and rapid sorption to the soil, and the amount of fipronil sulfide recovered from soil continued to increase over the 184 day lifetime of the experiment.

From analysis of the data in **Figures 2** and **3**, we speculated that once fipronil was applied to the water column, it either immediately sorbed to the soil or degraded to fipronil sulfide. We assume that fipronil so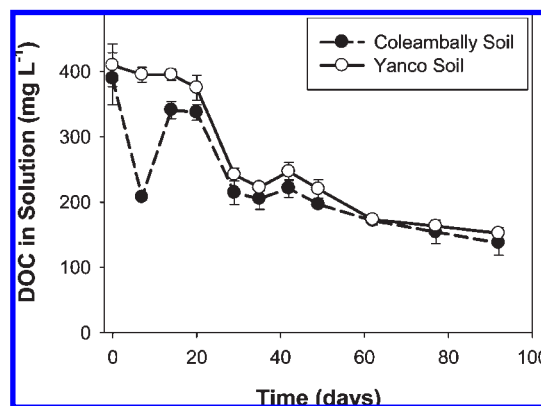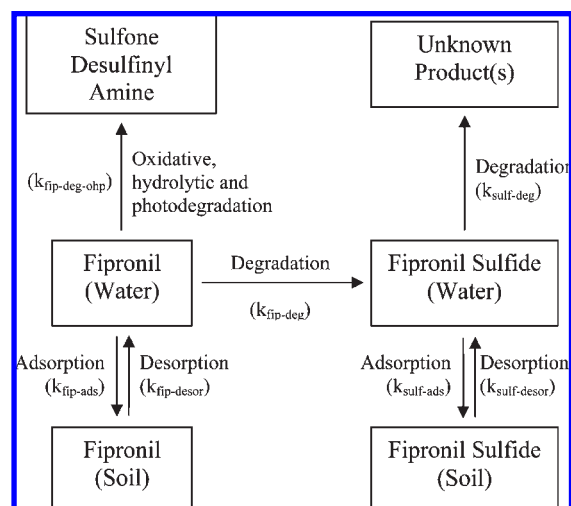rbed to the soil later desorbed and was immediately converted to fipronil sulfide, which, in turn, immediately sorbed to the soil and most likely did not desorb again based on the accumulation of fipronil sulfide in the soil (**Figures 2B** and **3B**). The total recovery of applied pesticide/metabolite declined by 25% over the first 28 days and was attributed to hydrolysis and oxidation as a result of the facultative conditions present in the water column. All fipronil sulfide was a terminal degradation product, because it did not desorb from the soil to allow for degradation.

Reaction Rate Constants and Conceptual Model. By careful analysis of **Figures 2** and **3** and using several assumptions, a model describing the behavior of fipronil can be deduced to aid in understanding the fate of fipronil in flooded soils (**Figure 5**). Rate constants for each process are shown in **Table 3**. The main assumptions of the model are that (1) fipronil cannot be degraded when sorbed to the soil and must desorb to degrade, (2) fipronil sulfide was not reoxidized to fipronil, and (3) no photodegradation occurred because the experiment was conducted in the dark. The fipronil sorption ($k_{\text{fip-ads}}$) constant was calculated from the increase in fipronil in the soil over the first 14 and 28 days on the Yanco and Coleambally soils, respectively. Conversely, the fipronil desorption rate constant ($k_{\text{fip-desor}}$) was calculated from the decrease in fipronil in the soil after the first 14 and 28 days on the Yanco and Coleambally soils, respectively. The rate constant for the reductive degradation of fipronil ($k_{\text{fip-deg}}$) was calculated on the basis of the rate of total fipronil sulfide production over the

Table 3. Sorption and Degradation Rate Constants for Fipronil as Predicted from **Figures 2** and **3** and Calculated Rate Values Using the Fipronil Distribution in Soil and Water
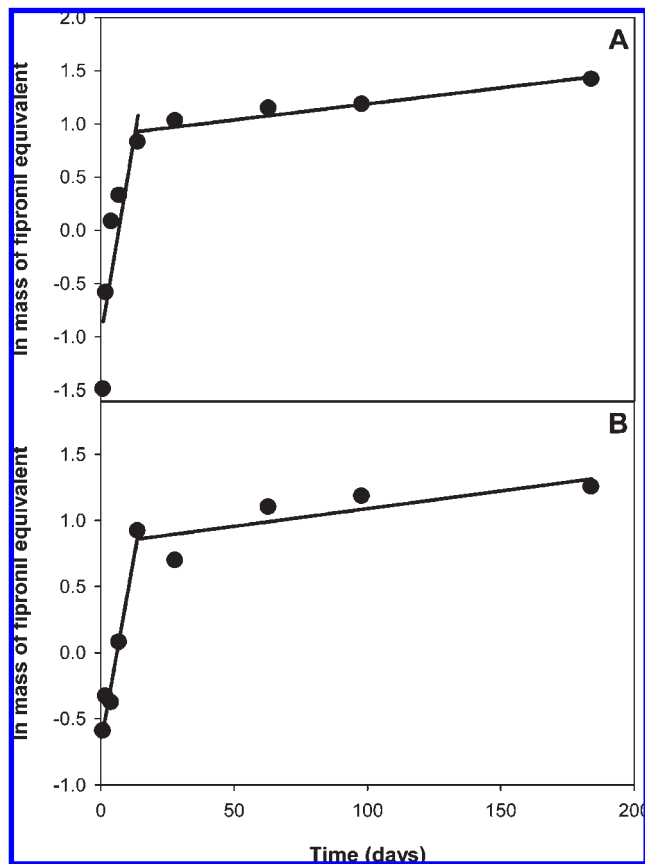
	rate constant ($\times 10^{-2}$ days^{-1})	
rate constant	Coleambally	Yanco
$k_{\text{fip-ads}}$	8.9	5.1
$k_{\text{fip-desor}}$	0.52	0.45
$k_{\text{fip-deg}}$[a]	13.7 (0.2)	11.1 (0.2)
$k_{\text{sulf-ads}}$	14.9	11.3
$k_{\text{sulf-desor}}$	0	0
$k_{\text{fip-deg-ohp}}$	8.8	5.5
$k_{\text{sulf-deg}}$	0	0

[a] $k_{\text{fip-deg}}$ values shown in parentheses represent rate constants for the slower of the two fipronil degradation processes.
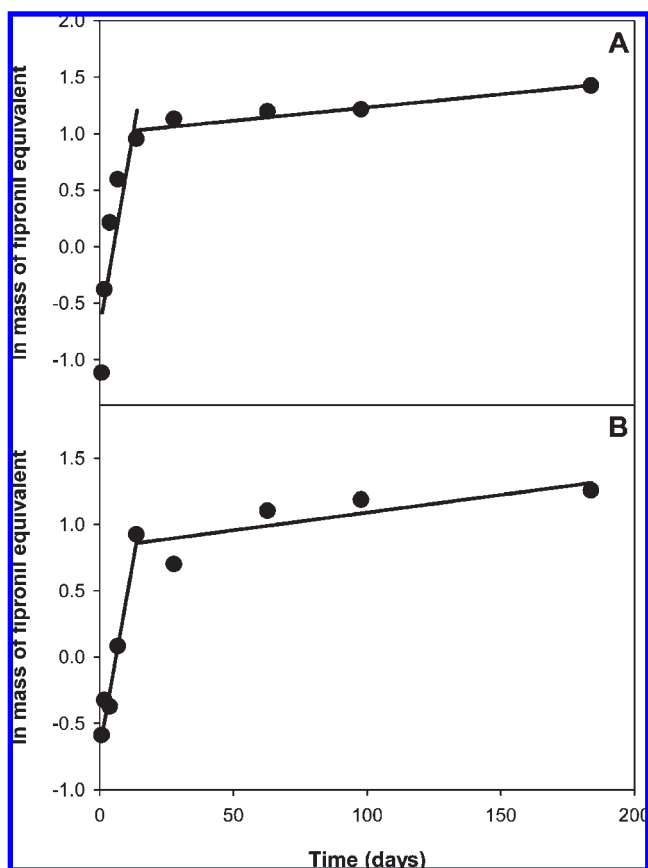
Figure 6. Logarithmic transformations of the total amount of fipronil sulfide in (A) Coleambally and (B) Yanco soils.

Figure 7. Logarithmic transformations of fipronil sulfide recovered from soil in (A) Coleambally and (B) Yanco soils.

Table 4. Comparison of Half-Lives for Fipronil Coleambally and Yanco Soils Based on Faster and Slower Degradation Rates

	half-life (days)	
soil type	faster reaction	slower reaction
Yanco	6.3	431
Coleambally	5.0	296

first 14 days, because logarithmic transformation indicated two separate degradation processes: a rapid phase occurring between days 0 and 14 and a slower phase occurring between days 14 and 184 (**Figure 6**). This type of dual rate degradation process has been reportedly previously for fipronil (*24*). We speculate that this two-stage process is most likely an indication of the availability of fipronil and, thus, its rate of desorption. This is evident from the initial fast rate of fipronil sulfide production because of rapid desorption from readily accessible soil sorption sites, followed by the slow rate of fipronil sulfide production because of slow desorption from less readily accessible soil sorption sites. Statistical comparison of the gradients indicated a significantly faster rate of fipronil degradation ($p < 0.05$) on the Coleambally soil compared to the Yanco soil.

Logarithmic transformation of the amount of fipronil sulfide in soil indicated two separate linear regions, suggesting two separate sorption processes taking place. The first region occurred between days 0 and 14, and the second occurred between days 14 and 184, with the latter having a slope less than 2% of the former (**Figure 7**). These results suggest that an apparent two-stage sorption process for fipronil sulfide occurred, but because of the very low application rate of fipronil, it is unlikely that soil sorption sites were saturated. It is more likely that the sorption was dictated by the fipronil degradation rate ($k_{\text{fip-deg}}$). The rate of fipronil sulfide sorption to the soil ($k_{\text{sulf-ads}}$) was therefore calculated on the basis of the faster of the two rates, which occurred over the first 14 days, because this rate was assumed to be less restricted than the slower of the two rates. The rate constant for the oxidation and hydrolysis of fipronil ($k_{\text{fip-deg-ohp}}$) was calculated from the amount of fipronil/fipronil sulfide lost from the system over the first 14 days and was assumed to have occurred in the facultative conditions present in the water column. The rate constant for fipronil sulfide degradation ($k_{\text{sulf-deg}}$) was assumed to be 0 because the concentration of fipronil sulfide did not decrease during the lifetime of the experiment.

Half-life calculations for fipronil were confounded by the sorption-dependent degradation observed in both soils. Fipronil degradation rate constants ($k_{\text{fip-deg}}$) for both the faster and slower reactions are shown in **Table 4**. Fipronil half-lives of less than a week for each soil are predicted using the faster reaction rate, and

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Fipronil half-lives of 300−400 days for each soil are predicted using the slower rate. Closer inspection of **Figures 2** and **3** suggests that half-lives of approximately 50 days are more realistic predictions, which is in accordance with previous studies on fipronil using the same soils (*24*).

The half-life for fipronil degradation in other studies (*32*) has been reported to be approximately 150 days in a model estuarine system compared to less than a week based on the faster of the two reaction rates in the current work. However, the obvious difference in salinity between rice bay soils and estuarine sediments would inevitably result in different microbial populations and, thus, the potential for different degradation rates. Additionally, the high salt concentration in the estuarine system may have promoted sorption to sediments and, hence, decreased the rate of degradation. A half-life of 68 days for fipronil was reported when the moisture content in soil was 60% of MWHC (*20*), with fipronil sulfide the predominant metabolite. The high water content of the soil resulted in conditions that were predominantly chemically reducing, but failure to fully pond the soil made comparison of their results to the results from the current experiment difficult.

No diffusion of fipronil or fipronil sulfide beyond the top 1 cm on Yanco soil and minimal diffusion beyond the top 1 cm on Coleambally soil suggests that diffusion plays little role in the mobility of the chemicals in these soils. Short half-lives predicted the rapid degradation of fipronil in both soils, which was accompanied by a rapid increase in the fipronil sulfide concentration. While fipronil sulfide accumulated in the soil, it remained relatively immobile, suggesting that the diffusion of fipronil sulfide or fipronil poses no significant risk to the contamination of subsurface water sources.

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