ABTIc PROCESSES INFLUENCING FIPRONIL AND DESTHIOFIPRONIL DISSIPATION IN CALIFORNIA, USA, RICE FIELDS

KENLEY K. NGIM and DONALD G. CROSBY*
Department of Environmental Toxicology, University of California, One Shields Avenue, Davis, California 95616, USA

(Received 29 February 2000; Accepted 31 October 2000)

Abstract—Fipronil insecticide dissipated in California rice fields, producing half-lives of 10.5 to 125 h in water and 44.5 to 533 h in soil, depending on the formulation applied and the resulting differences in water solubility. The major degradation products were desthiofipronil in water and fipronil-sulphide in soil, while the sulphone and amide were less abundant. Fipronil was photolysed rapidly to desthiofipronil in deionized water in the laboratory ($t_{\frac{1}{2}} = 7.97-9.42$ h) and even faster in the presence of H$_2$O$_2$ ($t_{\frac{1}{2}} = 0.874-4.51$ h). Fipronil was also hydrolysed to amide in base ($t_{\frac{1}{2}} = 542$ h at pH 9) and volatised slowly from water ($H = 6.60 \times 10^{-6}$ m$^3$ atm/mol), properties not explaining its rapid field water dissipation. Desthiofipronil was more stable than fipronil to direct photolysis ($t_{\frac{1}{2}} = 120-149$ h), was indirectly photolysed in the presence of H$_2$O$_2$ ($t_{\frac{1}{2}} = 0.853-3.76$ h), and was nonvolatile from water. The desthiofipronil observed in field water was formed photochemically from fipronil, accumulated due to slower photolysis and lack of volatility from water, but eventually dissipated.

Keywords—Phenylpyrazole Photodegradation Hydrolysis Volatility Pesticide

INTRODUCTION

Fipronil is a broad-spectrum insecticide applied to a number of crops worldwide [1]. Its phenylpyrazole structure is novel to the agrochemical industry [2], and its unique trifluoromethylsulphonyl sidechain may account for its toxic properties [3]. Fipronil exhibits high specificity toward insects [1], acts by blocking the $\gamma$-aminobutyric acid gated chloride channel [1,2,4,5], and is effective against insects with resistance or tolerance to pyrethroid, cyclodiene, organophosphorus, and carbamate insecticides [1,4]. In California flooded rice, fipronil has been tested as an alternative to carbofuran [6] to control rice water weevils (Lissorhoptrus oryzophilus).

We wished to characterize the abiotic fate of fipronil under California growing conditions, as little has been reported on its environmental fate [3,7,8]. During the June through October growing season, flooded fields (typically 4–6-cm water depth) are subjected to intense summer sunlight irradiance ($\approx 2,800$ $\mu$W/cm$^2$ at 365 nm) and to daily pH (6.8–8.3) and temperature (14–34$^\circ$C) fluctuations [9], making photolysis, hydrolysis, or aqueous volatilization possible. Oxidative transformations would prevail in water, while all but the top $\approx 1$ cm of flooded soil would be reducing [10].

The photodegradation of fipronil to its desthio analog may provide one route of its decomposition [3,7]. Desthiofipronil was insecticidal and stable on leaf surfaces [3], leading to possible persistence and nontarget toxicity in the environment. However, available reports [3,7] addressed neither the aqueous photodegradation of desthiofipronil nor other possible dissipation routes. Our purpose was to determine the dissipation kinetics of fipronil in rice field water and soil and the relative importance of photolysis, hydrolysis, and volatilization as potential aquatic dissipation routes for fipronil and desthiofipronil.

MATERIALS AND METHODS

Reagents

Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile, 99.4% purity) and its corresponding desthio (99.4%), sulphone (99.2%), sulphone (100.0%), and amide (98.7%) derivatives were provided by Rhône-Poulenc Agro (Research Triangle Park, NC, USA). Commercial formulations of fipronil (Icon®), including 80WDG (dry flowable), 1.67SC (soluble concentrate), and 1.5G (granular), were also supplied by Rhône-Poulenc. Hydrogen peroxide (30%, American Chemical Society [ACS] reagent grade) was purchased from Aldrich (Milwaukee, WI, USA) and Optima® grade organic solvents from Fisher Scientific (Pittsburgh, PA, USA). Other inorganic reagents (all certified ACS or ACS Plus) were from Fisher Scientific. Deionized water was prepared by a Corning Megapure® distillery (Dubuque, IA, USA).

Field application and analysis

During the 1995 to 1997 growing seasons, field treatments began prior to rice seeding from the last week of May through mid-June for unflooded treatments, while those at the rice three-leaf stage started roughly two weeks after flooding; field preparations and treatments were representative of California, USA, growing conditions. Dry flowable (28.0 g a.i./ha, 560 g a.i./ha), granular (28.0 g a.i./ha), and soluble concentrate (42.6 g a.i./ha) formulations of fipronil were applied to 18.6-m$^2$ (6.10 m × 3.05 m) plots enclosed by sheet-metal walls at the Rice Experiment Station (Biggs, CA, USA); the 560 g a.i./ha dosage rate was intended to ensure detectability but represents an unrealistic treatment. Also using the dry flowable (36.4 g a.i./ha), a similar 83.6-m$^2$ (9.14 m × 9.14 m) trial was made in a large commercial basin (Richvale, CA, USA), along with an unconfined 10,700-m$^2$ treatment (Pleasant Grove, CA, USA). For the soluble concentrate, a pair of unconfined trials (4,090 m$^2$, 12,100 m$^2$) were run at another commercial field (Sheridan,
CA, USA). Dry flowable and soluble concentrate were applied by backpack sprayer to the 18.6-m² enclosures and by ground rig to commercial fields; granules were distributed by hand in 18.6-m² trials. Treatments to unflooded soil were followed by irrigation after application to commercial fields; granules were distributed by hand in 18.6 m² trials. Treatments to unflooded soil were followed by irrigation after application to commercial fields; granules were distributed by hand in 18.6 m² trials.

### Table 1. Rice field applications of fipronil and resulting water and soil half-lives

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Location (CA, USA)</th>
<th>Plot size (m²)</th>
<th>Rate (g a.i./ha)</th>
<th>Application mode</th>
<th>Water ½ life (h)</th>
<th>Soil ½ life (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry flowable (80WDG)</td>
<td>Biggs</td>
<td>18.6 × 10⁴</td>
<td>28.0</td>
<td>Preflood spray, raked</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Pleasant Grove</td>
<td>1.07 × 10⁴</td>
<td>36.4</td>
<td>Preflood spray, rolled</td>
<td>NA</td>
<td>501</td>
</tr>
<tr>
<td></td>
<td>Richvale</td>
<td>83.6 × 10⁴</td>
<td>36.4</td>
<td>Preflood spray, rolled</td>
<td>22.1</td>
<td>462</td>
</tr>
<tr>
<td>Granule (1.5G)</td>
<td>Biggs</td>
<td>18.6 × 10⁴</td>
<td>28.0</td>
<td>Aqueous distribution, three-leaf rice</td>
<td>125</td>
<td>438</td>
</tr>
<tr>
<td>Soluble concentrate (1.67SC)</td>
<td>Biggs</td>
<td>18.6 × 10⁴</td>
<td>42.6</td>
<td>Preflood spray, raked</td>
<td>77.8</td>
<td>95.9</td>
</tr>
<tr>
<td></td>
<td>Sheridan</td>
<td>1.21 × 10⁴</td>
<td>42.6</td>
<td>Preflood spray</td>
<td>10.5</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>4.09 × 10⁴</td>
<td></td>
<td>42.6</td>
<td>Field drained, three-leaf rice</td>
<td>13.1</td>
<td>59.3</td>
</tr>
</tbody>
</table>

*a Plot confined by sheet metal.

*b Unconfined application.

*c Fipronil not detected within 24 h of treatment and trials discontinued.

*NA = not available.

*a Aqueous analytes undetected in unconfined application.

with a Model 5972A mass-selective detector (Wilmington, DE, USA) operated in full scan mode (m/z 50–500) and a 30-m × 0.25-mm i.d. × 0.25-μm film DB-5MS column (J&W Scientific). Instrument conditions included splitless injection, 275°C (injector), 280°C (transfer line), and a temperature program of 150°C to 270°C at 10°C/min followed by a 23.00-min hold.

### Photolysis

Solutions of fipronil and desthiofipronil (900 μg/L, 1.5 L) were prepared by adding standard to distilled deionized water, magnetically stirring for 24 h, and filtering (0.22 μm) through nylon membranes. Absorption spectra, obtained for fipronil and desthiofipronil (each 5 × 10⁻⁶ M in methanol) with a Hewlett Packard 8451A diode array spectrophotometer, ranged from 193 to 322 nm and 198 to 317 nm, respectively, with a λmax of 208 nm for each; ε₃₀₀ values of 1.53 × 10⁴/M/cm and 7.50 × 10⁴/M/cm were obtained for I and II, respectively.

Solutions were irradiated in borosilicate glass photoreactors [11] containing single 120-cm F40/350BL ultraviolet fluorescent lamps (Sylvania, Westfield, IN, USA). The lamp produced 285 to 480 nm radiation with a maximum output at 365 nm; transmission through the glass filtered out <300 nm light, ensuring representative sunlight ultraviolet (UV) irradiation.

Solution temperature was maintained at 35.0 ± 1.0°C with a tubing coil wrapped around each photoreactor and attached to a constant temperature circulator. For comparison, photoreactor solutions were also sparged with 20 ml/min of medical-grade air. Indirect photolysis experiments were similar except that H₂O₂ was added at 50:1, 200:1, and 500:1 molar ratios. Trials were run in triplicate until about 5% of starting chemical remained and a minimum of five time points were sampled. Duplicate dark controls (900 ml) were held in Teflon-capped amber glass bottles maintained in a 35°C water bath, and indirect photolysis dark controls employed only 500:1 H₂O₂.

Solution pH did not vary during the incubation period of photolysis experiments from the initial pH of 6.6 to 7.0. Samples (25 ml) were analyzed in a manner similar to field water except that 3-ml 500-mg C-18 SPE cartridges (Varian) were used.

### Hydrolysis

The hydrolysis of fipronil to its amide was measured in 0.1 M acetate (pH 5.15), phosphate (pH 7.07), and borate (pH...
9.00) buffers and in deionized water (initially pH 6.6–7.0). Aliquots of 1 L were transferred to Teflon-capped amber glass bottles, spiked with 250 μL of a 1.7 mg/mL solution of methanolic fipronil to give about 425 μg/L, and all trials were maintained at 24.0 ± 1.0°C. Samples (50 mL) were analyzed in the manner of the photolysis samples. Experiments were run in duplicate for 2,200 h or until about 5% of fipronil remained and a minimum of 10 time points were sampled.

Volatilization from water

Triplicate or duplicate borosilicate glass jugs (13 L) containing 7 L of deionized water solutions of fipronil (800 μg/L), desthiofipronil (800 μg/L), molinate (23 mg/L), or nitrobenzene (11 mg/L) were sparged with 200 to 220 mL/min of N₂ through a coarse glass dispersion tube. Solution temperature was 24.0 ± 1.0°C; total exposure time was 800 h for fipronil and desthiofipronil, 2,600 h for molinate, and 600 h for nitrobenzene; and duplicate controls were run simultaneously without gas flow. Aliquots (25 mL) were withdrawn periodically by volumetric pipet, and fipronil and desthiofipronil were analyzed like the photolysis samples.

Molinate was collected on 3-ml, 500-mg C-18 SPE cartridges and eluted with 2 mL of methanol, and the eluates were concentrated to 1 mL. Molinate was determined with an Isco high-performance liquid chromatograph fitted with a UV/Vis detector set at 240 nm (2360 gradient programmer, 2350 pump, high-performance liquid chromatograph fitted with a UV/Vis detector; Lincoln, NE, USA) and a 250-mm × 4.6-mm i.d., 5-μm Altima C-18 column (Alltech, Deerfield, IL, USA) with a matching 7.5-mm guard column carrying a 1-mL/min flow of isocratic acetonitrile:H₂O (70:30). Recoveries of 75% at 6.5-V detector set at 240 nm (2360 gradient programmer, 2350 pump, high-performance liquid chromatograph fitted with a UV/Vis detector; Lincoln, NE, USA) and a 250-mm × 4.6-mm i.d., 5-μm Altima C-18 column (Alltech, Deerfield, IL, USA) with a matching 7.5-mm guard column carrying a 1-mL/min flow of isocratic acetonitrile:H₂O (70:30). Recoveries of 75% at 6.5-

Between 12 and 20 time points were sampled for each trial, and H was calculated from the obtained first-order dissipation rate constant by the method of Mackay et al. [12], which used a similar sparging apparatus. Our calculations used the average of the starting and final solution volumes since the return of spectrophotometrically analyzed samples to the Mackay apparatus made solution volumes constant, while the low water solubility of fipronil (1.9 mg/L at 20°C [13]) and desthiofipronil (0.95 mg/L at 20°C [L. Hodges, Rhône-Poulenc Agro, personal communication]) precluded a nondestructive analysis in this study.

RESULTS AND DISCUSSION

Field studies

The dissipation of fipronil generally followed pseudo–first-order kinetics (r² = 0.85–0.95) for the various formulations applied to 18.6-m² confined plots and to unconfined sections of commercial fields (Fig. 1), resulting in t½ values of 10.5 to 125 h in water and 44.5 to 533 h in soil (Table 1). As a result, low to moderate rice field persistence of fipronil was indicated. An equilibration period up to 36 h in water and 100 h in soil (upon sampling) was necessary to reach maximum concentrations, most likely to allow release from its formulations. Field application rates correlated with the maximum soil concentrations, increasing from 25.3 μg/L for 28.0 g a.i./ha (granules), 37.8 μg/L for 36.4 g a.i./ha (dry flowable), and 52.4 μg/L for 42.6 g a.i./ha (soluble concentrate); field water concentrations showed no such correlation.

The dissipation of fipronil was influenced by formulation. Granular was the most persistent (t½ = 125 h in water, 438 h in soil) and soluble concentrate the least (t½ = 10.5–77.8 h in water, 44.5–95.9 h in soil) (Table 1). The dry flowable treatment was among the least persistent in water (t½ = 22.1–67.6 h) but the most stable in soil (t½ = 462–533 h). Fipronil apparently desorbed slowly from granules, while the soluble concentrate promoted its dispersion in water and soil sorption was minimized. The dry flowable formulation evidently solubilized fipronil similar to the soluble concentrate while retaining soil sorption capabilities comparable with that of granules. The variability in water and soil t½ of soluble concentrate and dry flowable trials are acceptable, given the differences in treatments (i.e., location, plot size and confinement, application mode).

Soil sorption, which apparently differed with the formulation of fipronil applied, would lead to decomposition in this compartment while delaying fipronil transport into water and any subsequent aqueous-phase decomposition. Soil organic matter content was shown to correlate positively with the sorption of various neutral organic compounds [14–16]. Also, the reduction of Fe(III) to Fe(II) in anaerobic soil like that of rice paddies may decrease the mineral surface area available for sorption, as shown for lindane [15]. However, such soil properties were not determined, nor were adsorption or desorption coefficients investigated in this study.

Dissolution was an important fipronil dissipation process. The persistence of fipronil applied as soluble concentrate was up to 7.4 and 2.2 times greater in the water and soil, respectively, of enclosed 18.6-m² unconfined sections of commercial fields at Biggs, CA, USA, and the water (C) and soil (D) of unconfined sections of commercial fields at Sheridan, CA, USA, treated with dry flowable, soluble concentrate, or granular formulations (28.0–42.6 g a.i./ha).

The variability in water and soil t½ of soluble concentrate and dry flowable trials are acceptable, given the differences in treatments (i.e., location, plot size and confinement, application mode).

Soil sorption, which apparently differed with the formulation of fipronil applied, would lead to decomposition in this compartment while delaying fipronil transport into water and any subsequent aqueous-phase decomposition. Soil organic matter content was shown to correlate positively with the sorption of various neutral organic compounds [14–16]. Also, the reduction of Fe(III) to Fe(II) in anaerobic soil like that of rice paddies may decrease the mineral surface area available for sorption, as shown for lindane [15]. However, such soil properties were not determined, nor were adsorption or desorption coefficients investigated in this study.

Dissolution was an important fipronil dissipation process. The persistence of fipronil applied as soluble concentrate was up to 7.4 and 2.2 times greater in the water and soil, respectively, of enclosed 18.6-m² plots than in the 4,090- to 12,100-m² unconfined sections of commercial fields. No residues were detected in water after an application of dry flowable formulation to a 1,070-m² area of commercial field at Pleasant Grove (CA, USA) that represented only a third of the total basin area and was both unconfined and subject to drainage into an adjacent field (Table 1). However, dissolution may be
Environmental fate of fipronil and desthiofipronil product

Fig. 2. Fipronil degradation routes in California, USA, flooded rice fields.

The major degradation products of fipronil were the desthio product in water and the sulfone in soil (Fig. 1) while the sulfoxide and the amide were detected intermittently in water and appeared to be minor. Desthiofipronil formed within 24 h of application in all treatments, attaining maximum concentrations of 1 to 2.3 µg/L (Fig. 1A and C), and was more persistent than fipronil. However, desthiofipronil dissipated to undetectable levels within about 150 h after soluble concentrations of 1 to 2.3 µg/L (Fig. 1A and C), and was more persistent than fipronil. Such rapid dissipation was not observed in confined dry flowable and granule applications. The formation of fipronil-sulfide at up to 14 µg/kg in soil treated with a small enclosures and unconfinned commercial fields treated with soluble concentrate.

Intense UV irradiation typical of field experiments (≥1.386 µW/cm² at 310 nm, ≤3.180 µW/cm² at 360 nm) was measured between May 24 and June 10, 1999, which was acquired to verify a photodechlorination mechanism [K.K. Ngim and D.G. Crosby, unpublished data] but also supported fipronil photodegradation as a rice field dissipation route. Overcast weather during this period diminished the maximum UV intensity (≥555 µW/cm² at 310 nm, ≤1,313 µW/cm² at 360 nm). Although such incidents were rare for fipronil field studies, photolysis would be less prevalent and the overall decomposition rate could decrease, possibly contributing to variability in t₁/₂ for given formulations. Furthermore, the daily ranges in field-water pH (6.8–9.1) and temperature (17.2–36.3°C) were consistently observed in the present study, suggestive of base hydrolysis and volatilization as possible dissipation routes for fipronil and indicating that the observed t₁/₂ variability could not be due to these factors. The decomposition pathways of I in California rice fields are summarized in Figure 2.

Direct and indirect photolysis

The greater persistence of desthiofipronil compared with fipronil in rice field water may be largely explained by their relative rates of photolysis in the laboratory. Pseudo–first-order kinetics (r² = 0.98–0.99) were observed in the direct photolysis of aerated and static trials (Table 2), producing t₁/₂ values of 7.97 ± 1.40 and 9.42 ± 2.62 h for fipronil and 120 ± 18 and 149 ± 39 h for desthiofipronil (n = 3 for all). The more rapid dissipation in aerated trials was likely from using different sets of UV lamps, although volatilization was also suggested. Similarly, variability among individual UV lamps likely explains the standard deviation of these t₁/₂ values (and corresponding rate constants) since excellent r² linear fits were obtained with little variability (up to ±0.02). Our findings with fipronil were similar to those of Bobe et al. [7], who reported a t₁/₂ of 4.1 h, the difference possibly attributable to the light source and their acidic solutions (pH 5.5) containing methanol.

Table 2. Half-lives and rate constants for the photolysis of I and II

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Experiment</th>
<th>t₁/₂ (h)</th>
<th>−k (h⁻¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fipronil</td>
<td>Direct (aerated)</td>
<td>7.97 ± 1.40</td>
<td>0.0855 ± 0.0195</td>
<td>0.98 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Direct (static)</td>
<td>9.42 ± 2.62</td>
<td>0.0789 ± 0.0254</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Direct (combined)</td>
<td>8.70 ± 2.04</td>
<td>0.0822 ± 0.0206</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Dark control</td>
<td>Stable for 45 h</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Indirect (500:1)</td>
<td>0.874 ± 0.200</td>
<td>0.825 ± 0.211</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Indirect (200:1)</td>
<td>1.09 ± 0.27</td>
<td>0.481 ± 0.150</td>
<td>1.0 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>Indirect (50:1)</td>
<td>4.51 ± 0.76</td>
<td>0.158 ± 0.032</td>
<td>0.97 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Dark control (H₂O₂, 500:1)</td>
<td>Stable for 30 h</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Desthiofipronil</td>
<td>Direct (aerated)</td>
<td>120 ± 18</td>
<td>0.00589 ± 0.0085</td>
<td>0.99 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Direct (static)</td>
<td>149 ± 39</td>
<td>0.00482 ± 0.00132</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Direct (combined)</td>
<td>134 ± 32</td>
<td>0.00535 ± 0.00115</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Dark control</td>
<td>Stable for 420 h</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Indirect (500:1)</td>
<td>0.853 ± 0.078</td>
<td>0.817 ± 0.071</td>
<td>1.0 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>Indirect (200:1)</td>
<td>1.44 ± 0.30</td>
<td>0.495 ± 0.105</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Indirect (50:1)</td>
<td>3.76 ± 1.77</td>
<td>0.209 ± 0.078</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Dark control (H₂O₂, 500:1)</td>
<td>Stable for 30 h</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

ᵃ nâ = 3 for trials, n = 2 for controls.
ᵇ NA = not available.
ᶜ Molar ratios of H₂O₂: fipronil or desthiofipronil.
Dark controls for fipronil and desthiofipronil were stable for the duration of experiments (45 and 420 h).

The photolysis of fipronil to desthiofipronil (Fig. 3A) started almost instantaneously and produced a maximum yield of about 50%, indicating that the presence of desthiofipronil in field water was due to a photochemical reaction. Using aqueous methanol solutions, Hainzl and Casida [3] proposed that desthiofipronil is formed by the direct photodesulfinylation of fipronil, while Bobe et al. [7] suggested that the reaction proceeds through the sulfone. We identified minor quantities of sulfone and amide (<5 µg/L total) in both UV and dark trials, which, with desthiofipronil, still did not provide a mass balance. It is possible that desthiofipronil was photolyzed to other products as it formed or that fipronil was oxidized to its sulfone, identified by gas chromatography-mass spectroscopy spectra interpretation. Furthermore, the stability of fipronil and desthiofipronil for 30 h in dark controls (500:1 molar ratio) verified that a photochemical reaction had occurred. Hydrogen peroxide is present in sunlit natural waters [17] and is readily converted to HO• by UV radiation [18]. Hydroxyl radical is known to react indiscriminately with pesticides [18,19] and other compounds [20] and has been quantified in various natural waters [21].

**Hydrolysis**

Fipronil was hydrolyzed at the nitrile group to amide in a base-catalyzed reaction following pseudo-first-order kinetics at pH 9 ($r^2 = 0.97 \pm 0.01$) to yield a $t_{1/2}$ of 542 ± 66 h ($n = 2$) (Fig. 3B). While the duplicate trials precluded statistical significance, the mean and standard deviation are reported here due to the quality and invariance of the $r^2$ linear fit. However, fipronil was stable to hydrolysis at pH 7 and pH 5 buffers (<5 and <1% of fipronil-sulfide formed after 2,200 h, respectively), the former also comparable with the deionized water trial. Traces of sulfone were observed in all hydrolysis solutions, in agreement with its previous detection in the solutions of photolyzed fipronil and its dark controls. Our results are comparable with those of Bobe et al. [7], who reported a $t_{1/2}$ of 770 h at pH 9 (22 ± 2°C), found 80% of fipronil unchanged after 100 d at pH 5.5 and 7.0, and showed that the rate of hydrolysis was directly proportional to pH between pH 9 and 12. The difference in the hydrolytic $t_{1/2}$ values could be due to the use of higher fipronil solution concentration (2.5 mg/L) and to aqueous methanol by Bobe et al. [7]. Since pH 9 is approximately the upper limit in rice field water, hydrolysis of fipronil was indeed possible during field studies. Still, the hydrolytic $t_{1/2}$ is rather long compared with that of photolysis (9.42 h), making it less important in the field dissipation of fipronil, consistent with the trace quantities of amide found in rice field water.

**Vaporization from water**

The Henry’s law constants (m³-atm/mol) measured experimentally with our bubble chambers ($H_{exp}$) were similar to calculated values ($H_{calc}$) (Table 3), as determined by the expressions

$$H_{calc} = P_v/S$$

$$H_{exp} = -kVRT/G$$

where $P_v$ is the vapor pressure (atm), $S$ is the solubility (mol/m³), $k$ is the first-order dissipation rate constant (s⁻¹) from a plot of ln($C/C_0$) versus time, $V$ is the solution volume (m³), $R$ is the gas constant (8.058 × 10⁻⁵ atm·m³/K·mol), $T$ is the temperature (K), and $G$ is the $N_2$ flow rate (m³/s). Equation 1 is used widely for estimating $H$, while Equation 2 was derived by Mackay et al. for the volatilization of nonpolar pollutants from water [12].

The similarity of $H_{exp}$ and $H_{calc}$ for nitrobenzene (1.78 ± 0.01 × 10⁻⁵ and 1.3 × 10⁻⁴, respectively) and molinate (7.25 ± 0.61 × 10⁻⁷ and 1.6 × 10⁻⁶, respectively) validated the sparging chamber for estimating Henry’s law constants. However, while nitrobenzene (n = 3) dissipated with an excellent linear fit ($r^2 = 0.99 \pm 0.01$), indicative of pseudo-first-order dissipation, that of molinate was relatively poor ($r^2 = 0.74 \pm 0.01$) and suggestive of nonequilibrium partitioning between the gas phase and aqueous solution. Although molinate trials
Environmental fate of fipronil and desthiofipronil product

Table 3. Comparison of Henry’s Law constants

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$H_{alc}$ (m$^3 \cdot$atm/mol)</th>
<th>$H_{exp}$ (m$^3 \cdot$atm/mol)</th>
<th>$-k$ (h$^{-1}$)</th>
<th>$r^2$</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fipronil$^b$</td>
<td>8.5 $\times$ 10$^{-10}$</td>
<td>6.60 $\pm$ 2.74 ($\times$ 10$^{-4}$)</td>
<td>5.18 $\pm$ 2.15 ($\times$ 10$^{-2}$)</td>
<td>0.91 $\pm$ 0.04</td>
<td>Stable for 800 h</td>
</tr>
<tr>
<td>Desthiofipronil$^b$</td>
<td>1.6 $\times$ 10$^{-8}$</td>
<td>Stable for 800 h</td>
<td>NA</td>
<td>NA</td>
<td>Stable for 800 h</td>
</tr>
<tr>
<td>Molinate$^b$</td>
<td>1.6 $\times$ 10$^{-6}$</td>
<td>7.25 $\pm$ 0.61 ($\times$ 10$^{-2}$)</td>
<td>5.70 $\pm$ 0.48 ($\times$ 10$^{-2}$)</td>
<td>0.74 $\pm$ 0.01</td>
<td>Stable for 2,600 h</td>
</tr>
<tr>
<td>Nitrobenzene$^a$</td>
<td>1.3 $\times$ 10$^{-5}$</td>
<td>1.78 $\pm$ 0.01 ($\times$ 10$^{-2}$)</td>
<td>1.40 $\pm$ 0.07 ($\times$ 10$^{-3}$)</td>
<td>0.99 $\pm$ 0.01</td>
<td>Stable for 600 h</td>
</tr>
</tbody>
</table>

$^a$H = 3.
$^b$n = 2 (including unsarged controls).
$^c$NA = not available.

were only performed in duplicate, the variability of $H_{exp}$ and the corresponding $r^2$ linear fit was minimal, so repeat trials would not have improved the results. Varying the N$_2$ flow rate could have improved the linear fit of molinate dissipation but was not pursued.

The $H_{alc}$ for fipronil and desthiofipronil (8.5 $\times$ 10$^{-10}$ and 1.6 $\times$ 10$^{-8}$, respectively) indicates that water ($H$ of 10$^{-7}$ atm-m$^2$/mol) volatilizes more rapidly, which would result in both compounds concentrating in field water in the absence of alternate degradation or transport. Indeed, duplicate desthiofipronil trials were stable to sparging for 800 h, which may contribute to its observed persistence in field water. However, the $H_{exp}$ of 6.60 $\pm$ 2.74 ($\times$ 10$^{-4}$) for fipronil ($n = 3$) indicated that it would volatilize slowly from rice fields; the $H_{exp}$ variability was to be expected for a chemical comparable in aqueous volatilization with water itself. Although the $H_{exp}$ of fipronil differs from its $H_{alc}$ by four orders of magnitude, the stability of fipronil in unsarged controls indicates no loss from glass adsorption or degradation, and the pseudo–first-order dissipation ($r^2 = 0.91 \pm 0.04$) attests to the quality of the $H_{exp}$ value. The discrepancy may be due to the errors in vapor pressure and solubility estimations, possibly to be expected for a compound with such low $P_c$ (2.8 $\times$ 10$^{-5}$ mm Hg [13]).

CONCLUSIONS

Overall, fipronil exhibited low to moderate persistence in California rice field water and soil, and the soluble concentrate formulation possessed the most favorable dissipation characteristics. The dissipation of fipronil and desthiofipronil in field water can be explained by a combination of photolysis, hydrolysis, and volatilization, as confirmed by laboratory experiments. In the laboratory, fipronil degraded in water principally by photolysis, while base hydrolysis and volatilization from water were less important; desthiofipronil was produced photochemically from fipronil and underwent slower photolysis and no volatility, although it eventually dissipated. Reduction to fipronil-sulfide was the principal degradation route for fipronil in soil.

Acknowledgement—We thank L. Godfrey, L. Beem, A. Moore, J. Scheidel, and B. and W. Vineyard for commercial field applications and Rhône-Poulenc Agro for a gift of materials. This work was supported by the California Rice Research Foundation and a Jastro-Shields Research Scholarship.

REFERENCES
