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# Photodegradation of Imidacloprid and Fipronil in Rice–Paddy Water

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**Abstract** Photodegradation of insecticides, imidacloprid and fipronil, in rice–paddy water under the ambient temperature was investigated. The initial concentrations were set at 58.8 and 3.1 μg/L for imidacloprid and fipronil, respectively, according to their reported initial concentrations in the rice–paddy field. The half-lives ($DT_{50}$) of imidacloprid and fipronil were 24.2 and 36.7 h, respectively. Fipronil desulfinyl was detected as a major metabolite and fipronil sulfone was found to be a minor metabolite of fipronil in the photodegradation process. Detected mass of fipronil, fipronil desulfinyl, and fipronil sulfone at 79 h were 12.9%, 45.8%, and 5.2% of initial fipronil mass, respectively.

**Keywords** Photodegradation · Imidacloprid · Fipronil · Rice–Paddy water

Imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidene-amine), and fipronil (5-amino-1-[2, 6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carbonitrile), are systemic insecticides that have been used popularly worldwide for controlling broad spectrum of insects (Liu et al. 2002; Aajoud et al. 2003). Imidacloprid has a low mammalian toxicity and high insecticidal effectiveness (Fossen 2006), meanwhile, fipronil has a high efficacy in pest control even at a low field application rate (Aajoud et al. 2003). In Japan, imidacloprid and fipronil are popularly used in rice nursery-box application for controlling of sucking insects, nephotettix cincticeps, planthoppers, and cnaphalocrocis medinalis in rice production. The dissipation of those insecticides in the rice paddy field has been reported for imidacloprid (Phong et al. 2009; Thuyet et al. 2011) and fipronil (Doran et al. 2009). However, the environmental fate of imidacloprid (Tisler et al. 2009) and fipronil (unpublished data) is rather inconsistent depending on various factors including environmental and field conditions. Recent reports indicated that photodegradation is the major degradation pathway for imidacloprid (Fossen 2006) and fipronil (Gunasekara et al. 2007) in the aquatic environment. The photodegradation of imidacloprid (Moza et al. 1998; Wamhoff and Schneider 1999; Schippers and Schwack 2008) and fipronil (Bobe et al. 1998; Ngim et al. 2000; Raveton et al. 2006) have been investigated under controlled conditions in the laboratory. However, photodegradation of imidacloprid and fipronil in rice–paddy water under ambient temperature have not been reported. In addition, several metabolites of fipronil have a higher toxicity than fipronil itself (Gunasekara et al. 2007), thus monitoring the fate of those metabolites is also important for the risk assessment. A better understanding of photodegradation pathway of those insecticides in the rice–paddy environment is required in the risk assessment and management of pesticides in the aquatic ecosystem for sustainable rice production. Therefore, the aim of this study was to monitor and investigate the behavior of imidacloprid and fipronil, and the formation of the toxic metabolites of fipronil during the photodegradation process in rice–paddy water.

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## Materials and Methods

Imidacloprid, fipronil, fipronil sulfone standards (≥99% purity), and acetonitrile analytical grade solvent (Wako, Japan); Fipronil desulfinyl, Fipronil sulfide standards (Accustandard, USA); and a Milli-Q Water Purification System (Millipore, USA) were used for chemical analysis.

Concentration of imidacloprid and fipronil was monitored under the ambient condition with and without sunlight. It was assumed that pesticide dissipation under the dark condition was due to the biochemical degradation, and that under the natural sunlight was due to the total effect of biochemical degradation and photodegradation. Therefore, the pesticide concentration solely due to photodegradation was determined by subtracting the pesticide concentration obtained in the experiments without light from that obtained under the natural sunlight condition.

Pesticide-free rice–paddy water was collected from the experimental paddy field of Tokyo University of Agriculture and Technology in Fuchu, Tokyo, Japan. Water samples were filtered through 1.2-μm glass fiber filters (GF/C; Whatman) then used for photodegradation experiments. The experiments were conducted at lysimeter facility ( Watanabe et al. 2008) in National Institute for Agro-Environmental Sciences (NIAES) from 12 to 15 October, 2010 for imidacloprid, and from 18 to 21 October, 2010 for fipronil, respectively.

Ten litters of each pesticide solution having a concentration of 60 μg/L for imidacloprid and 3 μg/L for fipronil were prepared separately. These concentrations were set from the field experimental data for imidacloprid (Phong et al. 2009; Thuyet et al. 2011) and fipronil (Thuyet et al. 2010a). The pesticide solution was divided 2.5 L each into four round glass containers (24 cm diameter × 7 cm height). Two containers, considered as replicates of the treatment, were covered by quart glass plates (Fujiwara Seisakusho, Japan), which allow about more than 90% of solar radiation (280–2,000 nm) to pass through, to minimize the UV attenuation (Watanabe and Takagi 2000). The other two containers, considered as replicates of the control, were covered by glass lids and wrapped with aluminum foils to prevent the sunlight from entering the solution. These solutions were kept under ambient condition for 53 and 79 h for imidacloprid and fipronil, respectively. The ultraviolet B range (280–315 nm) (UVB) radiation was monitored by MS-210 w UVB sensors (Eiko Co. Ltd., Japan) placed next to lysimeter facility. The water temperature was also monitored by temperature sensors placed in the water containers of the control and the treatment. The air temperature was downloaded from a weather station located about 2 km from the experimental facility.

In order to measure the concentration of pesticide in the solution, 4 mL of water sample was collected at 0, 0.5, 1, 2, 4, 7, 19, 24, 27, 31, 43, 48, 53 h for imidacloprid, and at 0, 0.5, 1, 2, 4, 6, 9, 21, 23, 26, 33, 45, 46.5, 51, 55.5, 75, 79 h for fipronil from each solution by using a 5 mL-syringe. They were, then, filtered through 0.2 μm syringe filters (Whatman). A part of filtered sample was kept in a 1.5 mL-vial and stored in dark at 4°C until analysis. All the samples were analyzed by ultra performance liquid chromatography (UPLC)-MSMS within 1 day after the sampling.

ACQUITY UPLC System (Waters, USA) linked with a Micromass Quattro micro API Tandem Quadrupole system (Waters, USA) was used for the chemical analysis. The chromatograph was equipped with a ACQUITY UPLC BEH Phenyl Column (1.7 μm, 2.1 × 100 mm), kept at 40°C. The pump was set in isocratic mode at a flow rate of 0.3 mL/min using a mobile phase of acetonitrile-water acidified with 0.1% of acetic acid (20:80, v/v) for imidacloprid and (55:45, v/v) for fipronil and its metabolites, respectively. Mass analysis of imidacloprid was reported in a recent publication (Thuyet et al. 2010b). Mass analysis of fipronil and its metabolites was performed with a Z-spray source for negative electrospray ionization (ESI) using multiple-reaction monitoring (MRM) scan mode. Both UPLC and MS/MS were controlled by MassLynx 4.1 software (Waters). The capillary voltage was adjusted to 3.5 kV. The ionization source was heated to 100°C and the desolvation temperature was set to 350°C. Dry nitrogen (≥99.5%) was used as the desolvation and nebulization gas. Argon (>99.999%) was used as the collision gas. Ions were fragmented by collision with argon gas at $5.9 \times 10^{-3}$ mbar. The nitrogen flow rate and cone gas flow were set to 500 L/h and 100 L/h, respectively. Dwell times of 0.1 s were used. The cone voltage and collision voltage ranged 20–25 V, and 5–20 eV, respectively. The products of 435, 451, 387, 383 m/z were used for qualification, and 330, 415, 351, 262 m/z were used for confirmation of fipronil, fipronil sulfone, fipronil desulfinyl and fipronil sulfide, respectively. The sample injection volume was 10 μL. The recoveries of imidacloprid, fipronil, fipronil sulfone, fipronil desulfinyl and fipronil sulfide were 100.0 ± 2.2%, 99.2 ± 3.4%, 97 ± 2.1%, 98 ± 3.2% and 97 ± 3.0%, respectively and the corresponding limits of detection were 0.3, 0.05, 0.05, 0.05, and 0.09 μg/L, respectively.

## Results and Discussion

Monitored temperatures of ambient air and tested water in imidacloprid and fipronil experiments were in a similar range (Fig. 1a, b). The average temperatures of tested water in the control, that in the treatment and the ambient air were 23.1 ± 2.8, 24.9 ± 5.6, and 21.3 ± 1.7°C for

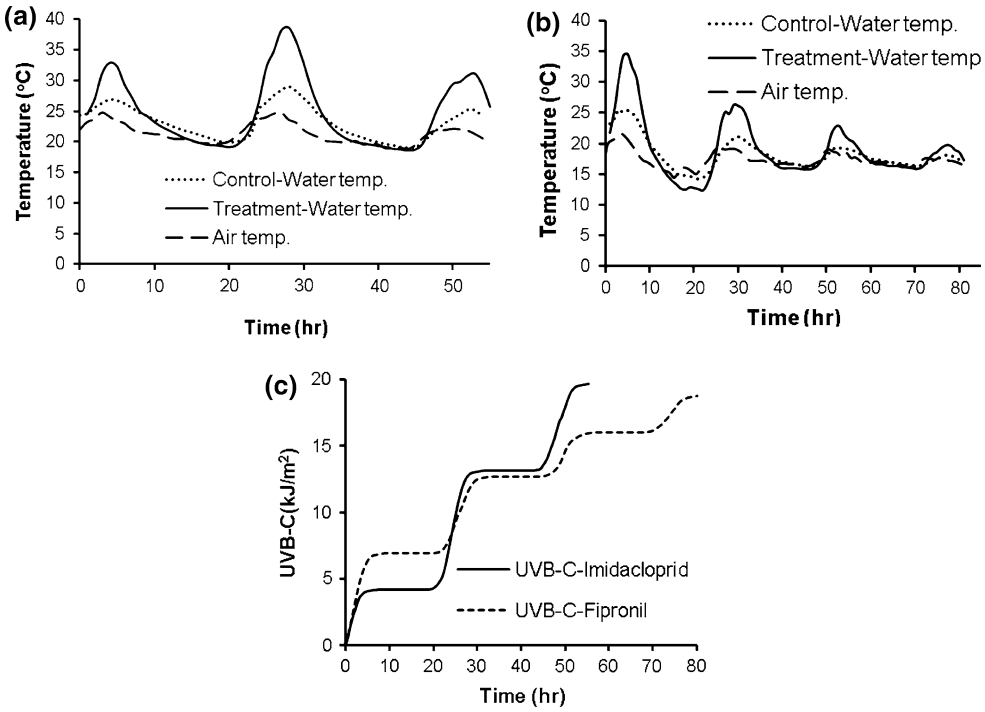


**Fig. 1** Air and water temperature of imidacloprid (**a**) and fipronil (**b**) experiments, and their cumulative UVB energy (**c**) at ambient condition

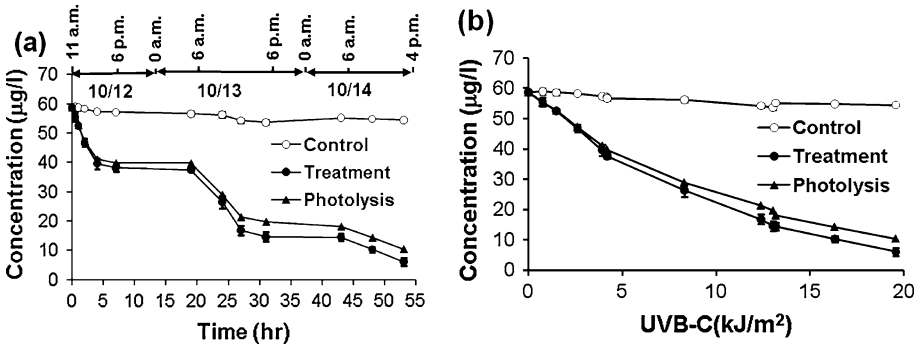


**Fig. 2** Concentrations of imidacloprid in rice paddy water for the control, the treatment and those due to photolysis with respect to time (**a**) and those with respect to cumulative UVB (**b**)

imidacloprid experiment and 18.3 ± 2.6, 19.1 ± 4.9 and 17.4 ± 1.4°C for fipronil experiment, respectively. Figure. 1a, b show that the temperature at noon of the treatment seems to be higher than the control due to the heat supplied by the sunlight. However, over the course of the experiment, the difference in the mean temperature between the control and the treatment in both imidacloprid and fipronil experiments was statistically insignificant ($t$ test, two tail, $p = 0.05$). The cumulative UVB energy (UVB-C) was shown in Fig. 1c, after 53 and 79 h of irradiation of the natural sunlight, the UVB-C was 19.6 and 18.7 kJ/m$^2$ for imidacloprid and fipronil experiments, respectively. The daily average of UVB-C was 6.8 ± 2.3 kJ/m$^2$. The paddy water had pH 7.8 ± 0.1, EC of 33.4 ± 0.2 µS/cm and Eh of 335.0 ± 2.9 mV, which were similar to the data monitored in micro paddy lysimeter and rice paddy field (Nhung et al. 2009).

The concentrations of imidacloprid in the treatment and the control are shown in Fig. 2a, b. The initial average concentration was 58.8 ± 0.1 µg/L, which was similar as the concentration range of imidacloprid in the actual paddy field (Phong et al. 2009; Thuyet et al. 2011). In the treatment, the initial concentration of imidacloprid rapidly decreased to 6.1 ± 1.4 µg/L, after three consecutive days of exposure under the natural sunlight. Meanwhile in the control, its initial concentration decreased slowly to 54.5 ± 0.3 µg/L during the same experiment period (Fig. 2a, b). Moreover, there is a clear difference in dissipation rate in the treatment between day and night (see Fig. 2a, b), indicating that the photodegradation is the major degradation pathway in the rice paddy water.

Figure 3a, b show the dissipation of fipronil (F) and the formation of its metabolites in the control and the treatment, respectively. The initial concentration of fipronil was 3.1 ± 0.1 µg/L. After 79 h of exposure under the sunlight in the ambient condition, the concentration of fipronil quickly decreased to 0.4 ± 0.0 µg/L (Fig. 3b), meanwhile, in the dark condition, the concentration slowly decreased to

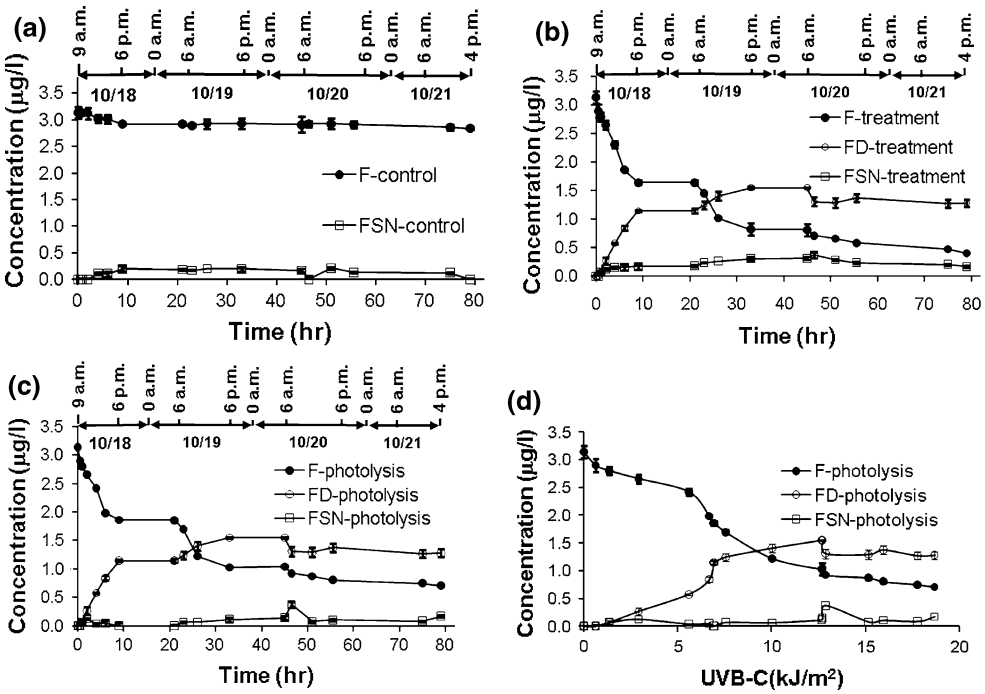


**Fig. 3** Concentrations of fipronil and its metabolites in rice paddy water for the control (**a**), the treatment (**b**) and those due to photolysis with respect to time (**c**) and those with respect to cumulative UVB (**d**)

2.8 ± 0.0 µg/L (Fig. 3a). In the control where hydrolysis and biodegradation supposed to be the driving process of metabolic reactions, fipronil sulfone (FSN) was the only detected metabolite and it peaked at 0.2 ± 0.1 µg/L at 51 h. Whereas, in the treatment, under the natural sunlight, fipronil desulfinyl (FD) and fipronil sulfone were detected as fipronil degraded. Fipronil desulfinyl peaked at 1.5 ± 0.0 µg/L at 45 h and fipronil sulfone peaked at 0.4 ± 0.0 µg/L at 46.5 h, respectively, with different rates (Fig. 3b).

Figure 3c, d show the change of concentrations with time and UVB-C for fipronil and its metabolites in rice paddy water due to photolysis. Fipronil decreased less steadily as compared to imidacloprid and the degradation rate may depend not only on the UVB radiation. Fipronil desulfinyl was detected as the major metabolite of fipronil in the photodegradation process as reported from previous findings (Hainzl and Casida 1996; Bobe et al. 1998; Ngim et al. 2000). Since the rates of decline of fipronil and increment of fipronil desulfinyl seem to have opposite trend, except at about 46 h, the source of formation of fipronil desulfinyl seems to be fipronil. Fipronil desulfinyl peaked at 45 h or 12.7 kJ/m$^2$ at 1.5 ± 0.0 µg/L, and then the level persisted until the end of the experiment. The concentration of fipronil sulfone due to photolysis has been very low during the experiment except sudden jump at 46.5 h. Fipronil sulfide was under the detection limit in this experiment.

The photodegradation rates of imidacloprid and fipronil, and corresponding half-lives ($DT_{50}$) were determined using a first-order kinetics. The photodegradation rate, $k_{photo}$ (1/h), was obtained as the slop of natural logarithm of pesticide concentrations (µg/L), ln(c), versus the exposure period (h). Also, the photodegradation rate, $k_{photo}$ (m$^2$/kJ), with respect to the UVB-C (kJ/m$^2$) was obtained. The results are summarized in Table 1.

Both imidacloprid and fipronil are very sensitive to sunlight. Their $DT_{50}$s were 24.2 and 36.7 h for imidacloprid and fipronil, respectively. However, regarding to the UVB-C, their photodegradation rates were similar such as 0.0870 m$^2$/kJ of imidacloprid and 0.0864 m$^2$/kJ of fipronil,

**Table 1** Photodegradation kinetics of imidacloprid and fipronil in the rice–paddy water

| | Imidacloprid | Fipronil |
|---|---|---|
| *Ln(c) versus time* | | |
| Equations | y = −0.0286t + 3.98 | y = −0.0189t + 0.93 |
| $r^2$ | 0.952 | 0.911 |
| #$k_{photo}$ (1/h) | 0.0286 (0.0329, 0.0243) | 0.0189 (0.0221, 0.0156) |
| #$DT_{50}$ (h) | 24.2 (21.1, 28.5) | 36.7 (31.3, 44.3) |
| *Ln(c) versus UVB-C* | | |
| Equations | y = −0.0870x + 4.07 | y = −0.0864x + 1.18 |
| $r^2$ | 0.997 | 0.976 |
| #$k_{photo}$ (m$^2$/kJ) | 0.0870 (0.0900, 0.0840) | 0.0864 (0.0938, 0.0789) |

y is a natural logarithm of pesticide concentration ln(c)

t is the time after experiment was started (h)

x is the cumulative of UVB energy (kJ/m$^2$)

$r^2$ is the square of the correlation coefficient of y and x, and y and t

#Lower and upper 95% confidence intervals are provided in parentheses

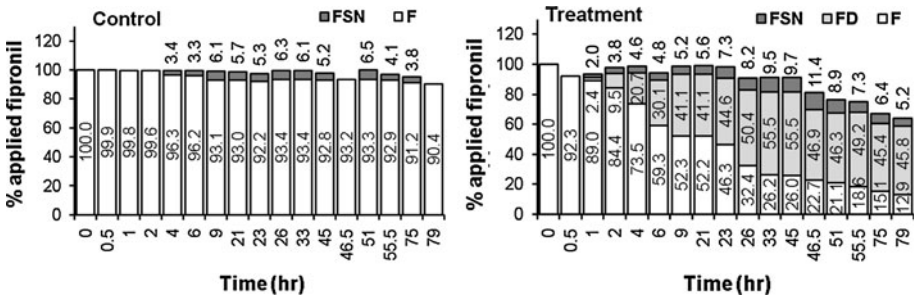


**Fig. 4** Mass balance of fipronil and its metabolites during experiment for the control and the treatment

respectively. According to the measured data, daily average UVB-C for actual cropping period of May 2010 at the same location was about 18.5 ± 8.5 kJ/m$^2$, whereas, during experiment, the daily average UVB-C was 6.8 ± 2.3 kJ/m$^2$. Although, it depends on the local weather, the $DT_{50}$ of both imidacloprid and fipronil in the actual cropping period may be shorter than 24.2 and 36.7 h, respectively.

In a photolysis study of imidacloprid in deionized water, under the irradiation of UV-light $\lambda \geq 290$ nm at 24°C, the $DT_{50}$ was 1.2 h (Moza et al. 1998). Another study using high-pressure mercury lamp reported that the $DT_{50}$ of imidacloprid were 43 min in HPLC grade water for analytical standard, 126 min in tap water for formulated as commercial product, Confidor, and 144 min in tap water in the presence of $TiO_2$ for formulated as Confidor (Wamhoff and Schneider 1999). A study at pH 5.5 using a solar simulator reported that the calculated $DT_{50}$ of fipronil was 4.1 h (Bobe et al. 1998). However, fipronil seem to be more stable in soil, the photolysis $DT_{50}$ in Sauguia, Banizoubou, and Montpellier soil were 147, 178, and 217 h at pH of 5.3, 5.8 and 8.3, respectively (Bobe et al. 1998).

In comparison with other pesticides, imidacloprid and fipronil in the rice–paddy water are more sensitive with solar radiation than herbicide pretilachlor (k = 0.00083 m$^2$/kJ) (Watanabe and Takagi 2000), and herbicide mefenacet (k = 0.0062 m$^2$/kJ) (Watanabe et al. 2006) but similar to insecticide methofluthrin ($DT_{50}$ = 1.1–3.4 day) (Nishiyama et al. 2010).

Figure 4 shows mass balance of fipronil and its metabolites during experiment for the control and the treatment. In the control, fipronil degraded only 9.6% over 79 h in the dark condition. Only small amount of fipronil sulfone was formed and maximum amount accounted for 6.5% of applied fipronil at 51 h. In the treatment, after 79 h of exposure under the natural sunlight condition 87.1% of applied fipronil was degraded. Fipronil desulfinyl and fipronil sulfone accounted for 45.8% and 5.2% of applied fipronil at 79 h, respectively (Fig. 4). The peak formation of fipronil sulfone and fipronil desulfinyl occurred around 45–46.5 h at 11.4% and 55.5% of applied fipronil, respectively. Fipronil sulfide was under the detection limit in this experiment. In both the control and the treatment, the total mass of fipronil and its metabolites at the end of experiment accounted less than 100% of applied fipronil, probably because fipronil was broken down to other minor metabolites or further mineralized over the course of experiment. In the treatment, the total masses of fipronil, fipronil desulfinyl and fipronil sulfone has been more than 95% of applied fipronil until 23 h and gradually decreased to 63.9% at 79 h, indicating that further mineralization occurred after 23 h. Several groups (Hainzl and Casida 1996; Bobe et al. 1998) found four photoproducts such as fipronil detrifluoromethylsulfinyl, fipronil desulfinyl, fipronil sulfide and fipronil sulfone.

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