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Behavior of nursery-box-applied fipronil and its sulfone metabolite in rice paddy fields

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ABSTRACT

The granular insecticide fipronil has been widely applied in rice nursery boxes, both before transplanting (BT) and during at-sowing (AS) treatments to control insect pests at the early stages of rice cultivation in Japan. Although a potential effect of fipronil on paddy ecosystems and downstream aquatic environments has been observed, the environmental effect of this substance in paddy fields remains unsought. Here we investigate the environmental behavior of nursery-box-applied granular fipronil and its sulfone metabolite in paddy water and paddy soils during BT and AS treatments performed in a paddy field in Japan. Although the fipronil concentrations in the paddy water in the AS treatment were significantly lower than those measured in the BT treatment, no significant differences were observed in the paddy soil between the two treatments. Fipronil was mainly found in the 0- to 5-cm surface soil layer of the rice-root zone, where its concentrations were approximately ten times higher than those in the soil of the inter-row zone. The insecticide concentration in the 0- to 1-cm layer of the inter-row zone in the surface soil was approximately 2.5 times higher than that in the 0- to 5-cm layer. The maximum concentrations of fipronil in the 0- to 1-cm surface soil layer ranged from 65.8 to 92.1 μg/kg on the first day after rice transplanting (DAT), and the corresponding values in the paddy water ranged from 0.9 to 2.5 μg/L. The dissipation of fipronil from the paddy water and paddy soil was described by first-order kinetics. The compound's half-life (DT_{50}) was 0.9–3.1 days in paddy water and 12.3–26.4 days in paddy soil. Compared to the BT treatment, the AS treatment may pose a smaller risk to the paddy water and the adjacent environment. Fipronil sulfone was found in every water and soil sample, with the maximum concentrations ranging from 0.4 to 0.9 μg/L in the paddy water and from 9.7 to 59.2 μg/kg in the paddy soil on the third DAT. These values gradually decreased over time. Ecotoxicological risk assessments of fipronil products in rice paddies should not only consider the toxicity of fipronil itself but also that of fipronil sulfone because of its relatively high concentrations in paddy water and paddy soil

1. Introduction

The application of pesticides in rice nursery boxes has become a popular method to control pests during the early periods of rice cultivation in Asia. Fipronil, 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carbonitrile, is a systemic insecticide (Aajoud et al., 2003), which is available as granular formulations and has been popularly used in rice nursery-box applications in Japan to control rice-leaf folders (*Cnaphalocrocis medinalis*) and brown plant hoppers (*Nilaparvata lugens*) (Syobu et al., 2002; Gyoutoku et al., 2007). The total application of granular fipronil has annually increased, and the average application of fipronil granules (1% a.i.) during 1998–2009 was 721 ton/year (JPPA, 2000–2010). In conventional rice cultivation, pesticides are directly applied to nursery boxes (30 cm × 60 cm) containing rice seedlings before these rice seedlings are transplanted into the rice paddy by rice transplanters (Kurogochi, 2003). Depending on the farmer's agricultural practice, fipronil granules can be applied at different periods, such as before transplanting (BT) or at the time of sowing (AS) (Thuyet et al., 2011a).

Flooded paddies are considered as a safe environment for many aquatic species (Tourenq et al., 2001; Bambaradeniya et al., 2004; Wilby et al., 2006). However, extensive use of fipronil may have unfavorable effects on nontarget aquatic organisms, and it has been reported to have a significant ecological impact on aquatic communities in paddy ecosystems (Hayasaka et al., 2012; Sánchez-Bayo et al., 2013). Fipronil and its metabolites have also been detected in aquatic environments, such as in the Sakura River, which flows through a region comprising many paddy fields, during the pesticide application period in May 2008 and 2009 in the Ibaraki prefecture, Japan (Iwafune et al., 2010, 2011). Many studies have

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shown that fipronil sulfone, a fipronil metabolite, has a similar or even greater toxicity to aquatic invertebrates than the parent fipronil (Schlenk et al., 2001; Aajoud et al., 2003; Gunasekara et al., 2007). Iwafune et al. (2011) studied Japanese aquatic organisms and found that the 48-h half maximal effective concentration (EC_{50}) values of fipronil and fipronil sulfone for the caddisfly *Cheumatopsyche brevilineata* (Iwata; Trichoptera: Hydropsychidae) were 0.133 and 0.066 μg/L, respectively, and those for *Daphnia magna* (Straus; Cladocera: Daphniidae) were 42.9 and 5.17 μg/L, respectively. The studies of the environmental impact of fipronil on paddy fields suggest that the dragonfly (*Sympetrum* species) population has rapidly decreased since 1989, and that the observed reduction was positively correlated with the increased use of nursery-box-applied fipronil and imidacloprid (Jinguji et al., 2009; Ueda, 2011). After only nine days of fipronil application in a micro paddy lysimeter, the survival of *Sympetrum infuscatum* decreased to 0% (Jinguji et al., 2012). The use of fipronil has been restricted in China since 2009 owing to its excessive application in fields and its harmful effects on shellfish, bees, and the river environment (Zhao et al., 2011).

Although a potential effect of fipronil on paddy ecosystems has been reported, the environmental fate of nursery-box-applied fipronil granules and its metabolites has not been thoroughly studied to date in rice paddies. The failure to account for the contribution of fipronil sulfone to the total toxicity of fipronil products can lead to a significant underestimation of the toxicity of fipronil containing product to the environment. A better understanding of the behavior of fipronil and its metabolite, fipronil sulfone, in rice paddies is required to minimize the effects of these substances on the environment and nontarget species, as well as to improve the risk assessment in aquatic ecosystems. Therefore, the aim of this study was to investigate the environmental fate of nursery-box-applied granular fipronil and its sulfone metabolite in a Japanese rice paddy under BT and AS treatments.

2. Materials and methods

2.1. Field experiments

Experiments were conducted in two paddy plots of 26 m × 7 m (1 BT and 1 AS) from May 15 to June 20, 2008 and in six paddy plots of 8 m × 6 m (3 BT and 3 AS) from May 15 to June 20, 2009 at the experimental paddy field of the Tokyo University of Agriculture and Technology (TUAT) in Fuchu, Tokyo, Japan. Prior to the experiments, a 15-cm-thick surface soil layer was collected from the experimental field to determine the physical and chemical properties of the soil. The soil's pH was measured by the glass electrode method (JSSSPN, 1997), and the organic carbon content and cation-exchange capacity of the samples were determined following the methods developed by Allison (1965) and Cantino (1944), respectively. The total carbon and total nitrogen contents were measured by the dry combustion method (JSSSPN, 1997). Measurements of the particle density and soil particle distribution were performed following the standard soil particle density test (JSA, 1990) and the pipette method (JSSSPN, 2004), respectively. The soil presented in the experimental plots was a light clay soil with an organic carbon content of 3% (Thuyet et al., 2011a). Further physicochemical properties of this soil are shown in Table 1. The field setup and water management of the paddy plots were similar to those reported in our recent study (Thuyet et al., 2011a). Briefly, the paddy plots were irrigated daily, up to 3 cm during the first week and up to 4 cm during the following weeks if the water level was <3 cm and <4 cm, respectively. Water was held in the paddy plots using plastic borders, and no runoff occurred during the monitoring period, except following large rainfall events. The water-balance components, such as rainfall, evapotranspiration, water level, and surface runoff, are shown in Fig. 1 and Table 2. Rainfall data was collected from the meteorological station at TUAT, evapotranspiration was measured using a lysimeter (30 cm × 50 cm × 30 cm) placed next to the experimental plots, and the water level and surface runoff were recorded using water-level sensors (LSP-100, UIJIN Co. Ltd., Tokyo). Percolation was calculated from the other monitored water-balance components using the water-balance equation (Watanabe et al., 2007). The redox potential (Eh), pH, and electrical conductivity (EC) of the paddy water and soil were also daily monitored during the experimental period (Thuyet et al., 2011a), and the results are shown in Table 1.

Table 1
Physicochemical properties of paddy water and paddy soil (0–15 cm) in the experimental plots.

Water	Value
pH[a]	8.4 ± 0.5
Eh (mV)[a]	528.6 ± 61.0
EC (μS/cm)[a]	206.1 ± 73.8
Soil	**Value**
Eh at 3 cm (mV)[a]	−119.9 ± 144.2
Eh at 1 cm (mV)[a]	333.4 ± 157.5
pH (H_2O)[b]	6.3
Organic carbon content (%)[b]	3.0
Total carbon content (%)[b]	5.2
Total nitrogen content (%)[b]	0.35
Cation exchange capacity ($cmol_c$/kg)[b]	20.1
Particle density (g/cm)[b]	2.58
Sand (%)[b]	40.7
Silt (%)[b]	32.9
Clay (%)[b]	26.4
Soil texture (ISSS)[b]	Light clay (LiC)

ISSS, International Society of Soil Science.
[a] Average values of daily monitored data at 4:00 PM during the experimental period.
[b] Measurement values prior to the experimental period.

The granular insecticide Prince® (1% fipronil; BASF Agro Ltd., Tokyo, Japan) was applied to nursery boxes at the recommended rate of 10 kg/ha. For the AS treatment, the nursery boxes were filled with approximately 2 cm of bed soil, followed by germinated rice seeds, the prescribed amount of granular fipronil, and approximately 1 cm of soil on top at sowing, approximately 14 days before transplanting. Prince® was applied on the surface of the BT-treatment nursery boxes immediately before transplanting. At the time of transplanting, the rice seedlings in the nursery box were 14-days old, approximately 10- to 15-cm tall, and at a leaf stage of around 2–2.5. The rice seedlings for both AS and BT treatments were transplanted to the surface soil with a spacing of 16 cm × 30 cm using a transplanting machine. The average transplanted depth was 4.4 cm from the surface soil in 2009 but was not measured in 2008.

2.2. Sampling and chemical analysis

Five soil samples were collected from each nursery box immediately before transplanting by driving a stainless core (2.5 cm in diameter) from the surface soil down to the bottom of the nursery box to examine the initial fipronil concentrations in the nursery-box soils for the BT and AS treatments performed in 2008 and 2009. Paddy water and a 0- to 1-cm surface paddy soil layer in the inter-row zone were collected on the 1st, 3rd, 7th, 14th, 21st, 28th, and 35th days after rice transplanting (DAT) in both 2008 and 2009, following the methods described by Thuyet et al. (2011a). Briefly, five 125-ml surface water samples were taken from five spots within each paddy plot (i.e., from a central spot and from the four corners) and were then combined into one representative water sample for each sampling day (Thuyet et al., 2011a). Similarly, a composite paddy-soil sample containing five 50-g surface