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Occurrence and ecological risks from fipronil in aquatic environments located within residential landscapes

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HIGHLIGHTS

- Fipronil and degradates evaluated in surface water in residential areas
- Ecological risks estimated for aquatic organisms
- Risks greatest for larval insects and crustaceans in ponds within high density developments

GRAPHICAL ABSTRACT

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ABSTRACT

This study investigated the occurrence of fipronil and its metabolites in aquatic environments in residentially-developed landscapes, including five canals and three retention ponds. Fipronil was detected at four of the sites, with concentrations of 0.5–207.3 ng L^{-1}. Fipronil sulfone and fipronil sulfide were detected at three sampling sites, with concentrations ranging from 0.46 to 57.75 and 0.40–26.92 ng L^{-1}, respectively. Multiple risk assessment methods were performed to characterize potential ecological risks, including deterministic screening and probabilistic risk assessment techniques. The deterministic method indicated no risk to certain biotic groups (i.e. aquatic plants, fish, molluscs, and algae–moss–fungi), but did indicate risks to larval insects and crustaceans. Results from the probabilistic risk assessment indicated significant ecological risks (acute and chronic) ranging from 0.75 to 58.9% and 3.9–35.0% when organisms were exposed to the maximum and median concentrations detected, respectively. The potentially affected fraction of species (PAF) likely to be acutely impacted ranged from 4.6 to 8.1% (fipronil), 0.2–1.6% (fipronil sulfone), and 1.9–3.1% (fipronil sulfide) in the ponds with frequent detectable concentrations. The PAF likely to be impacted at chronic toxicity levels ranged from 16.5 to 23.8% for fipronil. Joint probability curve analysis indicated that concentrations exceeded the LC50 of the most sensitive 5% of species 8.5–18.8% of the time at two of the sites with the most frequent detections. Using the more conservative NOEC/LOEC values, there was a 75–78% probability that concentrations were high enough to negatively affect the most sensitive 5% of species at the same two sites, indicating significant risks for chronic toxicity. JPCs indicated a ≤2.6% probability of fipronil sulfone exceeding the LC50 concentrations

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for the most sensitive 5% of species at the same two sites; and a 4.3–6.8% probability of fipronil sulfide exceeding the LC50 concentrations at the same sites. Results indicate that fipronil and its sulfone and sulfide degradation products may present significant risks to aquatic organisms in some residentially-developed areas.

1. Introduction

Possessing advantages of lower mammalian toxicity, selective insecticidal activity, and lower environmental persistence, phenylpyrazole pesticides have been increasingly used in agriculture, pest control, and landscape maintenance activities (Hainzl et al., 1998; Mize et al., 2008; Vidau et al., 2009). The phenylpyrazoles constitute a relatively new class of chemicals with insecticidal and herbicidal properties (Klis et al., 1991; Yanase and Andoh, 1989). A common phenylpyrazole insecticide is fipronil (average $K_{oc} = 803$, log $K_{ow} = 4.01$) (Mize et al., 2008), which can be transformed into the relatively toxic metabolites fipronil sulfide and fipronil sulfone (Brennan et al., 2009a, 2009b). Fipronil has played an essential role in pest control because of its effectiveness at low field application rates against insects that are resistant to other insecticides such as the pyrethroids, organophosphates, and carbamates (Gunasekara et al., 2007). Due to its widespread usage and chemical properties, occurrence of fipronil in different non-target environments is expected (Brennan et al., 2009b; Chiovarou and Siewicki, 2008; Gan et al., 2012; Mahler et al., 2009). Little information is available regarding the occurrence of fipronil in residential landscapes where it is widely used for fire ant and termite control.

Fipronil, fipronil sulfide, and fipronil sulfone are highly toxic to non-target aquatic larval insects and crustaceans, with median lethal concentration (LC_{50}) values reported as low as 0.008 μg L^{-1} for larval insects (Weston and Lydy, 2014), and 0.56 μg L^{-1} for crustaceans (U.S. EPA, 2000) (Table S1). However, risks of fipronil contamination to non-target aquatic ecosystems are uncertain (Mize et al., 2008). Ecological risk assessment, an important process evaluating the potential adverse environmental effects of chemical, physical, or biological entities (U.S. EPA, 1992), is attracting more and more attention (Hela et al., 2005; Peterson, 2006; Qu et al., 2011; Vryzas et al., 2011). Ecological risks of pollutants to ecosystems are often evaluated using multiple approaches (Hela et al., 2005; Qu et al., 2011; Wang et al., 2009) to obtain a more comprehensive and reliable prediction of risks and uncertainties. The traditional methods for ecological risk assessment often calculate the ratios of the predicted (Verro et al., 2009) or measured environmental concentrations (Hela et al., 2005; Qu et al., 2011; Vryzas et al., 2009, 2011) to some toxicity benchmark. The critical toxicity benchmark values used are usually the lethal concentration to 50% of test organisms (LC50), effective concentration for 50% of test organisms/processes (EC50), or the no observable effect concentration (NOEC) (Hela et al., 2005; Qu et al., 2011; Vryzas et al., 2009, 2011). The use of the HC_5 (hazardous concentration for 5% of the species in the ecosystem) has also been recommended as a toxicity benchmark criterion (Qu et al., 2011; Wang et al., 2009). A probabilistic risk assessment method, first developed by Kooijman (1987) and modified by van Straalen and Denneman (1989), has been used frequently to evaluate ecological risks (Hela et al., 2005; Qu et al., 2011). Likewise, the potentially affected fraction (PAF) of species, based on exposure concentrations of pollutants and species sensitivity distributions (SSD), has also been widely applied to probabilistically characterize ecological risks (Klepper and van de Meent, 1997; Rand et al., 2010; Schuler and Rand, 2008; Traas et al., 2002; Wilson and Boman, 2011).

Usage of fipronil for pest control in agricultural crops is currently banned in China and European countries due to its high toxicity to bees (MOA, 2009; PAN Europe, 2013). In the U.S., it is used for limited agricultural crop production (i.e. potatoes, turnips, and rutabagas) (U.S. EPA, 2005). Other uses include control of household and pet pests (e.g. ants, beetles, cockroaches, fleas, ticks, termites) as well as lawn and landscape pests (e.g. mole crickets, thrips, rootworms). Because of its high toxicity, this study was performed to evaluate its potential environmental impacts resulting from continued use in the U.S. This 11-month monitoring project was developed to: 1) characterize the occurrence of fipronil and its biologically active degradation products in surface water within drainage canals and retention ponds in residentially developed areas; and 2) estimate the ecological risks of fipronil, fipronil sulfide, and fipronil sulfone to the aquatic ecosystems using deterministic and probabilistic approaches.

2. Materials and methods

2.1. Fipronil and degradate occurrence in surface water

Surface water samples were collected from eight drainage canals and ponds located within residential areas in the Indian River Lagoon watershed (Saint Lucie County, FL, USA, Fig. S1). Sites 1 to 5 were canals receiving drainage and runoff water from surrounding residential communities. Sites 6, 7, and 8 were surface water retention ponds receiving runoff water from newer residential communities. Site 1 was in a canal draining part of a community with a housing density of 7–10 houses ha^{-1}. Most homes in this community did not have irrigated lawns. Landscape maintenance intensity varied by property, but most were not manicured. Site 2 was located within a canal draining a golf course community with a housing density of 5–10 houses ha^{-1}. Landscapes were all irrigated, well maintained, and controlled by home owner association (HOA) rules. Sites 3–5 were located on canals draining several high density (10–17 houses ha^{-1}) communities, a golf course, and some other mixed land uses. Landscapes within the communities were irrigated and maintained according to HOA rules. Sites 6 and 7 were terminal retention ponds for several high density communities (17 houses ha^{-1}). Within these communities, some retention ponds were connected to one another so that water would flow towards the terminal discharge ponds when the water holding capacities were exceeded. Excess water flowing into these terminal ponds was ultimately discharged into a tributary of the St. Lucie Estuary. These landscapes were all irrigated and maintenance was coordinated through the HOA. Site 8 was in a pond located within an area similar to Site 1.

Amber glass bottles (1 L) were submerged below the water surface to a depth of approximately 0.76 m to collect samples. All water samples were held on ice until transported back to the laboratory where they were stored in a refrigerator at 4 °C. Extraction of water samples occurred within 24 h of collection. Water samples were collected on a weekly basis from September 2009 to July 2010. In addition to the routine weekly monitoring, a 3-month short term investigation of another four residential lakes (Lake A, Lake B, Lake C, and Lake D) that were located in the same communities as Sites 6 and 7 was also performed to further characterize the presence of fipronil in these communities (sites were chosen based on frequent detections in Sites 6 and 7).

2.2. Sample analysis

The detailed extraction and analysis procedures were described by Wu et al. (2010). Briefly, a liquid–liquid extraction (LLE) method was used to extract pesticides from water samples. Methylene chloride (MeCl) and 4,4′-dibromooctafluorobiphenyl was used as extraction solvent and extraction surrogate, respectively. Each analysis batch always included a method blank, instrument blank, quality control check standard from a second source, matrix spikes (MS), and matrix