Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Comparison of fipronil sources in North Carolina surface water and identification of a novel fipronil transformation product in recycled wastewater

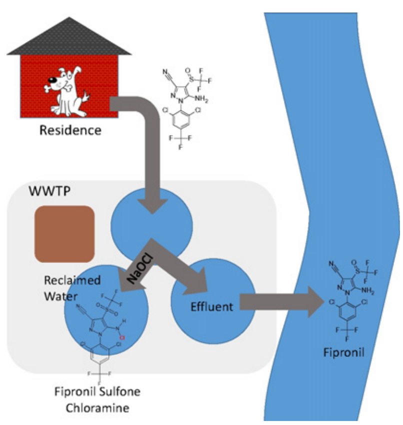
Rebecca L. McMahen [a], Mark J. Strynar [b,*], Larry McMillan [c], Eugene DeRose [d], Andrew B. Lindstrom [b]

[a] United States Environmental Protection Agency, National Exposure Research Laboratory, 109 TW Alexander Dr., Durham, North Carolina 27705, United States
[b] United States Environmental Protection Agency, National Exposure Research Laboratory, 109 TW Alexander Dr., Durham, North Carolina 27705, United States
[c] National Caucus and Center on Black Aged Employee, U.S. Environmental Protection Agency, National Exposure Research Laboratory, 109 TW Alexander Dr., Durham, North Carolina 27705, United States
[d] National Institute for Environmental Health Sciences, Nuclear Magnetic Resonance Facility, 111 TW Alexander Dr., Durham, North Carolina 27713, United States

HIGHLIGHTS

- The most important sources of fipronil in the environment have yet to be determined.
- Sampling was conducted to learn more about the origins of fipronil in surface water.
- High resolution mass spec analysis indicated that fipronil was routinely present.
- Concentrations were substantially elevated near wastewater treatment plant outfalls.
- In recycled water fipronil compounds are oxidized to a novel species.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form 12 May 2016
Accepted 13 May 2016
Available online xxxx

Editor: Adrian Covaci

Keywords:
Fipronil
Source evaluation

ABSTRACT

Fipronil is a phenylpyrazole insecticide that is widely used in residential and agricultural settings to control ants, roaches, termites, and other pests. Fipronil and its transformation products have been found in a variety of environmental matrices, but the source[s] which makes the greatest contribution to fipronil in surface water has yet to be determined. A sampling effort designed to prioritize known fipronil inputs (golf courses, residential areas, biosolids application sites and wastewater facilities) was conducted in North Carolina to learn more about the origins of fipronil in surface water. High resolution mass spectrometry (HRMS) analysis indicated that fipronil and its known derivatives were routinely present in all samples, but concentrations were substantially elevated near wastewater treatment plant outfalls (range 10–500 ng/L combined), suggesting that they predominate as environmental sources. Corresponding recycled wastewater samples, which were treated with NaOCl for disinfection, showed disappearance of fipronil and all known degradates. HRMS and nuclear magnetic resonance

Abbreviations: ACN, acetonitrile; DCM, dichloromethane; DI, deionized; EPA, environmental protection agency; FSC, fipronil sulfone chloramine; GABA, gamma-Aminobutyric acid; gHSQCAD, gradient heteronuclear single quantum coherence; HDPE, high-density polyethylene; HLB, hydrophilic-lipophilic balance; HPLC, high performance liquid chromatography; HRMS, high resolution mass spectrometry; LCL, lowest calibration level; LC/TOF, liquid chromatography time-of-flight mass spectrometry; MeOH, methanol; $MgSO_4$, magnesium sulfate; NaOCl, sodium hypochlorite; NMR, nuclear magnetic resonance; TOF-MS, time-of-flight mass spectrometry; US, United States; WWTP, wastewater treatment plant.

* Corresponding author.
E-mail address: strynar.mark@epa.gov (M.J. Strynar).

http://dx.doi.org/10.1016/j.scitotenv.2016.05.085
0048-9697/Published by Elsevier B.V.

Wastewater
Transformation
High resolution mass spectrometry
Water reuse

(NMR) analysis techniques were used to determine that all fipronil-related compounds are oxidized to a previously unidentified fipronil sulfone chloramine species in recycled wastewater. The implications of the presence of a new fipronil-related compound in recycled wastewater need to be considered.

1. Introduction

Fipronil is a phenylpyrazole insecticide used to control termites, fleas, roaches, ants, and other pests in residential and agricultural settings. Fipronil has been found in various environmental media (residential runoff (Gan et al., 2012; Sengupta et al., 2016), surface water (Karen et al., 2010; Stone et al., 2014), wastewater (Heidler and Halden, 2009), indoor and outdoor dust (Mahler et al., 2009), etc.). It is known to undergo degradation to form a number of transformation products, notably fipronil sulfone, fipronil sulfide, fipronil desulfinyl, and fipronil amide (Gunasekara et al., 2007).

A recent report from the US Geological Survey shows an upward trend for fipronil occurrence in surface water between 2002 and 2011, with approximately 70% of the urban streams exceeding an EPA chronic aquatic health benchmark for invertebrates set at 11 ng/L (Stone et al., 2014). Fipronil is a potent blocker of the gamma-aminobutyric acid (GABA) receptor in insects, causing disruption to the central nervous system and over-excitation of muscles and nerves (Hainzl and Casida, 1996; Hainzl et al., 1998; Ikeda et al., 2004). Fipronil and its degradates have recently been implicated as a partial causal agent for bee colony collapse disorder (Erickson, 2013; Vidau et al., 2011; Desneux et al., 2006), and other non-target populations have suffered as a result of fipronil contamination of surface water (Bedient et al., 2005; Overmyer et al., 2007). Fipronil has a high aquatic toxicity (EC_{50} values range from 32 to 730 ng/L for a variety of freshwater invertebrates), and the fipronil sulfone and sulfide metabolites are generally more toxic than fipronil itself (Weston and Lydy, 2013).

Although current production amounts are unknown, a 1997 Rhône-Poulenc report indicated production of 480 metric tons/yr at a site in France (Rhône-Poulenc, 1997). The US EPA estimates that fipronil is most often used in residential settings to control fire ants, termites, fleas, ticks, and cockroaches. In 2003 licensed pesticide applicators used approximately 181,000 kg (400,000 lbs) indoors (in the US) while consumers used approximately 1800 kg (4000 lbs) (Brassard et al., 2011). A major use is in topical applications to control fleas and ticks on domestic pets, with many preparations containing approximately 10% fipronil as the active ingredient. Research using fluorescent indicators has shown that after application to pets, fipronil residues are easily transferred to pet owners' hands and to household surfaces for at least a week (Dyk et al., 2012). This may lead to human exposure through normal hand-to-mouth activity and eventual discharge to sewer systems after such activities as hand washing, showering, toilet flushing, and laundering of contaminated fabrics. Heidler et al. (Heidler and Halden, 2009) have confirmed the presence of fipronil in municipal wastewater treatment plant effluents and sludges, with liquid effluents ranging from <10 to 70 ng/L.

We are unaware of any attempts to directly assess the importance of the known sources of fipronil in the environment despite the fact that this information is vital for adequate hazard identification. To learn more about which sources of fipronil predominate, we collected surface water samples up and downstream of areas hypothesized to be significant sources based on previous literature accounts and registered uses of fipronil-containing products. Potential inputs that were selected as targets for this study included golf courses, residential areas, wastewater treatment facilities, and rural areas located near permitted sewage sludge application sites in central North Carolina.

We specifically targeted wastewater treatment plant (WWTP) effluent that was discharged into the surrounding surface water and water samples that were designated as reuse water. As human populations continue to grow in many areas that lack sufficient water resources, water conservation has become a critical issue. To maximize the efficient use of water resources, there is a growing trend toward reuse of WWTP effluents in applications such as irrigation, cooling towers, and process flows. While standard practices vary, WWTP effluent for reclamation is often simply treated with a disinfection agent like sodium hypochlorite (NaOCl) to kill pathogens and maintain a chlorine residual during transport before reuse. How this disinfection treatment influences chemicals normally found in WWTP effluents remains almost completely undescribed. In this study we specifically analyzed wastewater effluent and corresponding recycled water samples via high resolution mass spectrometry (HRMS) for fipronil and its potential transformation products.

The goals of this study were to compare the potential importance of the various sources of fipronil in central North Carolina and to describe the distribution of fipronil-related compounds in the two types of wastewater (effluent and recycled water). This work led to the identification and confirmation by HRMS and nuclear magnetic resonance (NMR) of a novel fipronil transformation product found only in recycled water, which will be presented.

2. Materials and methods

2.1. Chemicals

Unlabeled fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-(trifluoromethylsulfinyl)-1-H-pyrazole-3-carbonitrile, >99%) and its metabolites: fipronil sulfone (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-[(trifluoromethyl)sulfonyl]-1*H*-pyrazole-3-carbonitrile, >99%), fipronil sulfide (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-[(trifluoromethyl)thio]-1*H*-pyrazole-3-carbonitrile, 98%), fipronil amide (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-[(trifluoromethyl)thio]-1*H*-pyrazole-3-carboxamide, >99%), and monochloro fipronil (5-amino-1-[2-chloro-4-(trifluoromethyl)-phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile, >97%) were procured as solid analytical standards from the US EPA's Pesticide Repository (Fort Meade, MD, USA). These analytical standards were each prepared as a solution in acetonitrile and used for subsequent experiments. The internal standard fipronil des-F_3 (see supporting information for structure) (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-(methylsulfinyl)-1-H-pyrazole-3-carbonitrile, 99%, 0.1 ng/μL in Acetonitrile) was ordered from Crescent Chemical Company (Islandia, NY, USA).

Acetonitrile (ACN), dichloromethane (DCM), and methanol (B&J Brand High Purity Solvent) were purchased from Honeywell Burdick & Jackson (Muskegon, MI, USA). T-butanol (≥99.7%), magnesium sulfate, sodium carbonate, and ammonium acetate were purchased from Sigma Aldrich (St. Louis, MO, USA). Silica gel (63–200 particle size) was purchased from Selecto Scientific (Norcross, GA, USA). Commercial household bleach was purchased from a local grocery store and was labeled as containing 8.25% NaOCl. Ultrapure deionized (DI) water was generated in house from a Barnsted Easypure UV/UF (Dubuque, IA, USA) coupled with activated charcoal and ion exchange resin canisters.

2.2. Surface water sample collection

Samples ($n = 54$) were collected up and downstream of potential sources of fipronil in the environment during the summer of 2014.

Please cite this article as: McMahen, R.L., et al., Comparison of fipronil sources in North Carolina surface water and identification of a novel fipronil transformation product in re..., Sci Total Environ (2016), http://dx.doi.org/10.1016/j.scitotenv.2016.05.085