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Characterization of selected organo-nitrogen herbicides in south florida canals: Exposure and risk assessments

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ABSTRACT

Much uncertainty exists regarding the discharge characteristics of terrestrial-use herbicides into aquatic systems. This study evaluated the temporal distribution and concentrations of five commonly used herbicides (atrazine, bromacil, metolachlor, norflurazon, and simazine) in a typical South Florida watershed. Surface water samples were collected weekly over a 3-yr period from four canals and Ten Mile Creek. These systems received drainage water from a variety of land-uses, including residential, pastures, and citrus production. Herbicides were extracted and analyzed by GC-MS/SIM. Atrazine was most frequently detected (87% of samples) in the canal serving the residentially developed sub-basin, with median and maximum concentrations of 0.43 and 6.67 $\mu g\ L^{-1}$, respectively. Norflurazon was most frequently detected (90–95% of samples) in the systems serving agricultural production areas, with median and maximum concentrations ranging from 0.37–0.63 $\mu g\ L^{-1}$ and 1.98–6.97 $\mu g\ L^{-1}$, respectively. Bromacil was detected in 14–36% of samples with median and maximum concentrations ranging from 0.50–0.67 $\mu g\ L^{-1}$ and 2.31–4.96 $\mu g\ L^{-1}$, respectively. Metolachlor was detected in 1.8–10% of the samples, with median and maximum concentrations ranging from 0.16–0.2 $\mu g\ L^{-1}$ and 0.17–1.55 $\mu g\ L^{-1}$, respectively. Simazine was detected in 10–35% of the samples, with median and maximum concentrations ranging from 0.18–0.28 $\mu g\ L^{-1}$ and 0.37–1.35 $\mu g\ L^{-1}$, respectively. Bromacil + norflurazon was the most commonly detected (240 samples of 1060 total) binary combination of herbicides; whereas bromacil + norflurazon + simazine was the most frequently detected tertiary combination (58 samples). While detectable concentrations were present for significant periods of time, risks of acute toxicity were relatively low; affecting <1% of the potentially affected fraction (PAF) of plant species based on 90th centile exposure concentrations and 10th centile effects concentrations from species sensitivity distributions.

1. Introduction

Pesticides are used throughout the world for agricultural and non-agricultural purposes. Depending on individual pesticide properties and environmental conditions, these pesticides may move from the sites of application into nearby aquatic systems. Losses of herbicides from applications in the surrounding landscape are especially important for aquatic plant communities since they are designed to control plants. Aquatic macrophytes and algae provide habitat structure and food for fish, invertebrates, water fowl, and other aquatic animals. Given their position within the landscape, discharge of herbicides in surface runoff and drainage water from surrounding land uses have potential to impact normal growth, reproduction, and health if exposure concentrations are high enough and exposure durations are long enough. Many of the streams, rivers, and lakes where these aquatic plant species occur are surrounded by land-uses that employ herbicides for controlling weeds, or that receive runoff/drainage water from those areas.

Several commonly used herbicides in agricultural and non-agricultural settings include atrazine [6-chloro-N-ethyl-N′-(1-methylethyl)-1,3,5-triazine-2,4-diamine], bromacil [5-bromo-3-*sec*-butyl-6-methyluracil], metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide], norflurazon [4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(*2H*)-pyridazinone], and simazine [6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine]. A summary of the properties of each is shown in Table 1. These herbicides have also been detected in non-target surface water bodies around the world (Gómez-Gutièrrez et al., 2006; Konstantinou et al., 2006; Cerejeira et al., 2003; Glotfelty et al., 1984; Zablotowicz et al., 2006; Coupe et al., 1998; Byer et al., 2011; Du Preez et al., 2005; Guo et al., 2007; Bocquene and Franco, 2005; Woudneh et al., 2009). Within the South Florida area, Miles and Pfeuffer (1997) and Carriger and Rand (2008a,b) reported frequent detections of atrazine, simazine, bromacil, norflurazon, and other pesticides in 72 surface water samples collected from 1991 to 1995 in drainage canals. They reported that spatial trends in pesticide detections followed use patterns, and that bromacil, norflurazon, and

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Table 1
Properties of herbicides monitored in this study.
All data adapted from Vencill (2002) unless otherwise noted.

Herbicide	CAS no.	Chemical family	Molecular weight (g mol^{-1})	Water solubility (mg L^{-1} at 25 °C)	Vapor pressure (mm Hg at 25 °C)	Log K_{ow}
Atrazine	1912-24-9	*s*-Triazine	215.7	33	2.9×10^{-7}	2.68
Desethyl atrazine	6190-65-4	*s*-Triazine	187.6[a]	3200[a]	9.3×10^{-5} [a]	1.51[a]
Desisopropyl atrazine	1007-28-9	*s*-Triazine	173.6	670[a]	nd	1.15[a]
Bromacil	314-40-9	Substituted uracil	261.1	700-815	3.1×10^{-7}	2.11
Metolachlor		Chloroacetamide		488	2.8×10^{-5}	
Norflurazon	27314-13-2	Fluorinated pyridazinone	303.7	28	2.9×10^{-8}	2.45
Simazine	122-34-9	*s*-Triazine	201.7	3.5	2.2×10^{-8}	2.18

[a] Data adapted from FOOTPRINT, 2006.

simazine were detected frequently at monitoring sites near citrus groves. Atrazine was detected regularly at all of their sites.

The presence of terrestrial-use herbicides in surface water is of concern due to the possibility of negative impacts on non-target aquatic plants and animals. Atrazine, bromacil, and simazine are all photosystem II inhibitors. They block electron transport from Q_A to Q_B by binding to the Q_B-binding niche on the D1 protein of the photosystem II complex in chloroplast thylakoid membranes (Vencill, 2002). While the blockage of electron transport stops CO_2 fixation and production of ATP and $NADPH_2$, plant death usually results from lipid and protein damage caused by free-radicals generated by the inability to reoxidize Q_A (Vencill, 2002). Norflurazon blocks carotenoid biosynthesis by inhibiting the enzyme phytoene desaturase, resulting in bleaching of foliage and destruction of chlorophyll. Metolachlor inhibits biosynthesis of several plant components, including fatty acids, lipids, proteins, isoprenoids, and flavonoids (Vencill, 2002). Using archived monitoring data from the South Florida Water Management District (SFWMD) from 1999 to 2006, Schuler and Rand (2008) conducted a risk assessment for aquatic plants within southern Florida freshwater ecosystems. They reported that the risks from individual herbicides were relatively low, but risks were higher for multiple simultaneous herbicide exposures at some sites, especially if bromacil, diuron, and norflurazon were present.

This study was initiated to 1) determine the temporal distribution and concentrations of atrazine, bromacil, metolachlor, norflurazon, and simazine in water discharged from a southern Florida watershed over a three-year period, and 2) estimate acute ecological risks to aquatic plants. These herbicides were chosen because of the prevalence of their use within the watershed and their confirmed presence in samples collected for the SFWMD's pesticide monitoring program (Pfeuffer, 2009). Two common degradation products of atrazine (desethyl-atrazine [6-chloro-2-N-propan-2-yl-1,3,5-triazine-2, 4-diamine] and desisopropyl-atrazine [2-amino-4-chloro-6-ethylamino-1,3,5-triazine]) were also included as indicators of previous atrazine/ simazine exposure.

2. Methods

2.1. Drainage basin descriptions

Due to the flatness of the landscape, surface water drainage throughout much of South Florida is achieved through use of man-made drainage canals that are managed by the SFWMD (West Palm Beach, FL) (Fig. 1). These canals are equipped with various types of water control structures to maintain water levels within the canals and to regulate discharges into the receiving waterbodies. Most of these canals function to 1) remove excess water from the drainage basins, 2) supply water for agricultural needs (except ELKAM), and 3) maintain water table elevations high enough to prevent salt water intrusion into the groundwater (Table 2). The canals within this sub-basin normally drain by gravity flow through the discharge structures. Each sub-basin is relatively flat, with slopes of less than 9.3 cm km^{-1}. The network of canals and the estuary drain or recharge the groundwater depending on head differential between the canals and the water table (Janicki et al., 1999). Samples were collected at five different sites for the duration of this study (Table 2, Fig. 1). Sampling sites were located at the discharge structures for Canal-23 (C-23/S97), Canal-24 (C-24/S49), Canal-25 (C-25/S99), Ten Mile Creek (TMC), and the ELKAM canal in Port St. Lucie (Table 2). Ten Mile creek, the ELKAM, C-23, and C-24 canals all discharge into the St. Lucie estuary, which is connected to the Indian River Lagoon estuary and the Atlantic Ocean (St. Lucie Inlet). Canal-25 discharges into the Indian River Lagoon estuary, which is connected to the Atlantic Ocean through the Fort Pierce and Sebastian inlets. A description of drainage basins for each sampling site is provided in Table 2.

2.2. Sample collection

Surface water samples were collected at least once per week from May 9, 2005 through April 8, 2008. Samples were collected upstream from each structure using Environmental Protection Agency (EPA) standard operating procedures and a modified grab sampler (U.S. EPA, 2001). Samples were collected directly into amber glass bottles by submersion to a depth of 0.76 m. Water pH was measured and recorded at the time of sampling. All samples were stored on ice upon collection. All extractions were performed within 7 d of collection and analyses were carried out within 30 d.

2.3. Sample preparation and extraction

The target herbicides were extracted from water samples using a modified version of EPA Method 3535. Samples were first filtered through a 1 μm glass fiber filter (Millipore, Billerica, MA, USA). Sample pH was adjusted to 7.0 by addition of 5–50 mL sodium phosphate buffer. HyperSep C_{18} extraction columns (500 mg/25 mL; Thermo Electron Corporation, Bellefonte, PA, USA) were initially washed with 10 mL methylene chloride, followed by sequential activation using 10 mL acetone, 10 mL methanol, and finally 10 mL reagent-grade water. Following extraction, pesticides were eluted from the columns sequentially using two 6 mL aliquots of acetone followed by two 6 ml aliquots of methylene chloride. To facilitate evaporation, the combined acetone:methylene chloride extract was first chemically dried by addition of sodium sulfate, followed by evaporation to dryness using a Labconco RapidVap system (Labconco Corp., Kansas City, MO, USA). The extracted analytes were re-dissolved in 1-mL of pesticide grade acetone. The extracts were stored at −16 °C until analyzed.

2.4. Analysis

2.4.1. Identification and quantification

Analytes were identified and quantified using an Agilent 6890 N gas chromatograph equipped with a 5975 mass spectrometer (GC-MS) (Agilent Technologies, Santa Clara, CA). The GC conditions included: inlet temperature 250 °C, transfer line 280 °C, and oven temperatures of 50 °C initial, increasing to 320 °C at a rate of 15 °C/min. with a final hold time of 0.5 min. The helium carrier gas flow rate was maintained