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Sulfonylurea herbicides in an agricultural catchment basin and its adjacent wetland in the St. Lawrence River basin

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HIGHLIGHTS

- Presence of sulfonylurea herbicides in streams and an adjacent wetland was assessed.
- Herbicide presence depended on stream hydrology and water quality characteristics.
- Maximum concentrations in streams were above level for aquatic plant toxicity.
- Presence of herbicides in wetland poses less toxicological risk to wetland flora.

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ABSTRACT

The use of sulfonylurea herbicides (SU) has increased greater than 100 times over the past 30 years in both Europe and North America. Applied at low rates, their presence, persistence and potential impacts on aquatic ecosystems remain poorly studied. During late-spring to early fall in 2009–2011, concentrations of 9 SU were assessed in two agricultural streams and their receiving wetland, an enlargement of the St. Lawrence River (Canada). Six SU in concentrations >LOQ (10 ng L^{-1}) were detected in 10% or less of surface water samples. Rimsulfuron was detected each year, sulfosulfuron and nicosulfuron in two years and the others in one year only, suggesting that application of specific herbicides varied locally between years. Detection frequency and concentrations of SU were not significantly associated with total precipitation which occurred 1 to 5 d before sampling. Concentrations and fate of SU differed among sites due to differences in stream dynamics and water quality characteristics. The persistence of SU in catchment basin streams reflected the dissipation effects associated with stream discharge. Maximum concentrations of some SU (223 and 148 ng L^{-1}) were occasionally above the baseline level (100 ng L^{-1}) for aquatic plant toxicity, implying potential toxic stress to flora in the streams. Substantially lower concentrations (max 55 ng L^{-1}) of SU were noted at the downstream wetland site, likely as a result from dilution and mixing with St. Lawrence River water, and represent less toxicological risk to the wetland flora. Sporadic occurrence of SU at low concentrations in air and rain samples indicated that atmospheric deposition was not an important source of herbicides to the study area.

1. Introduction

Sulfonylurea herbicides (SU) are selective systemic weed control products most frequently applied postemergence to major crops such as corn, wheat, barley, canola and potato. Registered uses of SU include around 30 active ingredients (Russell et al., 2002). Unlike many other herbicides, SU are phytoactive at low application rates ranging from 2 to 40 g active ingredient (a.i.) per hectare (Beyer et al., 1988). The world-wide use of SU has increased over the past two decades from 129 tonnes in 1992 to 2135 tonnes in 2011, with major increases in Europe and North America (Food and Agriculture Organization, 2013). In the province of Quebec (Canada), SU sales increased from 275 kg a.i. in 1992 to 11976 kg a.i. in 2006 (MDDEP, 2012) but decreased to 2928 kg a.i. in 2010, indicating variability in the use of these herbicides.

SU herbicides are weak acids (pK_a values ranging between 3 and 5) and are highly water soluble ($\log K_{ow} < 1$). Their half-lives in soil vary from 5 to 70 d depending on the herbicide, soil pH and other soil characteristics (Cessna et al., 2006; Hollaway et al., 2006). In soil, they are degraded either by hydrolysis or microbial activity and the degradation products of some SU may persist in soil for years (Rosenbom et al., 2010). Given their field half-lives and relatively high water solubility (Table 1), SU can leach to groundwater as well as enter surface waters

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Table 1
Physical–chemical characteristics of the sulfonylurea herbicides analyzed in this study.

Herbicide	Water solubility (mg L^{-1} @ pH 7, 25 °C) Tomlin (2006)	Field half-life (day) University of Hertfordshire (2013)	Field half-life (day) Sanseman (2007)	Field half-life (day) Tomlin (2006)	Vapor pressure (mPa × 10^5 @ 25 °C) Sanseman (2007)	Henry's Law constant (Pa m^3 mol^{-1} @pH 7, 25 °C) Tomlin (2006)	Soil sorption coefficient K_{oc} (mL g^{-1}) Sanseman (2007)
Ethametsulfuron-methyl	50	35–70	–	63	0.000077	6.34×10^{-12} (calc)	–
Metsulfuron-methyl	2790	10	30	52	0.033	4.5×10^{-11}	35
Nicosulfuron	70	19–26	21	24–43	0.0000016	$<1.48 \times 10^{-11}$	29–79
Primisulfuron-methyl	390	17–30	30	4–29	0.51	–	4–20
Prosulfuron	4000	16	9–20	5–23	0.35	–	18–41
Rimsulfuron	7300	10–24	2–5	–	150	–	–
Sulfosulfuron	1627	24	14–75	11–47	8.8	8.83×10^{-9}	5–89
Thifensulfuron-methyl	2240	4–10	2–6	4–7	1.7	9.7×10^{-16}	45
Tribenuron-methyl	2040	10–14	10	3–5	5.2	1.08×10^{-8}	46

of streams and rivers via soil erosion and surface runoff (Almvik et al., 2011; Battaglin et al., 2000; Cessna et al., 2006; Kreuger and Adielson, 2008; Struger et al., 2011). Cessna et al. (2006) reported dissipation half-lives of 16 to 84 d for 3 SU in weakly alkaline waters (pH = 8.0–8.7). Consequently, SU are of concern for their potential impacts on aquatic ecosystems, as suggested from laboratory exposure experiments with duckweed (*Lemna minor*) (Fairchild et al., 1997), sago pondweed (*Potamogeton pectinatus*) (Coyner et al., 2001) and submerged Eurasian water-milfoil (*Myriophyllum spicatum*) (Michael, 2003). SU can also be toxic to micro-algae including cyanobacteria and dinoflagellates (Nyström et al., 1999) and reported EC_{50} values suggest a toxicity threshold of around 100 ng L^{-1} for various algal species (Battaglin et al., 2000). By contrast, aquatic flora would exhibit toxic impact only when exposed to very high SU concentrations (>100,000 ng L^{-1}) (Michael, 2003). Although widely used for nearly three decades, the presence, concentrations and distribution dynamics of SU remain poorly studied for surface waters of major agricultural watersheds.

One such watershed is the Yamaska River watershed (4898 km^2) in the province of Quebec, Canada which has the largest cultivated area (2230 km^2) and accounts for 20% of all agricultural activities in the province (Poissant et al., 2008a; Roy, 2002). This major agricultural basin drains into the southwestern sector of Lake Saint-Pierre, an enlargement of the St. Lawrence River, which supports large emergent marshes and extensive macrophyte beds covering 260 km^2 (85%) of the lake surface area (Hudon and Carignan, 2008 990/id). The objective of the present study was to assess over three growing seasons (2009 to 2011) the presence and the spatio-temporal variation in SU concentrations in surface waters of the Baie Saint-François (BSF; 39.8 km^2) catchment basin, a sub-watershed within the Yamaska River watershed. Surface water samples were collected from late spring through early fall (late April to September) incorporating the time of pesticide application. In addition, SU concentrations in air and precipitation were measured to investigate the possibility of atmospheric deposition of SU to the BSF catchment basin. The results from this study would provide data necessary to assess whether these herbicides occurred in surface waters at sufficiently high concentrations to exert detrimental effects on non-target aquatic organisms.

2. Materials and methods

2.1. Study area

Located between the Yamaska River and the Saint-François River, the Baie Saint-François (BSF) catchment basin (Fig. 1) has been extensively used in recent years for corn (59%), soya (13%) and hay (15%) production (Poissant et al., 2008a). The catchment basin streams drain into a major fluvial wetland (9.5 km^2 — adjacent to the mouths of the Yamaska and Saint-François Rivers) which is part of the Lake Saint-Pierre wetland ecosystem (112 km^2). Estimated pesticide loads applied to the BSF catchment basin totaled 2.7 metric tons in 2006, of which 0.41% represented SU, due, in part, to the low SU application rates rather than to the extent of land application (Poissant et al., 2008b). Based on sales in 2006, nicosulfuron, rimsulfuron, primisulfuron and prosulfuron were the top four SU used in corn culture within the entire Yamaska watershed (Poissant et al., 2008b). However, details on application times and applied rates are not compiled in Quebec; thus, quantifying local or regional sources of SU over time and space was not possible.

2.2. Study sampling sites and environmental conditions

Information on the top soil characteristics, vegetation cover and general environment of the BSF catchment basin was summarized in a previous study (Poissant et al., 2008b). Surface water sampling was carried out at three sites (Fig. 1). The sites on the "Bois-de-Maska" and "Castorerie" streams were situated in the agricultural sector of the catchment basin used mainly for corn production. The Bois-de-Maska site was near a forested area whereas the Castorerie site was proximal to large open fields. This latter site was moved upstream approximately 1.2 km between 2010 and 2011 so that it was situated in closer proximity to cultivated fields. Both streams flow directly into the BSF wetland. The "BSF" site was positioned at the wetland outlet near the St. Lawrence River and downstream of the catchment basin. This site was more than 5 km away from the nearest agricultural field and was, therefore, not directly influenced by pesticide applications. Except for the Castorerie site which was not sampled in 2009, sites were sampled for three consecutive years: 2009, 2010 and 2011. In 2009, sampling was conducted bi-weekly between 24 April and 12 June and then monthly until 10 September (n = 8). In 2010, monthly samples were taken between 30 April and 18 August (n = 5). In 2011, weekly sampling was from 5 May until 27 July (n = 13). At each sampling in each year, duplicate water samples were collected at 0.1- to 0.2-m depth in 1-L amber glass bottles rinsed three times with stream water and the bottles capped with Teflon-lined caps. Each year, samples, preserved at 4 °C in the dark until analysis (1 to 4 mo), were accumulated and then analyzed as single batches.

In order to determine whether rainfall washout of the SU from the atmosphere may have contributed to concentrations detected in the surface water samples, time-integrated samples of air and precipitation were collected once in 2009 (11 June, air sample only) and on a monthly basis in 2010 (n = 4; 11 June, 9 July, 6 and 30 August) and 2011 (n = 3; 7 and 28 July and 2 September) at a weather station (WS) located in the BSF wetland (Fig. 1). Air samples were collected using a high-volume sampler (Model PS-1, General Metal Works, Village of Cleves, OH) installed at 1.5 m above the ground. Air was pumped continuously (flow rate of ~300 m^3 d^{-1}) for 1 mo through a glass fiber filter for particle collection and subsequently through a polyurethane foam (PUF)/XAD-2 resin/PUF cartridge for vapor collection. Rain samples were collected by an automated Meteorological Instruments of Canada (MIC type B) wet-only precipitation sampler in which water passed through XAD-2 resin contained in a column made of Teflon. Each rain sample