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Current-use pesticides in urban watersheds and receiving waters of western Lake Ontario measured using polar organic chemical integrative samplers (POCIS)

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ABSTRACT

Surface water contamination with current-use pesticides (CUPs) is usually associated with inputs from agriculture. However, there are several urban sources of these compounds, including pesticides used in public spaces, golf courses, and lawns and gardens; discharges of municipal wastewater containing fungicides from pharmaceuticals and personal care products (PPCPs); and runoff of biocides that are used in construction materials. Polar organic chemical integrative samplers (POCIS) were used to monitor the occurrence of fungicides and selected herbicides in surface waters in the densely populated urban area near Toronto, Canada. Samplers were deployed in five urban streams, one agriculturally dominated stream, and at five locations in the nearshore zone of western Lake Ontario adjacent to urban areas. Sampling rates for target compounds in POCIS determined in laboratory calibration experiments ranged between 0.03 and 0.65 L/day. For herbicides, atrazine was detected at all sites, and diuron, 2,4-D, and mecoprop were frequently detected. The fungicides carbendazim and thiophanate-methyl were detected at all sites, and a hydroxy-metabolite of the fungicide chlorothalonil was also widely detected. Fungicides used in PPCPs (e.g. fluconazole, climbazole) were primarily detected in POCIS deployed in locations impacted by municipal wastewater. Estimated time-weighted average (TWA) concentrations of iprodione and carbendazim in urban streams were consistent with the number of golf courses in the watershed. However, runoff of biocides from building materials may also be a source of these fungicides. Overall, these data indicate that urban environments, as indicated by the Toronto area, have several point and non-point sources of fungicides and other CUPs.

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Introduction

Herbicides used in both agricultural and urban settings to control weeds have been previously detected in surface waters in Canada (Byer et al., 2011; Kurt-Karakus et al., 2010a; Poissant et al., 2008; Segura et al., 2011; Struger et al., 2004; Struger and Fletcher, 2007; Todd and Struger, 2014). Fungicides are another class of current-use pesticides (CUPs), but there are few data from Canada on the distribution of these compounds in surface waters. In Ontario, Canada, the use of pesticides for cosmetic purposes in urban areas has recently come under strict regulation, while agricultural and other intensive uses of pesticide products are subject to fewer restrictions. Golf courses are recognized sources of pesticides that can be transported into surface water (Vincelli, 2004; Metcalfe et al., 2008). However, several classes of pesticides, including fungicides, are not routinely included in pesticide monitoring programs.

Recent data from Europe have shown that there are many sources of pesticides in urban areas besides applications to public spaces, lawns, and gardens. Kahle et al. (2008) detected several fungicides from the azole class in untreated and treated municipal wastewater resulting from their use as human pharmaceuticals, and in wood coatings and preservatives. Wick et al. (2010) detected several pesticides in municipal wastewater that are used as herbicides or fungicides in building materials, in pharmaceuticals, and in anti-dandruff hair shampoo. Several herbicides and fungicides have been detected in urban storm water as a result of their use as biocides in building materials and paints (Bollmann et al., 2014; Burkhardt et al., 2007; Schoknecht et al., 2003).

Monitoring for pesticides and other contaminants of emerging concern in surface waters is often a challenge due to wide temporal variations in concentrations. The transport of pesticides into surface waters from agricultural and urban landscapes varies with the time of application and with the frequency and intensity of rain events or snow melt. Therefore, low-frequency grab sampling strategies are not optimal for detecting these compounds in surface waters (Bundschuh et al., 2014). Contaminant discharges in domestic wastewater vary daily and seasonally (Ort et al., 2010), also limiting the effectiveness of

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grab sampling as a strategy for detecting contaminants discharged from wastewater treatment plants into surface waters.

Passive sampling is a relatively simple and practical way to screen and monitor surface waters for pesticides and other contaminants of concern (Kot-Wasik et al., 2007). Passive samplers deployed in surface waters accumulate contaminants over time and time-weighted-average (TWA) concentrations can be estimated from the amounts accumulated over the deployment period when sampling rates for the target analytes have been determined. Passive samplers can concentrate the chemicals from the surrounding water to detectable levels, even when they are present at ultra-trace concentrations, such as those found in lake environments (Helm et al., 2012). The polar organic chemical integrative sampler (POCIS) was developed for passive sampling of hydrophilic contaminants in water (Alvarez et al., 2004) and has shown promise as a monitoring tool for pesticides (Bartelt-Hunt et al., 2011; Mazzella et al., 2008; Charlestra et al., 2012; Dalton et al., 2014; Mazzella and Mazellier, 2014; Ahrens et al., 2015). However, due to uncertainty in the application of sampling rates determined in the laboratory to field conditions, passive sampling results are considered semi-quantitative (Miège et al., 2015). The results reported in the present study provide a screening level indicator of occurrence that will guide additional monitoring studies.

In this preliminary study, we evaluated the benefits and challenges of monitoring pesticides in surface waters using passive samplers. We used POCIS to monitor the occurrence of fungicides and selected current-use herbicides in urban streams and rivers draining into western Lake Ontario, and in surface waters in Lake Ontario that are impacted by runoff and discharges from wastewater treatment plants (WWTPs). The pharmaceutical meprobamate was included as an indicator of wastewater contamination (Dickenson et al., 2011). We used a static, non-renewal laboratory system to determine sampling rates for the target compounds in POCIS because sampling rates for many of the fungicides and some herbicides have not been determined experimentally. The methods for solid phase extraction (SPE) of target fungicides and herbicides from water for these experiments were developed for this study, as were the quantitative analysis methods using liquid chromatography with tandem mass spectrometry (LC-MS/MS).

Methods

POCIS deployments and site characteristics

Samplers were deployed in 2010 at selected locations in streams in the vicinity of Toronto, ON, Canada, and in nearshore waters of western Lake Ontario, Canada (Fig. 1). The POCISs were deployed in streams for 31–36 days in September–October. Watershed characteristics, including size, population, and the degree of urbanization upstream of the deployment locations are listed in Table 1. The Mimico and Highland Creek watersheds are highly urbanized, while the Etobicoke Creek and Don River watersheds are predominantly urban, but with some agriculture in headwater regions. The Don River site is also located downstream of a WWTP effluent discharge. The Humber River watershed, the largest included in the study, has agricultural land uses in about half of the watershed area. The downstream deployment site was located in a portion of the river dominated by urban (commercial, industrial, residential) land uses, while the East Humber site, located in the agricultural area, was included as a reference site. All sites were located upstream of any influence from Lake Ontario, and each were co-located at Water Survey of Canada monitoring stations that record water level and discharge, except the downstream Humber River site.

In nearshore waters of western Lake Ontario, POCIS were deployed for 28–29 days from mid-June to mid-July at locations influenced by urban wastewater discharges and runoff (Fig. 1). The region around the western portion of the lake has the greatest population density on the Canadian side of the Great Lakes. Deployment sites 1 and 2 were located in Hamilton Harbour, a Great Lakes Area of Concern, which

receives effluents from three wastewater treatment plants (WWTPs) and urban runoff from the municipalities of Hamilton and Burlington. Site 1 was located at the head of the Windermere Arm, where Red Hill Creek and effluent from the Woodward WWTP, servicing the City of Hamilton, enter the harbor. Site 2 was located in the center of the harbor. Site 3 was located in Humber Bay adjacent to Toronto within 250 m of the diffuser outfall of the Humber WWTP, and was also influenced by the Humber River plume. Site 4 was located within 250 m of the Duffins Creek WWTP diffuser outfall and is also influenced by Duffins Creek. Site 5 was not directly impacted by urban wastewater discharges and runoff and is more representative of nearshore Lake Ontario waters.

The POCIS, consisting of 200 mg of Oasis HLB solid sorbent enclosed between two polyethersulfone membranes, were purchased from Environmental Sampling Technology (St. Joseph, MO, USA). The samplers were stored frozen ($-18\text{ }^{\circ}\text{C}$) within their shipping containers until assembled for deployment. The samplers were assembled on clean foil surfaces on the deck of the monitoring vessel *Great Lakes Guardian* for the nearshore locations, or on the shore adjacent to the streams. Three POCIS were mounted within a perforated stainless steel cage secured on a stainless steel cable. At lake sites, the cages were suspended in the water at approximately 4 m depth beneath a pre-cleaned subsurface float anchored to weights on the lake bottom, except for site 1 where the samplers were suspended from a bridge to a depth of approximately 1.5 m. Cages at stream sites were suspended approximately 30 cm above the bed between steel posts driven into the stream bed, except at Etobicoke Creek where the cage was laid on the stream bed in a non-depositional area. Upon retrieval, the POCIS were removed from their cages and mounts, wrapped individually in foil, and stored in re-sealable polyethylene bags on ice until return to the laboratory where they were stored at $-18\text{ }^{\circ}\text{C}$ until analysis. POCIS field blanks were exposed to air at a subset of sites during deployments and retrievals.

At stream sites, the temperature and pH was measured using a calibrated hand-held YSI multi-parameter sensor array (Hoskin Scientific, Burlington, ON) at the time of deployment and retrieval. At the nearshore sites, a temperature sensor (Onset Stowaway Tidbit, Hoskin Scientific, Burlington, ON, Canada) was attached to each cage to log the water temperature at hour intervals. Average temperatures over the deployment period were $22.2\text{ }^{\circ}\text{C}$ and $21.2\text{ }^{\circ}\text{C}$ at sites 1 and 2, respectively, in Hamilton Harbour, and between 12.3 and $13.8\text{ }^{\circ}\text{C}$ at the other Lake Ontario stations. The pH at the Lake Ontario stations varied between 8.1 and 8.3, based on long-term monitoring data at these sites. Water temperatures in the streams varied from 10 to $14\text{ }^{\circ}\text{C}$ at the start of the deployment to 9 – $12\text{ }^{\circ}\text{C}$ at the end, and pHs varied from 8.2 to 8.5. During the fall stream deployments there were several rain events where stream discharges sharply increased (e.g. Electronic Supplementary (ESM), Fig. S1).

Chemicals

Analytical standards ($>99\%$ purity) of all target chemicals and stable isotope internal standards and their suppliers are listed in Table 2. Standards were prepared individually in methanol and stored in amber glass vials at $4\text{ }^{\circ}\text{C}$. A mixture of the deuterated and ^{13}C stable isotope labeled compounds was used as internal standards. In cases where no mass-labeled analog for a particular compound was available, the internal standard with the closest chromatographic retention time to that compound was selected (Table 2). HPLC grade water, methanol and acetone, and ACS grade sulphuric acid (96%) were purchased from Fisher Scientific (Ottawa, ON, Canada).

Sampling rates

The sampling rates for the target compounds into POCIS were determined using 8-day static, non-renewal experiments in stirred deionized

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