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Organic contaminants in Great Lakes tributaries: Prevalence and potential aquatic toxicity

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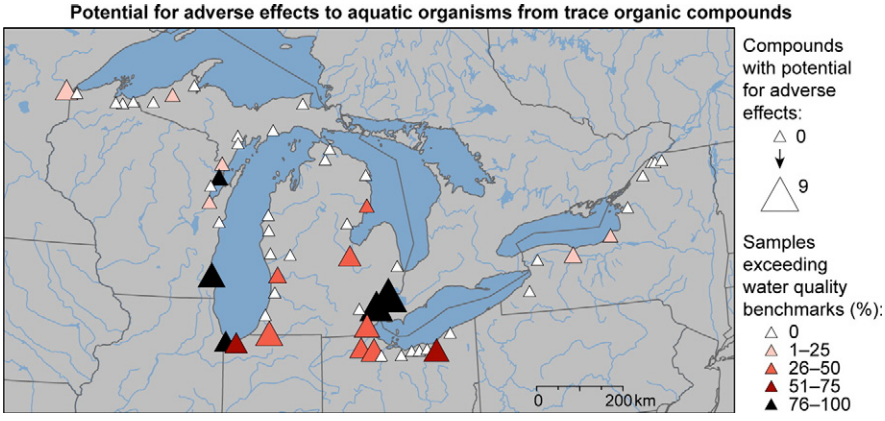
HIGHLIGHTS

- 709 samples were collected from 57 tributaries and analyzed for 69 compounds.
- Compounds commonly occurred as complex mixtures of 10 or more.
- Water-quality benchmarks were exceeded at 35% of the sampled sites.
- Estrogenic effects from nonsteroidal compounds alone were estimated at 18% of sites.
- Urban-related land use characteristics were important predictors of concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic compounds used in agriculture, industry, and households make their way into surface waters through runoff, leaking septic-conveyance systems, regulated and unregulated discharges, and combined sewer overflows, among other sources. Concentrations of these organic waste compounds (OWCs) in some Great Lakes tributaries indicate a high potential for adverse impacts on aquatic organisms. During 2010–13, 709 water samples were collected at 57 tributaries, together representing approximately 41% of the total inflow to the lakes. Samples were collected during runoff and low-flow conditions and analyzed for 69 OWCs, including herbicides, insecticides, polycyclic aromatic hydrocarbons, plasticizers, antioxidants, detergent metabolites, fire retardants, nonprescription human drugs, flavors/fragrances, and dyes. Urban-related land cover characteristics were the most important explanatory variables of concentrations of many OWCs. Compared to samples from nonurban watersheds (<15% urban land cover) samples from urban watersheds (>15% urban land cover) had nearly four times the number of detected compounds and four times the total sample concentration, on average. Concentration differences between runoff and low-flow conditions were not observed, but seasonal differences were observed in atrazine, metolachlor, DEET, and HHCB concentrations. Water quality benchmarks for individual OWCs were exceeded at 20 sites, and at 7 sites benchmarks were exceeded by a factor of 10 or more. The compounds with the most frequent water quality benchmark exceedances were the PAHs benzo[*a*]pyrene, pyrene, fluoranthene, and anthracene, the detergent metabolite 4-nonylphenol, and the herbicide atrazine. Computed estradiol equivalency quotients (EEQs) using only nonsteroidal endocrine-active compounds indicated medium

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to high risk of estrogenic effects (intersex or vitellogenin induction) at 10 sites. EEQs at 3 sites were comparable to values reported in effluent. This multifaceted study is the largest, most comprehensive assessment of the occurrence and potential effects of OWCs in the Great Lakes Basin to date.

1. Introduction

Anthropogenic activities related to industrial, agricultural, domestic, and urban water uses introduce an untold number of organic compounds into the Great Lakes and their tributaries on a daily basis (Bennie et al., 1997; Blair et al., 2013; Venier et al., 2014). Flame retardants, drugs, herbicides, plasticizers, polycyclic aromatic hydrocarbons (PAHs), and other types of compounds enter waterways through wastewater treatment plant (WWTP) discharges, combined sewer overflows, leaking septic and municipal sewer systems, urban and agricultural runoff, industrial discharges, and atmospheric deposition, among others (Barber et al., 2015; Kolpin et al., 2002).

Many of these compounds are associated with endocrine disruption or toxicity in aquatic organisms, resulting in tumors and other deformities, reproductive problems, and declines or collapses in populations (Collier et al., 2013; Ingersoll et al., 2002; Johnson et al., 2013). The ability of these compounds to bioaccumulate (Ismail et al., 2014; Jenkins et al., 2014) creates a risk to organisms higher up the food chain including mink, river otter, bald eagles, osprey, and humans (Hinck et al., 2009; Nilsen et al., 2014). Most drinking water treatment plants do not currently remove many of these compounds from the water supply, creating another exposure route for humans (Kingsbury et al., 2008; Stackelberg et al., 2004).

Studies on OWCs in environmental waters in the United States have generally reported concentrations of individual compounds at concentrations in the nanogram or microgram per liter range, often below water quality benchmarks and drinking water standards (Kolpin et al., 2013; Lee and Rasmussen, 2006; Thomas, 2009). However, low concentrations may still pose a risk to aquatic organisms, as well as organisms at higher trophic levels, because of low-dose effects (Hayes et al., 2003; Oehlmann et al., 2006; Vom Saal and Welshons, 2006), nonmonotonic dose-response curves (Vandenberg et al., 2012), additive and synergistic mixture effects (Brian et al., 2005; Sobolewski et al., 2014; Vandenberg et al., 2012), transgenerational effects (Bhandari et al., 2015; Daughton and Ternes, 1999), and a lack of established water quality benchmarks for many compounds (Stackelberg et al., 2004).

A number of factors may influence the occurrence of OWCs in environmental waters. Among them, land use may be the most important. Streams with upstream urban and (or) agricultural uses have been shown to have more frequent detections and higher concentrations of many organic compounds, compared to streams draining dominantly undeveloped areas (Bryant and Goodbred, 2009; Kingsbury et al., 2008; Nowell et al., 2013). Streamflow may be another important factor. Compounds associated with runoff, such as PAHs, may be found at higher concentrations during higher flow conditions (Baldwin et al., 2013; Thomas et al., 2007). Conversely, compounds with a constant source such as those contributed by wastewater effluent or groundwater may be diluted during high flow conditions and therefore show an inverse relation with streamflow (Kingsbury et al., 2008; Kolpin et al., 2004). For some compounds, concentrations may vary by season. Herbicide concentrations have shown a distinct seasonal pattern in some Midwestern agricultural watersheds, with summertime concentrations one to two orders of magnitude greater than wintertime (Gilliom et al., 2006; Thomas et al., 2007).

The Great Lakes represent 84% of the fresh surface water in North America (US EPA, 2015). Understanding the types of compounds entering the lakes, their spatial distribution, their sources, and the potential biological effects to aquatic communities is crucial to watershed management. Such information helps identify at-risk watersheds and serves as a benchmark for future contaminant reduction strategies and remediation efforts.

During 2010–13, the U.S. Geological Survey (USGS) conducted a study of organic compounds in Great Lakes tributaries across six states in the U.S. The goal of the study was to assess the occurrence and possible adverse biological effects of these compounds in the aquatic environment, and how they vary by land cover, flow regime, and season. A total of 709 water samples were collected from 57 tributaries, representing approximately 41% of the total inflow to the lakes (based on an average inflow of 209,500 cubic feet per second (cfs), Neff and Nicholas, 2005). Each sample was analyzed for 69 organic waste compounds (OWCs), making this the largest study of OWCs in the Great Lakes Basin to date.

2. Methods

2.1. Sampling design

Great Lakes tributary and harbor sites were sampled and samples of surface water were analyzed for OWCs between September 2010 and September 2013. Sampling sites were in Minnesota, Wisconsin, Michigan, Indiana, Ohio, and New York, collocated with existing National Monitoring Network for U.S. Coastal Waters sites (Table 1; Fig. 1). Watershed characteristics for the sites are in Table *SI*-1. Drainage areas ranged from 39 to 6330 mile^2 (mi^2), with mean annual flows from 91 to 7751 cfs (October 2010–September 2013). Watershed land cover varied from dominantly urban (up to 92% of watershed) to agricultural (84%) to forest and wetland (93%). Watershed population densities ranged from as few as 3.3 up to 2498 people/mi^2. Each watershed had at least one wastewater treatment plant (WWTP), and as many as 192. The portion of river flow from WWTP effluent ranged from <1% up to 47%.

OWCs were sampled at 57 tributary and harbor sites. In total, 709 environmental samples were collected. Thirty-eight sites were sampled 1–2 times each, generally during low-flow and medium-flow periods. Though samples at these sites were few, the large number of sites and broad geographic extent provide valuable background information on typical concentrations in Great Lakes tributaries, while also identifying tributaries of potential concern for future studies. The remaining 19 sites were sampled more frequently, with 7–64 samples each, during both runoff and low-flow conditions. The more intense sampling at these sites enabled evaluation of the effects of different streamflow conditions and seasons, and better characterization of concentration ranges.

2.2. Sample-collection

In accordance with USGS protocols (Shelton, 1994), samples were collected and processed in a manner consistent with minimal contamination of organic compounds. Glass or Teflon equipment was used during sample collection and processing, whenever possible. Samples were chilled at 4 °C and shipped overnight to the USGS National Water Quality Lab (NWQL) for analysis.

Sampling methods for OWCs varied by site type. All but eight sites were sampled manually, with whole-water samples were collected using the equal-width-increment (EWI) method (Edwards and Glysson, 1999). Subsamples were composited in a 14-L Teflon churn, homogenized, and churned into a 1-L baked amber-glass bottle. When