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Endocrine disrupting alkylphenolic chemicals and other contaminants in wastewater treatment plant effluents, urban streams, and fish in the Great Lakes and Upper Mississippi River Regions

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HIGHLIGHTS

- Wastewater treatment plants (WWTPs) are sources of endocrine disrupting chemicals (EDCs).
- Sources, concentrations, and exposure pathways of EDCs persist over long time periods.
- Although some EDCs are removed by WWTPs, many are discharged to the environment.
- Many alkylphenolic EDCs undergo little attenuation during stream transport.
- Fish from WWTP effluent impacted streams have signs of endocrine disruption.

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ABSTRACT

Urban streams are an integral part of the municipal water cycle and provide a point of discharge for wastewater treatment plant (WWTP) effluents, allowing additional attenuation through dilution and transformation processes, as well as a conduit for transporting contaminants to downstream water supplies. Domestic and commercial activities dispose of wastes down-the-drain, resulting in wastewater containing complex chemical mixtures that are only partially removed during treatment. A key issue associated with WWTP effluent discharge into streams is the potential to cause endocrine disruption in fish. This study provides a long-term (1999–2009) evaluation of the occurrence of alkylphenolic endocrine disrupting chemicals (EDCs) and other contaminants discharged from WWTPs into streams in the Great Lakes and Upper Mississippi River Regions (Indiana, Illinois, Michigan, Minnesota, and Ohio). The Greater Metropolitan Chicago Area Waterways, Illinois, were evaluated to determine contaminant concentrations in the major WWTP effluents and receiving streams, and assess the behavior of EDCs from their sources within the sewer collection system, through the major treatment unit processes at a WWTP, to their persistence and transport in the receiving stream. Water samples were analyzed for alkylphenolic EDCs and other contaminants, including 4-nonylphenol (NP), 4-nonylphenolpolyethoxylates (NPEO), 4-nonylphenolethoxycarboxylic acids (NPEC), 4-*tert*-octylphenol (OP), 4-*tert*-octylphenolpolyethoxylates (OPEO), bisphenol A, triclosan, ethylenediaminetetraacetic acid (EDTA), and trace elements. All of the compounds were detected in all of the WWTP effluents, with EDTA and NPEC having the greatest concentrations. The compounds also were detected in the WWTP effluent dominated rivers. Multiple fish species were collected from river and lake sites and analyzed for NP, NPEO, NPEC, OP, and OPEO. Whole-body fish tissue analysis indicated widespread occurrence of alkylphenolic compounds, with the highest concentrations occurring in streams with the greatest WWTP effluent content. Biomarkers of endocrine disruption in the fish indicated long-term exposure to estrogenic chemicals in the wastewater impacted urban waterways.

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1. Introduction

Urban waterways provide critical functions including water supply, wastewater disposal, transportation, recreation, and aquatic habitat.

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Managing the multiple uses requires an understanding of the sources, fates, and effects of chemical contaminants. Although there are many potential sources of chemicals to surface waters, discharges of effluent from municipal wastewater treatment plants (WWTPs) can provide a major source of stream-flow and chemical flux (Barber et al., 2006, 2011a; Brooks et al., 2006). When evaluating the effects of WWTP discharges on surface-water chemistry, a range of time scales from hours (chemical transformation rates) to decades (demographic, chemical use, and infrastructure changes) need to be considered. Depending on flow conditions, stream hydraulic residence times (HRTs) can be short relative to in-stream removal rates, resulting in "pseudo" persistence of contaminants that have continuous input (Daughton and Ternes, 1999).

Many chemicals make their way into sewage collection systems from domestic and commercial activities and are not completely removed by WWTPs, resulting in their discharge to the stream environment where they are subject to further attenuation by biotic and abiotic processes (Barber et al., 2011b, 2013). An important issue related to surface water systems receiving WWTP effluent discharges is the effect of biologically-active chemicals on aquatic organisms. Certain contaminants present in WWTP effluents can interfere with endocrine system functions in wildlife and humans (Norris and Carr, 2006) and are collectively known as endocrine disrupting chemicals (EDCs). Fish living in wastewater-impacted streams have been shown to experience endocrine disruption due to exposure to EDCs (Jobling et al., 1998; Vajda et al., 2008) including naturally occurring hormones and synthetic compounds, such as 4-nonylphenol (NP), 4-*tert*-octylphenol (OP), and bisphenol A, which are common in treated sewage effluent (Johnson and Sumpter, 2001). A major source of NP and OP in WWTP effluents and receiving waters is the use of alkylphenolpolyethoxylate nonionic surfactants in industrial, commercial, and domestic activities (Talmage, 1994). Due to the relatively rapid biodegradation of the polar side-chain of the nonionic surfactants (typically containing 10 to 20 ethylene oxide, EO, units), the parent compounds can be removed during wastewater treatment, although the short-chain (0 to 4 EO unit) acidic and neutral metabolites can persist and are commonly detected in WWTP effluents (Ahel et al., 1994a; Field and Reed, 1996; Barber et al., 2000, 2012; Planas et al., 2002; Loyo-Rosales et al., 2007a). In addition to having endocrine disrupting properties (Jobling et al., 1996; Routledge and Sumpter, 1996), NP and OP also are toxic to aquatic organisms (McLeese et al., 1981; Servos, 1999; US Environmental Protection Agency, 2005). Investigations into the fate of EDCs during wastewater treatment indicate that low concentrations can be discharged in the treated effluent (Clara et al., 2007; Barber et al., 2012).

This paper describes a decade-long investigation (1999–2009) into the occurrence of alkylphenolic EDCs and other contaminants in WWTP effluents and surface waters of the Great Lakes and Upper Mississippi River Regions. The objective of this research into the sources, occurrence, and effects of EDCs in aquatic resources was not intended to be a symmetric monitoring of trends, but rather to establish an understanding of the nature and implications of contaminant exposure pathways in urban streams. The interdisciplinary investigation used a tiered experimental approach carried out over a 10-year period using consistent chemical and biological assessment tools. The results are integrated to provide information at a variety of spatial and temporal scales (1) using water chemistry data collected from a regional survey of influents and effluents of major WWTPs and receiving waters, (2) a focused study of contaminant behavior within the urban water cycle including assessing point sources within the sewage collection system, determining relative removal and loading within various treatment units at a single WWTP, (3) an investigation of receiving stream assimilation capacity, and (4) an assessment of bio-uptake and potential endocrine disruption impacts on resident fish populations.

2. Methods

2.1. Study sites

The occurrence of alkylphenolic EDCs and other contaminants in WWTP effluents and influents was evaluated at nine facilities, of which five were paired with receiving streams, between 1999 and 2009 (Fig. 1A; Tables SI-1 and SI-2). A focused investigation at a single WWTP was conducted at different points along the sewage collection system, wastewater treatment train, and receiving stream ecosystem (Tables SI-2 and SI-3). Fish samples were collected at 15 locations from various surface waters associated with the WWTP discharges (Fig. 1; Table SI-4). The WWTPs represent a range of treatment processes and source characteristics and serve a combined population of over 15 million people. The Mississippi River was sampled upstream and downstream from the St. Paul, Minnesota WWTP outfall, and the Cuyahoga River was sampled downstream from the Akron, Ohio, WWTP.

Detailed sampling was conducted in the waterways of the Greater Metropolitan Chicago Area, Illinois (Chicago Area Waterways; Fig. 1B), which consist of 125 km of canals that support navigation, provide drainage for urban storm water runoff, and receive WWTP effluent (Metropolitan Water Reclamation District of Greater Chicago, 2011). Approximately 75% of the Chicago Area Waterways consist of constructed channels in which flow is controlled by hydraulic structures, and three WWTPs (Calumet, Stickney, and North Side — subsequently renamed Terrence J. O'Brien) contribute up to 90% of the flow in the system. Samples were collected at various points along the treatment processes at the Calumet WWTP, which treats an average of 280 million gallons per day (MGD; design flow 350 MGD or 15.3 m^3/s) of sewage collected from an area of approximately 780 km^2 (serving a population of 2,000,000). The Calumet WWTP also treats combined sewer overflow stored in the Chicago Tunnel and Reservoir Plan (TARP) system during storm events. Effluent from the Calumet WWTP is discharged to the Calumet-Sag Channel (CSC) of the Calumet River system, a 37-km stream segment from O'Brien Lock and Dam to the confluence with the Chicago Sanitary and Ship Canal (CSSC). Flow in the CSSC is almost entirely derived from effluent discharged from the Stickney WWTP. The CSSC discharges into the Des Plaines River near Romeoville, Illinois, below the Lockport Lock and Dam located 15-km downstream from the confluence of the CSC and CSSC. The Des Plaines River discharges into the Illinois River downstream from Joliet, Illinois. The Chicago waterways are generally well mixed due to heavy barge traffic.

2.2. Sampling

Multiple water and fish sampling events were conducted between 1999 and 2009 at various WWTP and surface water sites (Tables SI-1 to SI-4). This study used a tiered sampling design that involved a preliminary regional survey of WWTP influents, effluents, and receiving streams to confirm and expand on previous findings (Barber et al., 2000). Based on the results from the regional survey, several sites were selected for additional sampling, including the St. Paul, Duluth, Chicago North Side, and Chicago Calumet WWTPs. Focused studies were conducted at the Calumet WWTP to characterize contaminant sources in the sewer collection system, evaluate the effect of internal unit processes on the wastewater composition, and assess stream transport in the Calumet River System.

Grab water samples were collected by stainless steel containers from 0.5-m below the surface from the outflow channels of the WWTPs and from the mid-point (by boat) or near-bank of the surface water. Samples for organic analysis were collected unfiltered in pre-cleaned amber glass bottles and stored at 4 °C. A subset of samples was preserved with 1% (v/v) formalin. Samples for trace-element analysis were filtered through 0.2-μm polycarbonate membranes, collected in