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Spatial distributions and temporal trends in polybrominated diphenyl ethers in Detroit River suspended sediments

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HIGHLIGHTS

- PBDE spatial distribution associated with shoreline urban/industrial activity.
- PBDE concentrations decreased after 2000 concomitant with production and usage.
- Congener profiles shifted in response to cessation of use of penta- and octa-PBDEs.

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ABSTRACT

Suspended sediments from the Detroit River were collected using sediment traps at sites ranging from western Lake Erie to southern Lake St. Clair to assess spatial distributions and temporal trends of polybrominated diphenyl ethers (PBDEs). The distribution of PBDEs in suspended sediments in the Detroit River appeared influenced by shoreline-based contemporary urban and industrial activities, which stood in contrast to PCBs that were associated with areas of historic industrial activity. Temporal trend data indicate that total PBDE concentrations decreased in the period after 2000 in response to cessation of production of the penta- and octa BDE formulations. Concentrations of total PBDEs ranged from roughly 7 ng g^{-1} (4 ng g^{-1} BDE 209) in southern Lake St. Clair to several hundred ng g^{-1} (60–180 ng g^{-1} BDE 209) in the lower reaches of the Detroit River. The widespread occurrence of PBDEs in Detroit River suspended sediments suggests that large urban areas can act as diffuse sources of these chemicals that are used in modern industrial applications and consumer products.

1. Introduction

The Detroit River lies in the heart of the Great Lakes basin and is one of four major connecting channels, providing the link between western Lake Erie and Lake St. Clair. The binational watershed includes the metropolitan areas of Detroit, Michigan and Windsor, Ontario, with an associated combined population of approximately five and a half million people. Water resources are heavily used by millions of residents in Michigan and Ontario for recreational boating and angling, navigation and drinking water. The corridor supports shipping, manufacturing and fishing industries.

The highly urbanized and industrialized watershed represents a variety of sources of chemical contaminants to the river, including urban runoff, sewage treatment plant effluents, combined sewer overflows and industrial wastes. The river has been designated by the International Joint Commission (IJC) as an Area of Concern (AOC) due to impairments of the environmental health of the river, which include fish consumption advisories (Ontario Ministry of the Environment, 1999). These impairments are due in part to contamination of bottom sediments by persistent organic pollutants (POPs). The Trenton Channel area of the lower Detroit River contains areas of sediment contaminated by polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals due to historic industrial activities (Michigan Department of Environmental Quality, 1987). High concentrations of contaminants including PCBs and PAHs have been reported in Detroit River sediments (Furlong et al., 1988; Kaiser et al., 1985; Hamdy and Post, 1985; Thornley and Hamdy, 1984). Investigations have also reported the presence of other POPs including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) and polychlorinated naphthalenes (PCNs) (Kannan et al., 2001; Kauss, 1994; Furlong et al., 1988; Marvin et al., 2002). The presence of POPs in Detroit River bottom sediments has been linked to the impairment of benthic communities (Farara and Burt, 1993), and abnormalities and tumors in fish (Leadley et al., 1998, 1999). The Detroit River is also a primary vector for many POPs to enter western Lake Erie (Stevens and Nielson, 1989).

Suspended sediment quality in the western Lake Erie – Detroit River corridor is routinely monitored to assess the occurrence and spatial distribution of contaminants in order to understand the role

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anthropogenic activities play in discharging these compounds, and to provide information to devise strategies to mitigate potentially deleterious health impacts (Jia et al., 2010). Some Detroit River suspended sediments can originate in areas of severe chemical contamination, and thereby can represent significant sources to downstream areas including the western basin of Lake Erie. A program was initiated in 1997 to investigate contaminants associated with suspended sediments in the Detroit River. Suspended sediments were chosen over bottom sediments due to the non-depositional nature of the middle and upper reaches of the river, and as a measure of particle-associated contaminants in the water column with potential to be deposited in downstream locations, including the western basin of Lake Erie. The goals of this program are to assess the relative importance of sources of contaminants both to the corridor and downstream in western Lake Erie, and to assess the effectiveness of remedial measures to address areas of historically-contaminated sediment. Our most recent work with legacy contaminants including PCBs, PAHs and mercury (Jia et al., 2010) reported on trends in contamination throughout the western Lake Erie – Lake St. Clair corridor, including the Detroit River. This study showed the continued importance of local sources of contaminants, including zones of contaminated sediments, in areas including the Trenton Channel and the mouth of the Rouge River.

Although program work has historically focused on legacy pollutants such as PCBs, the analyte suite has been expanded to assess the occurrence and distribution of other compounds. Polybrominated diphenyl ethers (PBDEs) are flame retardants used globally in thermoplastics, polyurethane foams and textiles and other materials since the 1970s. Although the penta- and octa formulations are no longer produced in North America, the fully-substituted BDE 209 is still currently used; however, this formulation has been banned in electrical equipment in the European Union (Betts, 2008) and is scheduled to be phased out of US production by the end of 2013 (USEPA, 2010). As a result of its high molecular weight, BDE-209 is typically the most predominant congener detected in sediments (Song et al., 2005). A major vector for PBDEs to enter the aquatic environment is through the atmosphere; these semi-volatile compounds are released to the atmosphere from the products where they partition onto particulates. There is also evidence that less volatile compounds like BDE 209 enter the atmosphere from weathering and abrasion of polymers from commercial products (Webster et al., 2009). For many compounds associated with consumer products, the bulk of the releases occur through weathering and leaching from landfills at the end of the product life cycle. These compounds are very persistent and do not degrade efficiently, or at all, in sewage treatment plants (STPs); therefore, they may be directly released in treated effluent or via agricultural application of sewage sludges. The PBDEs pose an environmental concern because they are classified as persistent, bioaccumulative and toxic (Alaee et al., 2003; Covaci et al., 2003; Darnerud, 2003). In this paper, we present an overview of the occurrence, spatial distributions and temporal trends of PBDEs in the Detroit River.

2. Experimental section

2.1. Sample collection

Sediment traps were based on a design previously used for study of suspended sediment quality in the Detroit River (Jia et al., 2010). The key parameter in design of the traps is the aspect ratio (ratio of internal diameter of the trap tube to length). This aspect ratio determines if material collected passively in the tubes can be resuspended and flushed from the collection cups by *in situ* currents. This design has proven to be a simple, yet effective, method for collection of suspended particulates in both riverine and open lake environments. Single-point sediment trap moorings were deployed from April to November in the Detroit River ranging from the mouth at the outflow to western Lake Erie to the head in southern Lake St. Clair (Fig. 1). Each sediment trap mooring consisted of five individual 1-m length sections of core tubing (7 cm internal diameter) affixed to a steel rack. The assembly was anchored using a railway wheel in order to maintain the stability of the mooring in strong current regimes. A removable cup of high-density polypropylene was fitted to the bottom of each tube to provide a receptacle for sediment accumulation. Moorings were refurbished monthly; accumulated material was removed, refrigerated at 4 °C and transported to the laboratory. Physical characterization of samples is described in Jia et al., 2010.

2.2. Sample analyses

The PBDE analyses were conducted by AXYS Analytical Services using high resolution gas chromatography (HRGC) coupled with High Resolution Mass Spectrometry (HRMS) according to EPA Method 1614 (AXYS, 2008). Samples were spiked with isotopically labeled BDE surrogate standards; solvent extracted and cleaned up on a series of chromatographic columns including layered acid/base silica, florisil and alumina columns. The final extract was spiked with isotopically-labeled standards prior to instrumental analysis. Analysis of the extract was performed using HRGC (DB-5HT, 30 m, 0.25 mm i.d., 0.10 um film thickness) coupled with HRMS. Method blanks were processed with each set of 10 field samples. When non-detects were reported, 1/2 detection limit values were substituted for calculation of total PBDE concentrations. Total 1/2 detection limit substitutions did not exceed 8% of total PBDE concentrations.

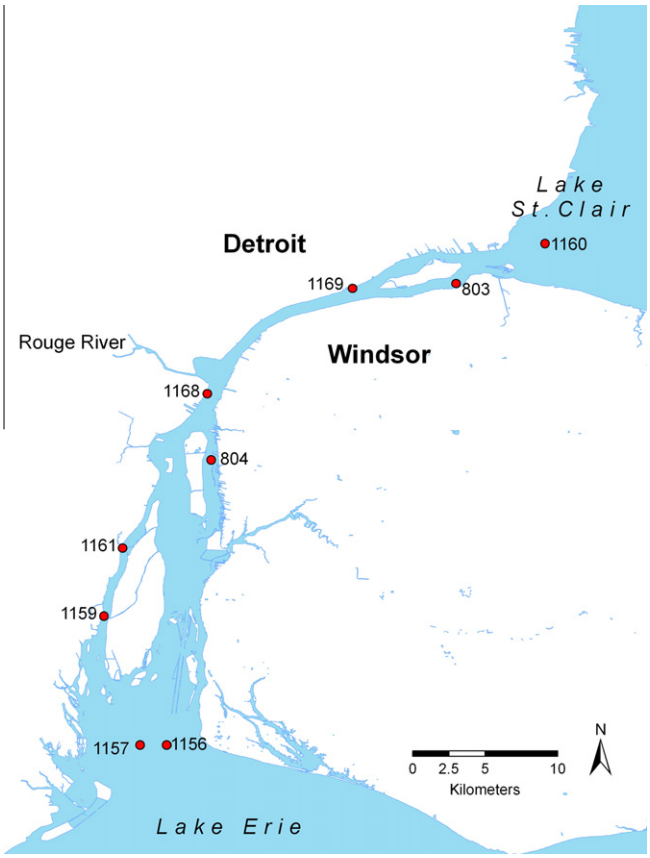

Fig. 1. Station locations for suspended sediments in the Detroit River.