POLYBROMINATED DIPHENYL ETHERS IN DETROIT RIVER SEDIMENT

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Introduction

The Detroit River is a major connecting channel system in the Great Lakes–St. Lawrence Seaway. This waterway is an important binational resource shared by the United States and Canada. Water resources are heavily used by millions of residents in Michigan and Ontario for recreational boating and angling, commercial navigation, and drinking water. The corridor supports multi-million dollar shipping, manufacturing, mining, and fishing industries. The corridor has long suffered from loadings of persistent toxics from a variety of sources, including over ten thousand commercial and industrial discharges, sewage treatment plants and combined sewer overflows, and urban runoff. The Trenton Channel area of the lower Detroit River contains areas of sediment contaminated by PAHs, PCBs and heavy metals due to historic industrial activities. The Detroit and St. Clair Rivers have been designated as Areas of Concern (AOCs) by the International Joint Commission (IJC). The Detroit River watershed is reportedly a primary source of contaminants to the western basin of Lake Erie. Environment Canada routinely measures the occurrence and spatial distribution of toxic substances in AOCs to further understand the role human activities play in releasing these compounds to the environment, and to provide information on transport and fate of contaminants in aquatic systems. 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 (1).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. 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 newer compounds. In this paper, we present an overview of the occurrence, spatial distributions and temporal trends of contaminants focusing on polybrominated diphenyl ethers.in the Detroit River.

Methods

Suspended sediment samples were collected from May to October using single-point sediment trap moorings. These sediment trap assemblies were modified from a design previously used for the study of the downflux and composition of particulate matter in the Great Lakes. The key parameter in the design of the traps is the aspect ratio, defined as the ratio of the internal diameter of the trap tube to the length. The moorings were refurbished monthly and accumulated material deposited in the traps was removed, transferred to Nalgene® containers and refrigerated. Samples were returned to the laboratory and frozen.

Samples were spiked with isotopically labeled BDE surrogate standards, solvent extracted and cleaned up on a series of chromatographic columns which may include layered acid/base silica, florisil, and alumina columns. The final extract was spiked with isotopically labeled recovery (internal) standards prior to instrumental analysis. Analysis of the extract is performed on a high resolution mass spectrometer (HRMS) coupled to a high-resolution gas chromatograph (HRGC) equipped with a DB-5HT chromatoghraphy column (30 m, 0.25 mm i.d., 0.10 um film thickness).

Results and Discussion

Many of the new compounds measured in the environment are produced for use in consumer products. The PBDEs are heavily-produced flame retardants used in thermoplastics, polyurethane foams and textiles. Although the penta- and octa formulations are no longer produced in North America, the fully-substituted BDE 209 is still heavily used and is typically the most predominant congener detected in sediments. A major vector for PBDEs to enter the aquatic environment is through the atmosphere. The semi-volatile compounds are released to the atmosphere from the products where they partition onto particulates. There is also evidence that the less volatile compounds like BDE 209 enter the atmosphere from weathering and abrasion of polymers from commercial products (2, 3) Indoor air has been reported at levels 20-30 times higher than outdoor air which is in turn vented to the outside environment. (4) For many compounds associated with consumer products the bulk of the releases occur thru weathering and thru land filling 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). Thus they may be directly released in treated effluent or via application of sewage sludges.

The occurrence and spatial distribution of PBDEs in suspended sediment for 2001 is shown in Figure 1. Background levels from Lake Huron were 12 ng/g and did not change significantly downstream through the St. Clair River, despite the heavy chemical industrialization of the area. There was little change in these concentrations in 2006. Increased levels of PBDEs were observed in the upper reaches of the Detroit River, and subsequently increased downstream along the American side of the river. Cross-river differences in levels of total PBDEs at the mouth of the river indicate the majority of PBDE loadings are along the western shoreline. The distribution of PBDEs in the Detroit R. is comparable to the distributions of other modern chemicals, including the brominated flame retardant hexabromocyclododecane (5). While the highest concentrations of legacy chemicals like PCBs are typically observed in the lower reaches of the river in the Trenton Channel (1), elevated levels of PBDEs were also observed upstream in the middle and upper reaches of the river.

The temporal trend from 1999-2009 for the two cross-river stations at the mouth of the Detroit R. are shown in Figure 2. The graph shows declines in concentration from 2001-2003 followed by a general leveling off. The overall decline in total BDEs over this time period is about 20% for both stations. The decreasing temporal trend during the 2001-2003 presumably is a result of the phasing out of the penta- and octa formulations; continued production and use of BDE 209 is reflected in the more consistent trend since 2003. The temporal trend of the contribution of BDE 209 to the total PBDE burden (Figure 3) exhibits a general increase over the past decade; this observation also supports our interpretation of the overall total PBDE temporal trend we attribute to the phasing out of the penta- and octa formulations and continued production and use of BDE 209.

The distribution of PBDEs in suspended sediments in the Detroit River appeared to be heavily influenced by shoreline-based contemporary urban and industrial activities, which stands in contrast to PCBs that are associated with areas of historic industrial activity. The widespread occurrence, but relatively low concentrations, of PBDEs in suspended sediments suggest that large urban areas can act as diffuse sources of these chemicals that are used in modern industrial applications. (5)

References

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Acknowledgements

We thank Jake Kraft at Environment Canada and the crew of the C.C.G.S. Limno,

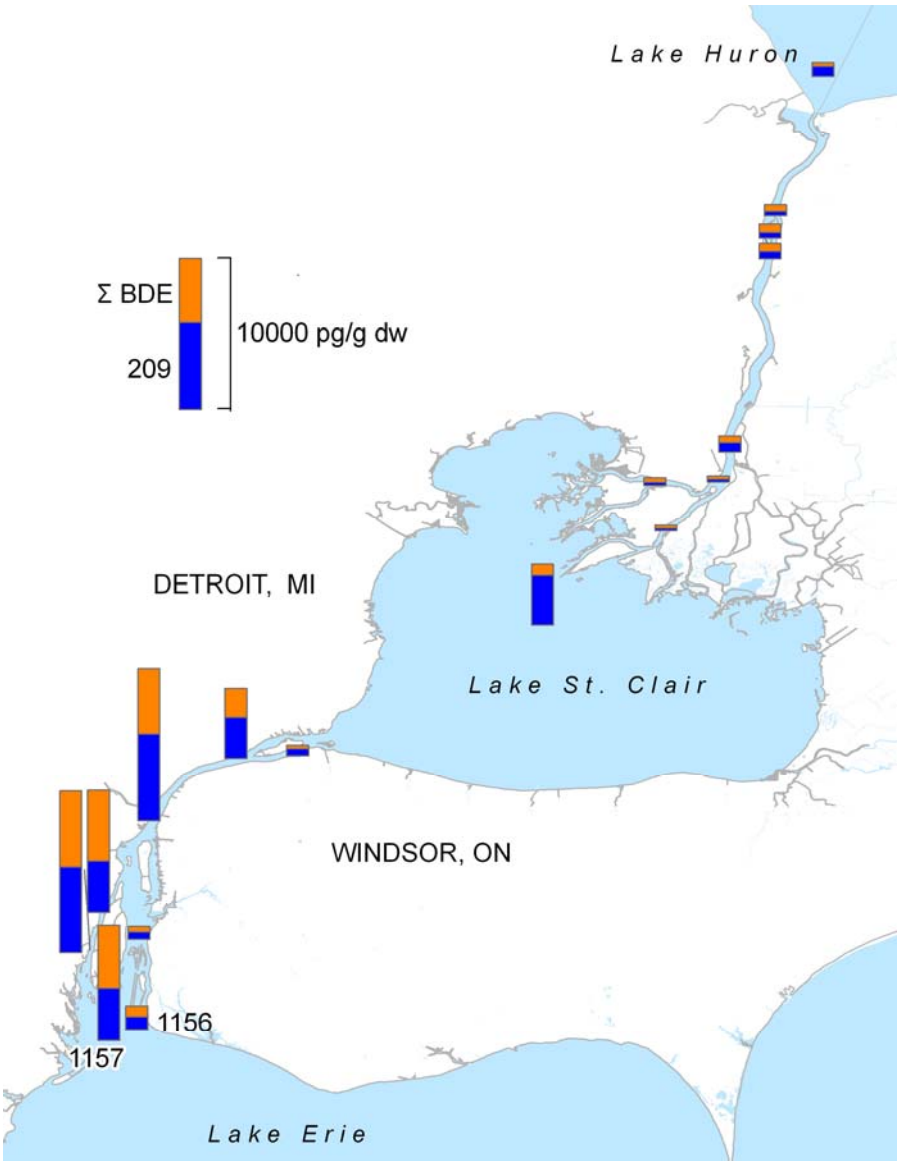

Figure 1.PBDE concentrations in suspended sediment in the Detroit R. 2001

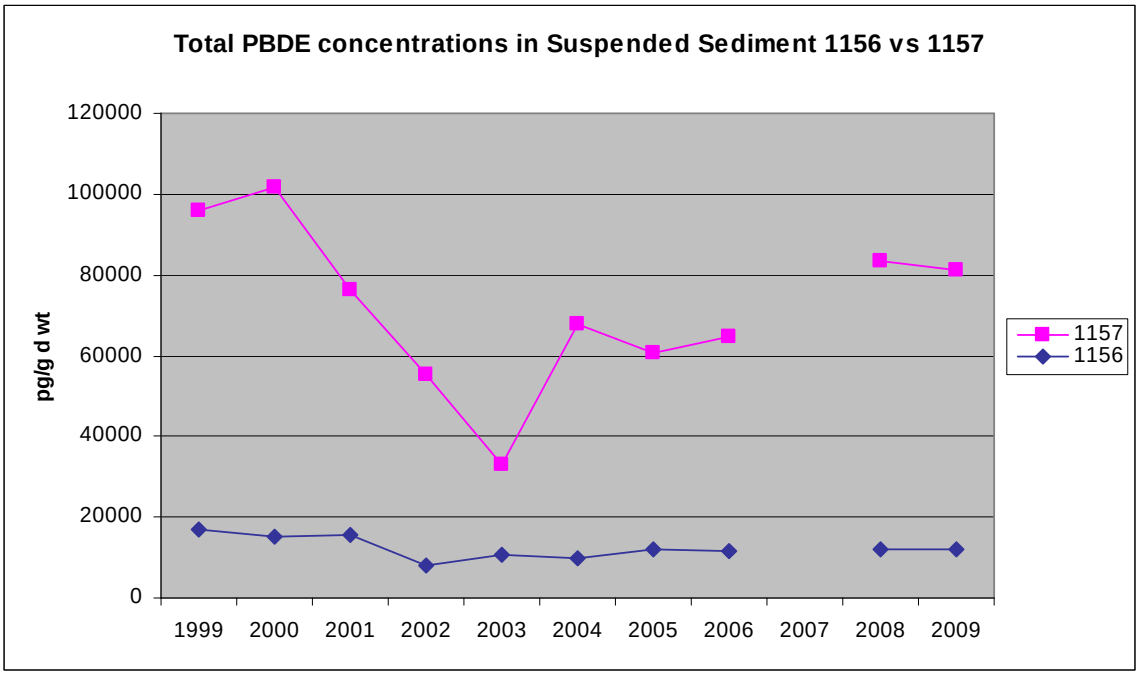

Figure 2. Concentration of PBDEs on suspended sediment 1999-2009

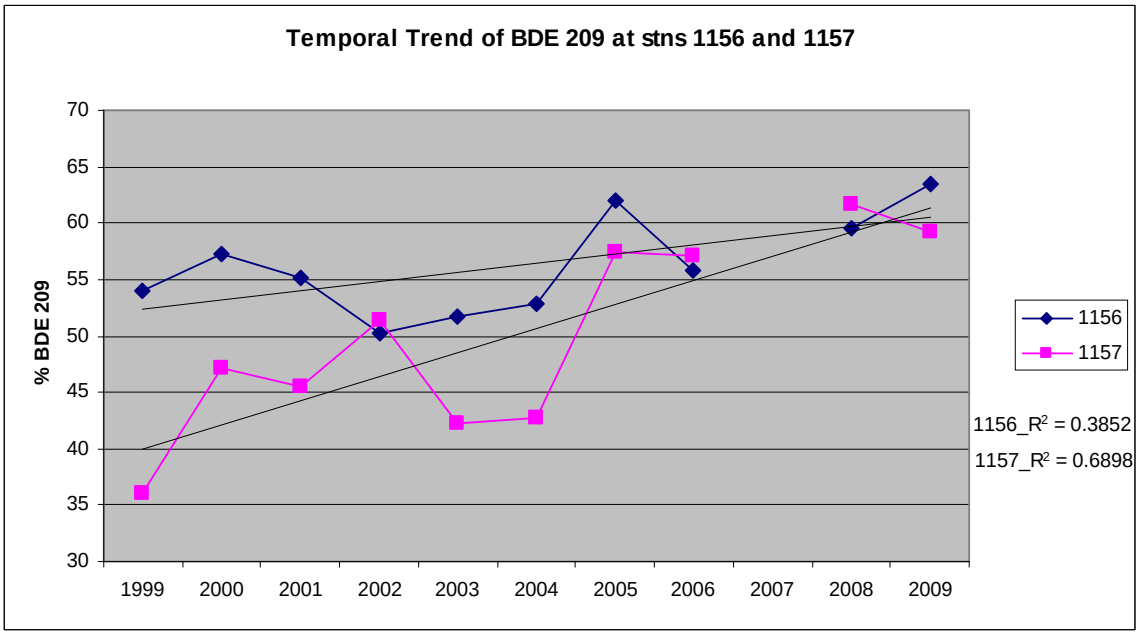

Figure 3. % BDE 209 in suspended sediment from stations 1157 and 1156