PBDES IN SURFICIAL SEDIMENTS OF THE GREAT LAKES: LAKES SUPERIOR, HURON AND MICHIGAN

Li Shen[1,2], Sarah Gewurtz[1,2], Eric Reiner[2], Terry Kolic[2], Karen MacPherson[2], Paul Helm[2], Todd Howell[2], Debbie Burniston[3], Ian Brindle[1], Chris Marvin[1,3]*

[1]Department of Chemistry, Brock University, Canada;
[2]Ontario Ministry of the Environment, Canada; [3]Environment Canada, Canada

Introduction

The watersheds of the upper Great Lakes (Lakes Superior, Huron and Michigan) are less urbanized and industrialized compared to the lower Great Lakes (Lakes Erie and Ontario), but these upper lakes have the potential to trap and accumulate contaminants because of their large surface areas and long water retention times. Polybrominated diphenyl ethers (PBDEs) have been detected in the upper Great Lakes sediments[1,2]; however, information on PBDEs in sediments on a lake-wide basis is limited. Environment Canada conducted sediment surveys on open water of Lake Superior (L Superior) in 2001, Lake Huron (L Huron) including Georgian Bay and North Channel in 2002, and Lake Michigan (L Michigan) in 2002 to evaluate the current extent of sediment contamination, determine spatial trends of contaminants, and identify areas of potentially associated sources. Environment Canada also conducted a tributary screening survey on L Superior in 2006 and L Huron in 2004 by sampling surficial sediments near the mouths of Canadian tributaries, which provides an indicator of water quality and contaminant loadings in Canadian watersheds around the lakes. Water quality in the nearshore areas of the Great Lakes is regularly monitored by the Ontario Ministry of the Environment (OMOE) through the Great Lakes Nearshore Monitoring and Assessment Program. Long term index and reference stations have been selected in areas representative of background conditions and in areas where there is a natural integration of the anthropogenic stressors from a larger area. These sites are visited on a lake-by-lake cycle, measuring a routine set of water quality parameters to indicate status and changes in environmental quality, including sediment-associated chemical contamination. Index and reference station sediments analyzed for PBDEs were collected from L Superior, the connecting channel St. Mary's River, and the North Channel in 2005 and from L Huron and Georgian Bay in 2002. In this study, we combine these unique and extensive databases of Environment Canada and the Ontario Ministry of the Environment from surveys of L Superior, L Michigan and L Huron to determine PBDE concentrations, their spatial trends, and congener profile patterns throughout these lakes.

Materials and Method

Surficial sediment samples were collected from more than 100 stations throughout the L Superior, L Huron, and L Michigan. Offshore samples were collected using a mini box core sampler, nearshore samples using a Shipek grab sampler, and tributary samples using a stainless steel spoon, or a Wildco Petite Ponar sampler when necessary. All samples were homogenized, stored in pre-cleaned glass jars, and refrigerated or frozen for transport to the laboratory. Methods for analysis of PBDEs in surficial sediments are described in detail elsewhere[3]. Briefly, frozen samples were thawed, air-dried, ground, and homogenized, and then fortified with ^{13}C-labelled PBDE quantification standards with one for each homologue group. Fortified samples were Soxhlet extracted overnight in toluene. Cleanup was performed using an acid/base/silver nitrate silica column. Seventeen PBDE congeners (BDE-17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -183, and -209) were determined using gas chromatography (GC)-high resolution mass spectrometry (HRMS) using a Hewlett-Packard HP6890 GC equipped with a DB-5HT column (15m x 0.25mm x 0.10 μm, J&W Scientific, USA) in splitless mode, coupled to a Waters/Micromass Autospec-Ultima HRMS system tuned to 9000+ RP (10% valley definition).

Results and Discussion

PBDEs in surficial sediments

The sum of seventeen PBDE concentrations is shown in Figure 1. PBDEs are widely dispersed and display a large variation across the watersheds of L Superior, L Huron, and L Michigan. Normalizing concentrations to organic carbon content (TOC) did not alter the spatial distribution pattern for PBDE concentrations. In general,

the open water areas of L Huron and L Michigan exhibit slightly higher levels of PBDEs than L Superior (Figure 2). The PBDE concentrations in offshore sediments were in the range of 0.2 ~ 5, 0.3 ~ 13, and 1.5 ~ 16 ng/g dry wt for L Superior, L Huron, and L Michigan, respectively. Nearshore sediments had PBDE concentration ranges similar to offshore sediments in L Superior and L Huron (Figure 2). PBDE contamination in offshore and nearshore sediments is at the lower end of the concentration range reported in the literature[4]. The greatest PBDE concentrations were found in several of the tributary samples. For example, tributary sediments collected from ST2 (40 ng/g dry wt) and HT13 (53 ng/g dry wt) had the highest concentrations, followed by ST6 (15 ng/g dry wt), ST3 (17 ng/g dry wt), ST4 (24 ng/g dry wt), and HT1 (21 ng/g dry wt). PBDE concentrations in surficial sediments collected from open water areas of the Great Lakes were reported previously and the lower Great Lakes had higher PBDE concentrations in surficial sediments than the upper Great Lakes, reflecting the influence of urbanization[1,2,5]. In this study, the sum of PBDE congener concentrations excluding BDE209 is comparable to those previously reported for L Superior, L Huron, and L Michigan, but the BDE 209 concentrations in this study were lower[1,2,6]. Qiu et al also found more than one order of magnitude difference in BDE209 concentration in Lake Ontario surficial sediments between their work[7] and that of Song et al[1,2].

PBDE congener profiles

Most of surficial sediments are dominated by BDE209, varying from 50% to 95% of total concentrations of the seventeen PBDE congeners. In general, L Huron and L Michigan offshore sediments had similar congener profile patterns in which BDE209 accounted for more than 80% of PBDEs (*e.g.* H43, H100, GB17, GB21, M18, and M48 in Figure 3), while the congener profiles in L Superior offshore sediments had higher proportions of BDE47 and 99 (S127 and S157). Surficial sediments at the mouths of several tributaries not only had high PBDE concentrations but also were characterized by shifts in congener profiles compared to open waters of L Superior (ST2 *vs.* S127 and S157) and L Huron (HT1 and HT13 *vs.* H43, H100, GB17, and GB21). In L Superior, BDE47, 99, 100, 153, 153, and 183 accounted for ~ 30% of the total PBDEs in the tributary ST3 sample and ~ 50% in the ST4 sample; while BDE47 and 99 were the most detected congeners in the ST2 sample (Figure 3). In L Huron, the HT1 sample had a similar congener profile to the ST3, and the HT13 similar to the ST4.

PBDE source to the upper Great Lakes

The upper Great Lakes are characterized by watersheds that are significantly less urbanized and industrialized compared to the lower lakes; therefore, the major inputs of contaminants are believed to be primarily from atmospheric deposition with accumulation in the depositional areas of the lakes. However, the relatively higher PBDE concentrations at mouths of several tributaries could not be accounted for by atmospheric deposition. Although sediment contamination relating to industrial activities is known in many areas of L Superior, L Huron, and L Michigan as they are listed as Areas of Concern (AOC) by the International Joint Commission (IJC), it is unknown if the same activities (mining, metals refining, pulp and paper, etc.) impact PBDE concentrations. For instance, the area of the St. Mary's River is one of AOCs that receives effluents of steel and paper industries from ST3 and ST4[8,9] where high PBDE levels were observed in this study. A high dioxin-like PCB (DLPCB) concentration was also found at ST4[10]. The ST2 site is located in the area of Thunder Bay, which is also an AOC and known for its forest products (pulp and paper mills, sawmills, and wood treatment plants). However, each of these areas is also associated with relatively higher population density within these lake basins and may be affected by municipal wastewater and storm water inputs. Similarly, the offshore samples from H100 in L Huron and M48 in L Michigan showed relatively high PBDE concentrations (Figure 1) which may be related to industrial activities from the Saginaw River/Bay and the Kalamazoo River areas, but may also reflect higher PBDE usage as both have relatively high population densities in the basins. The depositional area in southern L Michigan, M18 (16 ng/g dry wt) (Figure 1), may be influence by the urban Chicago area. Environmental releases of PBDEs to the Great Lakes are believed to be from the use of the penta- and/or deca-technical products. North America accounted for 98% of the global demand for penta-BDE in 1999[11]. Hale et al[12] also reported that the deca-BDE mixture accounts for greater than 70% of total PBDE production in North America.

Acknowledgements

We thank the EC and OMOE staff and the crew of the *C.C.G.S. Limnos*, *Monitor VI*, and *Great Lakes Guardian* for sample collection and Tereza Gobran at Laboratory Services Branch, OMOE for sample preparation.

References

1. Song W, Ford J, Li A, Mills W, Buckley D, Rockne K. *Environ. Sci. Technol.* 2004; 38:3286.
2. Song W, Li A, Ford J, Sturchio N, Rockne K, Buckley D, Mills W. *Environ. Sci. Technol.* 2005; 39:3474.
3. Ontario Ministry of the Environment. *Laboratory Services Branch Method BDE-3430.* 2004.
4. Hites R. *Environ. Sci. Technol.* 2004; 38:945.
5. Song W, Ford J, Li A, Sturchio N, Rockne K, Buckley D, Mills W. *Environ. Sci. Technol.* 2005; 39:5600.
6. Zhu L, Hites R. *Environ. Sci. Technol.* 2005; 39:3488.
7. Qiu X, Marvin C, Hites R. *Environ. Sci. Technol.* 2007; 41:6014.
8. Lake Superior Lakewide Management Plan (LaMP). Lake Superior Binational Program. 2004.
9. St. Marys River Remedial Action Plan (RAP). The St. Marys River Area of Concern: Remedial strategies for ecosystem restoration, Stage 2 Report.
10. Shen L, Gewurtz S, Reiner E, MacPherson K, Kolic T, Khurana V, Helm P, Howell T, Burniston D, Brindle I, Marvin C. *Environ. Pollut.*; submitted.
11. Renner R. *Environ. Sci. Technol.* 2000; 34:452A.
12. Hale R, Alaee M, Manchester-Neesvig J, Stapleton H, Ikonomou M. *Environ. Int.* 2003; 29:771.

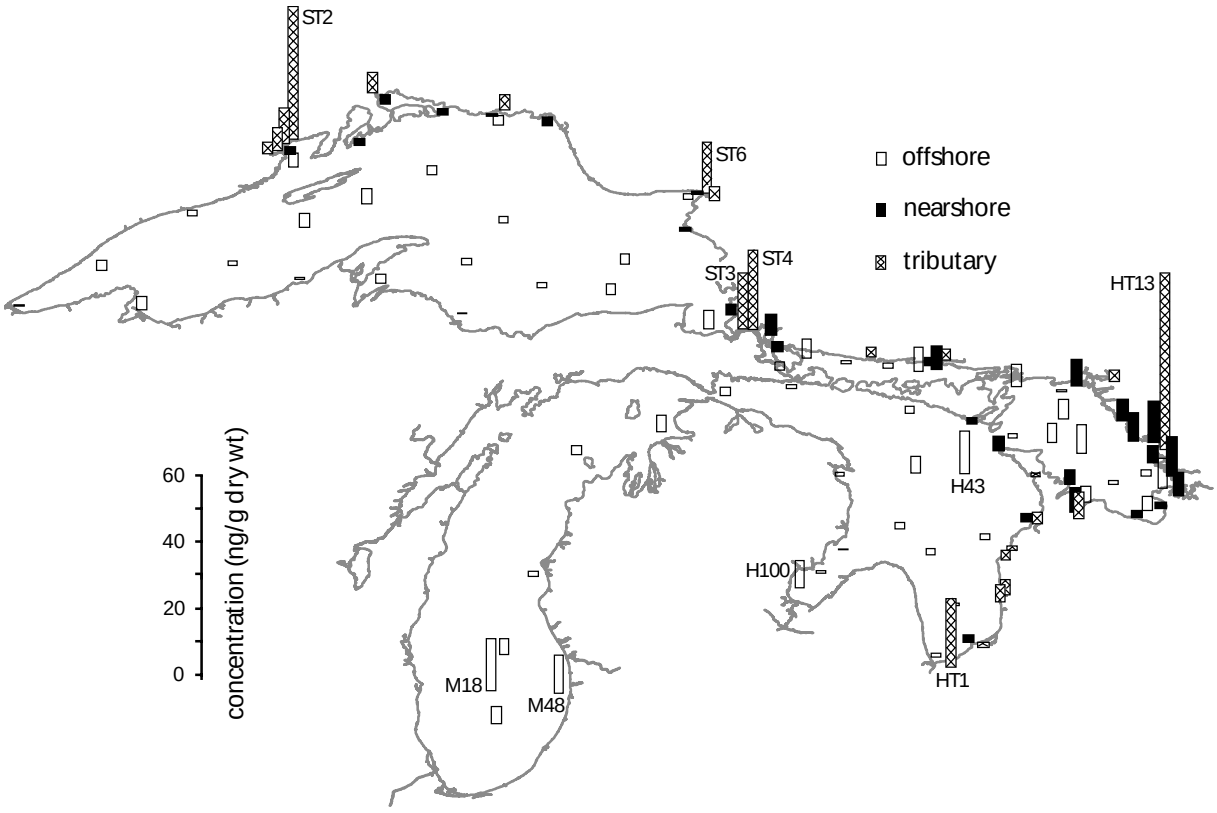

Figure 1: Map of PBDEs in surficial sediments of Lakes Superior, Huron and Michigan

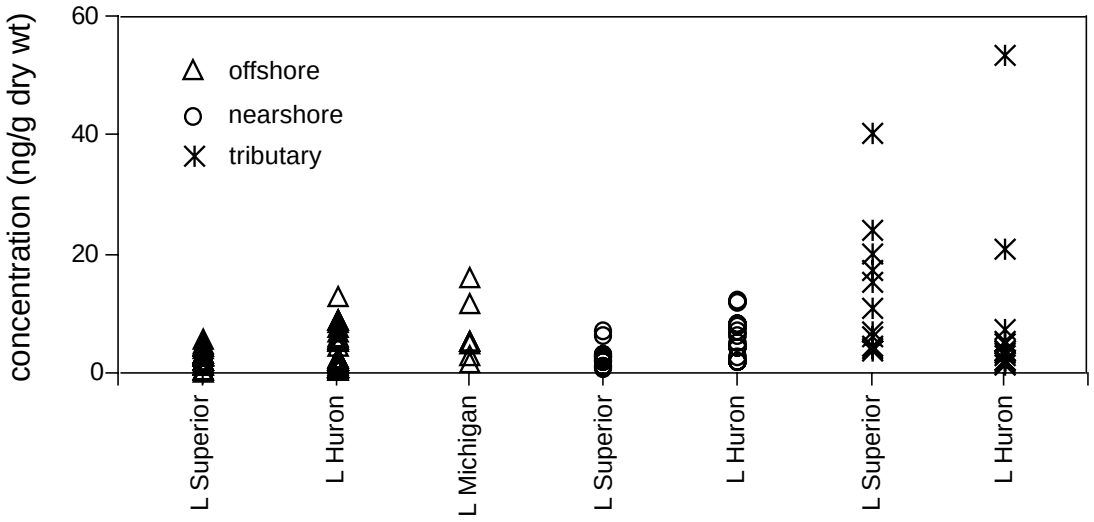

Figure 2: PBDE concentrations in surficial sediments of Lakes Superior, Huron and Michigan

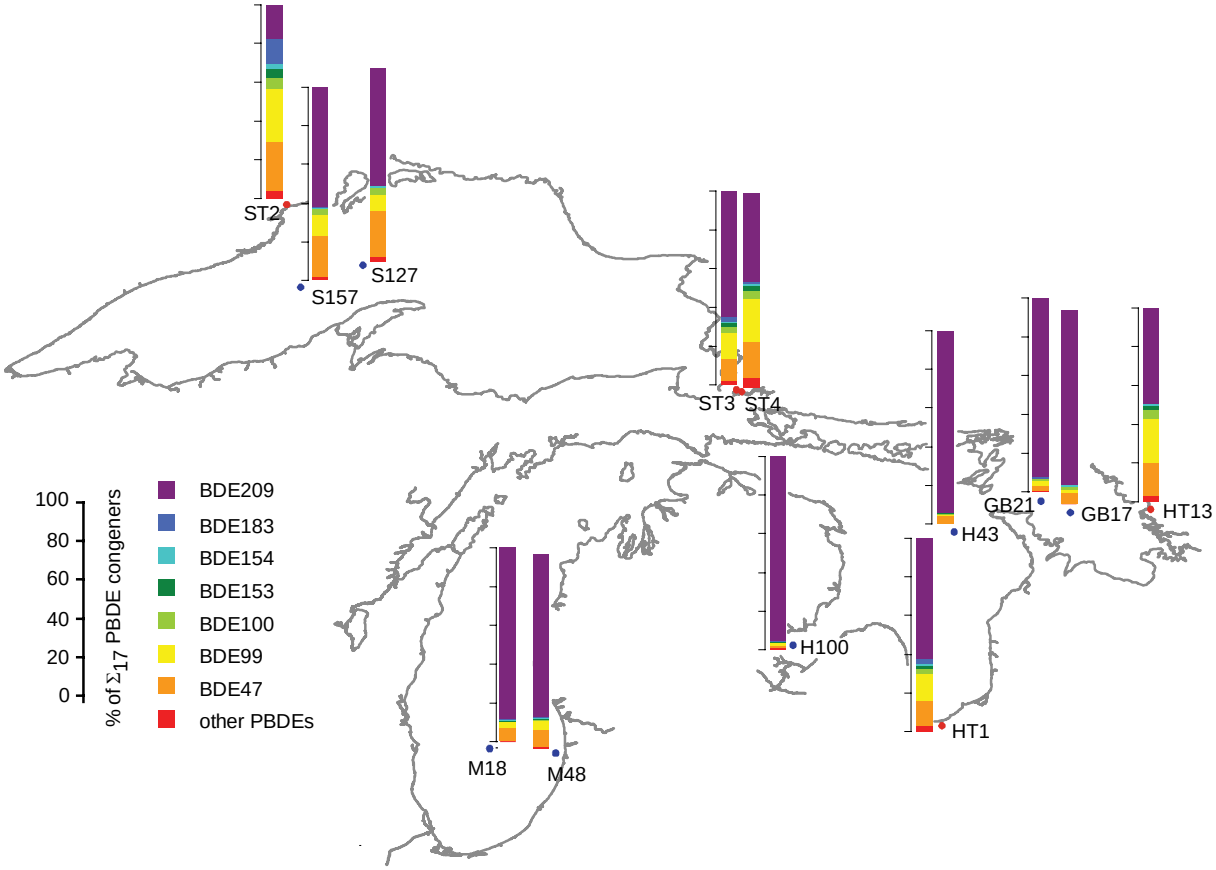

Figure 3: PBDE congener profiles in surficial sediments of Lakes Superior, Huron and Michigan.