

## TEMPORAL TREND AND SPATIAL DISTRIBUTION OF PBDEs IN THE SEDIMENTS OF THE GREAT LAKES

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### Introduction

The adverse health effects and rapid accumulations of polybrominated diphenyl ethers (PBDEs) in the environment and in human have caused great concerns.<sup>1</sup> Since first reported in soil and sludge from the USA in 1979<sup>2</sup> and in fish from Sweden in 1981,<sup>3</sup> PBDEs have been found in measurable amounts in various samples around the world including air, water, soil, sediment, biota, and human milk, blood, and adipose tissues. In the Great Lakes region, the concentration of PBDEs in the air at four land locations ranged from 5 pg m<sup>-3</sup> near Lake Superior to 52 pg m<sup>-3</sup> in Chicago.<sup>4</sup> PBDEs were also found in the fish of all the five Great Lakes.<sup>5-7</sup> This research was carried out to investigate the temporal trend and spatial distribution of PBDEs in the Great Lakes as recorded in the sediments.



Figure 1. Sampling Locations

### Methodology

Sixteen sediment cores were collected in the summers of 2001 and 2002. The sampling was performed using a 0.084 m<sup>3</sup> box corer deployed from the USEPA *RV Lake Guardian*. Sampling locations are shown in Figure 1. At each location, 4 or 5 subcores were taken from the box corer using pre-cleaned acrylic tubes of 7.0 cm I.D. Individual subcores were extruded using an aluminum foil-covered push plunger and sectioned on the ship. Most cores were sectioned at 1.0 cm intervals for the first 10 cm, then in 5 cm increments for the remainder of the core. The sediment segments at corresponding depth were composited into a pre-cleaned amber glass jar in order to obtain sufficient amount of sample for laboratory analyses. The samples were then refrigerated onboard the ship at 4°C until transport to the laboratory where they were stored frozen until analysis.

Each sediment sample was characterized for percent solids, wet and dry bulk density, particle density, and porosity. The contents of organic matter, organic carbon, soot carbon, non-soot carbon, nitrogen, and oxygen, were also determined. Each segment was dated using <sup>210</sup>Pb radiological method, and the results were used to determine the year of sediment deposition, and to estimate the sedimentation rate and focusing factor. Detailed procedures are presented elsewhere.<sup>8-9</sup>

Ten PBDE congeners were analyzed, including tri- (BDE28), tetra- (BDE47 and BDE66), penta- (BDE85, BDE99, and BDE100), hexa- (BDE153 and BDE154), hepta- (BDE183), and deca- (BDE209) bromodiphenyl ethers. Selected PCB congeners were also analyzed for all the sediment samples for comparison. In the laboratory, wet sediment was ground with anhydrous Na<sub>2</sub>SO<sub>4</sub> or Hydromatrix, and spiked with known amounts of PBDE surrogate <sup>13</sup>C labeled 2,3',4,4',5-penta bromodiphenyl ether (BDE118), PCB surrogate 2,3,5,6-tetrachlorobiphenyl (PCB65),

and BDE209 surrogate  $^{13}\text{C}$  labeled BDE209. The sediment was Soxhlet-extracted for 20 hr with 1:1 (v) hexane:acetone mixture. Elemental sulfur was removed by adding activated granular copper to the Soxhlet flask during extraction. The extract was then concentrated on a Kuderna-Danish (K-D) concentrator, solvent-exchanged to hexane, and cleaned-up by elution through a glass column filled with activated silica gel with 75 mL 9:1 (v) hexane:dichloromethane mixture. The eluant was again concentrated using K-D concentrator and  $\text{N}_2$  to 2.0 mL.

Quantitative analyses of PCBs and PBDEs were performed on an Agilent Model 6890 gas chromatograph (GC) coupled with a Model 5973 mass spectrometer (MS). Separate runs were made for PBDEs and PCBs using a DB-5MS (30 m  $\times$  0.25 mm  $\times$  mm) J&W capillary column, with helium as the carrier gas at flow rate of 1 mL  $\text{min}^{-1}$ . BDE209 was analyzed using a 15 m DB-5MS column. Internal standards (PCB204 for PBDEs, PCB30 and PCB204 for PCBs, and BDE190 for BDE209) were added to each sample before GC injection. Samples were introduced into GC/MS through a programmable temperature vaporization (PTV) large volume injection port. A total of 60 mL was injected in each run, with three injections of 20 mL each. Electron impact mass spectrometry (EI-MS) was used for all analytes except BDE209. The MS was operated in selected ion monitoring (SIM) mode. For BDE209, NCI-MS was used with the fragment ion of  $m/z$  486 for quantitation, and the  $m/z$  485 and 487 ions were used for confirmation. For  $^{13}\text{C}$ -BDE209, the  $m/z$  494 ion was used for quantitation and confirmation ions were  $m/z$  495 and 497.

Matrix blanks were pre-1900 segments for all dated cores except five cores from Lake Superior, for which the segments dated before 1850, were used as matrix blanks. The averages of chemical concentrations in the matrix blanks of each core were subtracted from the results of chemical analysis. The surrogate recoveries were in the range of 60% to 170%, and those for  $^{13}\text{C}$ -BDE209 were from 25% to 97%. All reported results are after corrections based on surrogate recoveries. One sediment sample in each core was analyzed in duplicate. NIST SRM 1939a (river sediment) was analyzed using the same analytical procedure. Our results were within 70% to 120% of the certified PCB congener concentrations.

## Results and Discussions

The concentration profiles as a function of depth are presented in our previous publications.<sup>8-10</sup> The maximum concentrations generally appeared in the top layers of the sediment cores, reflecting well the increasing production and usage of PBDEs in recent decades. The fact that maximum concentrations appear in the top layers of sediments implies the possibility that the increasing trend of PBDE inputs to the lake continues after 2002.

The inventory and flux of the chemicals to the sediment were estimated using equations [1] and [2], respectively.

$$\text{Inventory} = S C_i r_b d_i \quad [1]$$

$$\text{Flux}_i = C_i R_i / \text{FF} \quad [2]$$

where  $C_i$  is the concentration in sediment segment  $i$  ( $\text{ng g}^{-1}$  dry weight),  $r_b$  is the dry mass bulk density ( $\text{g cm}^{-3}$ ),  $d_i$  is the thickness of segment  $i$ , FF is the focusing factor of the location, and  $R_i$  is the sedimentation rate in  $\text{g cm}^{-2} \text{yr}^{-1}$ .

Inventories of the contaminants represent the total integrated mass of the compound of interest per unit area. Figure 2 shows that Lakes Ontario and Erie have accumulated much more PBDEs than the other lakes. The inventories are found to be related to the proximity of the sampling locations to urban areas. Also, a decreasing trend of PBDE inventory with increasing latitude is observed, but additional data over a much longer distance in the North America are needed to examine the dependence of PBDE inventory on latitude.

In all samples, the dominance of BDE209 in the total PBDEs in sediments is unquestionable. It counts from 70% to 98% of the total inventories. Among the other nine congeners, BDE47 and BDE99 are apparently more abundant than the others, and congeners 100, 153, 154, and 183 were also found in all the cores.

As expected, the PBDE fluxes at all locations were generally in continuous and obvious increase since the 1970s, while those of PCBs have been leveled or decreased at most locations (Figure 3). The fluxes seem to depend more strongly on the sediment movement and transport within a lake than the inventories, and do not always show a

dependence on the distance of the location from large urban centers.

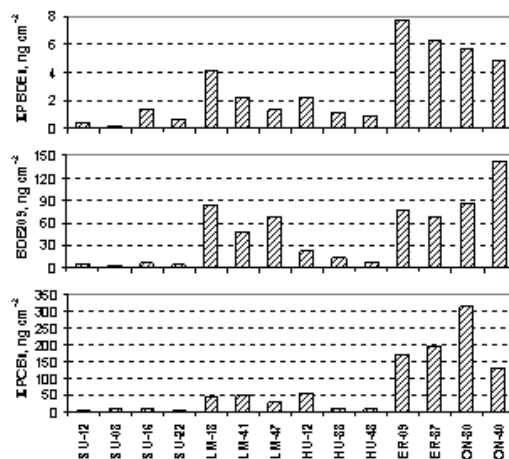


Figure 2. Comparison of Inventories among the Great Lakes.

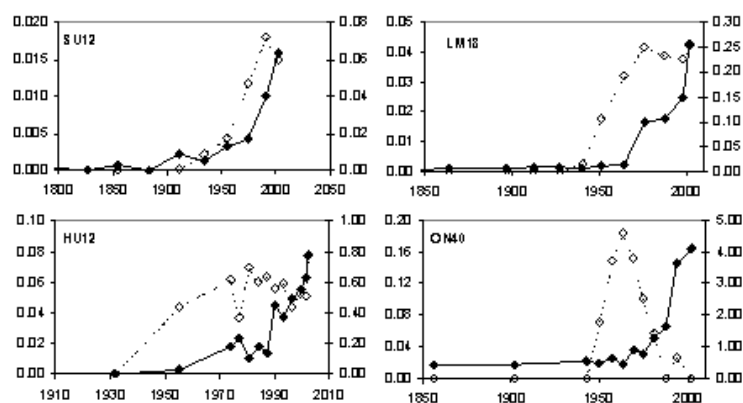


Figure 3. Flux of PBDEs (filled diamonds and solid lines, left scale) and PCBs (empty diamonds and dashed lines, right scale) into Great Lakes.

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