

## **A DEPTH PROFILE OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND POLYCHLORINATED BIPHENYLS (PCBs) IN SEDIMENTS FROM LAKE MICHIGAN**

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### **Introduction**

Polybrominated diphenyl ethers (PBDEs) are used around the world principally as flame retardants, but they have also become ubiquitous global contaminants.<sup>1,2</sup> Recent figures (1999) for worldwide demand from the Bromine Science and Environmental Forum (reported in de Wit<sup>1</sup>) indicate that about 67,000 metric tons of PBDEs are sold annually. Slightly more are used in North America (51%) than elsewhere.

Meironyte et al.<sup>3</sup> report the concentrations of PBDEs (measured as congeners BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-153, and BDE-154) in Swedish breast milk from samples spanning a twenty five year period from 1972 to 1997. During this period, PBDE concentrations increased more than fifty-fold, from 0.07 ng/g lipid to 4.02 ng/g lipid. This data set was reportedly paramount in the decision process that has led to the European Union banning the import and use of penta-BDE and octa-BDE by July 1, 2003<sup>4</sup>. Hooper and McDonald<sup>5</sup> compare the data generated by the Meironyte study and data depicting the concentration of the sum of toxic equivalents (TEQs) resulting from the presence of dioxins, furans and PCBs in breast milk. The researchers report that longstanding contaminants of concern have decreased over the past three decades, while PBDEs (which have toxicological endpoints not unlike dioxins, furans and PCBs) have increased exponentially.

PBDEs have been quantified in sediments of rivers, lakes and seas.<sup>6-10</sup> The presence of PBDEs in sediments underscores their resistance to degradation. Also, sediment records can sometimes be used to reconstruct historical inputs of persistent compounds, and so provide an important tool in the assessment of transport and fate of environmental contaminants. In this paper, we report recent concentration measurements of PBDEs in the sediments of Lake Michigan, which to our knowledge are the first such measurements.

### **Methods and Materials**

Sediment samples from a depth of approximately 80 m were collected from southeastern Lake Michigan in August 2001. Sediments were retrieved using a 30 cm x 30 cm box corer. The intact box core (with undisturbed sediment-water interface) was sub-sampled using coring tubes and gentle vacuum. Cores were hydraulically extruded and sliced into 1 cm sections from surface to 12 cm depth. Sediment samples were placed in ashed glass containers with screw top lid and stored at 4°C. Samples were analyzed upon return to the shore. Separate sub-cores from the same box were sectioned to create samples for ancillary analyses (not discussed here).

A 50 g aliquot of sediment from each sample was placed in a Petri dish and slowly brought to a water content of 50-60% w/w. The samples were completely transferred to an Erlenmeyer flask and a recovery spike was added. Samples were extracted with 75 ml of acetone, followed by 50 ml of dichloromethane (DCM), using a sonicating water bath at 35°C. The extracts were filtered over ashed quartz fiber filters directly into separatory funnels containing 200 ml of purified water and 25 ml of saturated NaCl solution. The DCM phase and two subsequent 40 ml DCM extractions were collected and combined. Volume was reduced and the analytes transferred to hexane using rotary evaporation. PBDEs were separated from most other trace components using 5 g of 3% w/w deactivated silica in 1 cm columns, eluted with 60 ml of hexane. Volume was reduced and solvent was changed to iso-octane. The extracts were placed in a 2 ml volumetric flask with 100 µl of internal standard and brought to volume.

Extracts were analyzed using gas chromatography (DB-5, 30 m, 0.25 mm, 0.25 µm) and a three-point calibration based on standards from Cambridge Isotope Laboratories, Inc., Andover, Massachusetts, USA. All solvents were trace analysis grade.

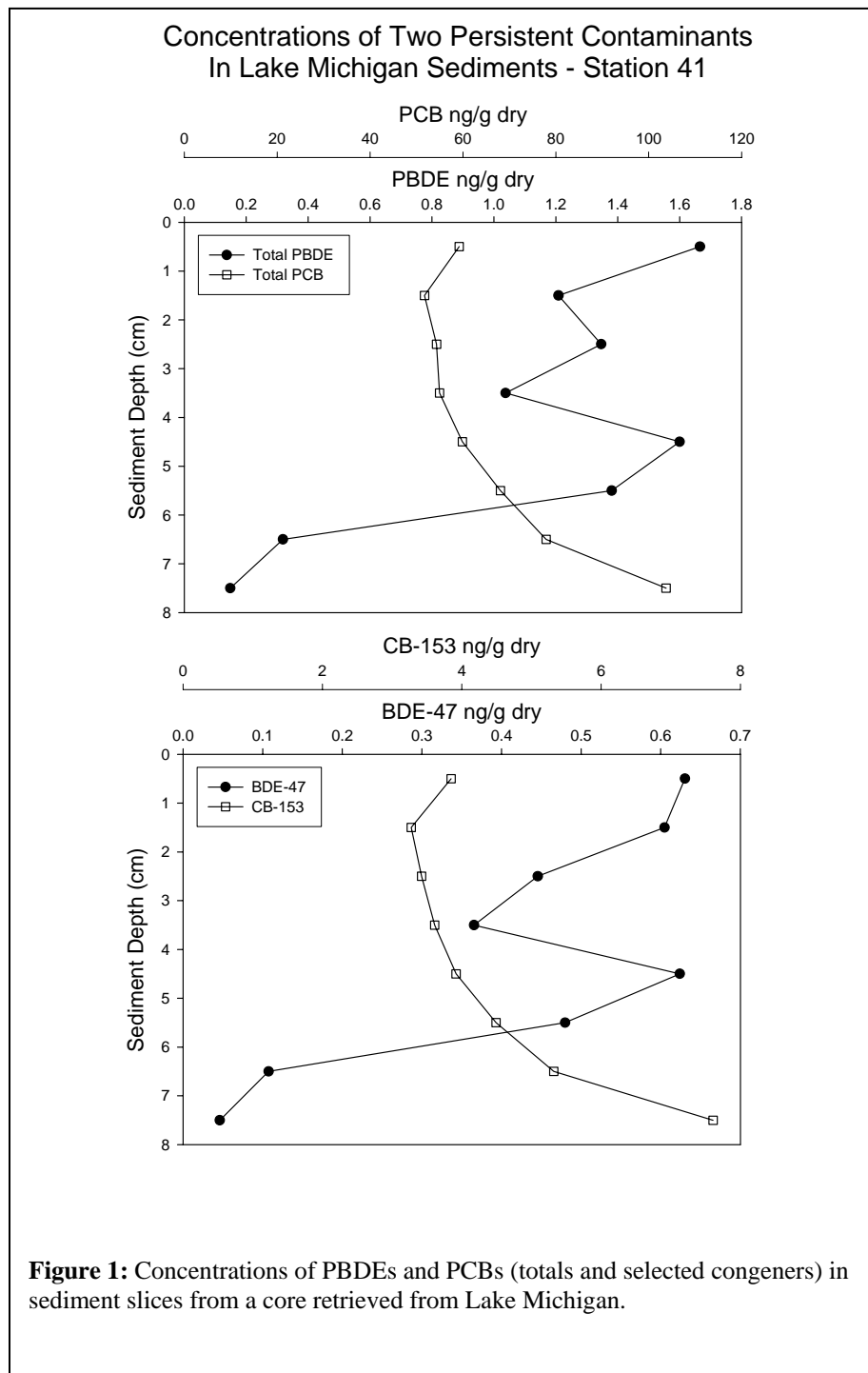
### Results and Discussion

Six PBDE congeners (BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, and BDE-154) were detected and quantified in each of the first eight core sections. Also, using the same extracts but a different GC method and calibration table, about 70 PCB congeners were quantified in the eight core sections. The measured concentrations are plotted with sediment depth in Figure 1.

The average concentration of total PBDEs (sum of the above congeners) at this location in Lake Michigan is 1.1 ng/g dry weight. This is about sixty times less than the concentration of total PCBs in the same samples. Concentrations of major congeners in each group are more similar. BDE-47 has an average concentration of 0.4 ng/g dry weight, and CB-153 is present on average at 4.4 ng/g dry weight.

Average concentrations mask the important trend in the concentration values as a function of sediment depth. The trend is like that described above in the context of breast milk samples: PBDEs are rapidly increasing in concentration even as PCBs are declining. Also, PBDEs have been accumulating in the sediments of the Lake for less time than PCBs. The PBDE profile is near zero at eight centimeters of depth, but the PCBs reach a maximum below this depth, before falling to zero at even greater depths. From the visible trends in the profiles, PBDEs will probably overtake PCBs as the dominant contaminant in these sediments if inputs continue.

Radionuclide data for Cesium-137 in sediments at this location show that this isotope has a maximum concentration at a depth of eighteen centimeters, indicating that sediment at this depth was at the sediment surface in 1963 (see Manchester-Neesvig et al.<sup>11</sup> for a description of radionuclide techniques). Thus, sediment is accumulating at this station at an approximate linear rate of 0.5 cm/yr. Therefore, given that PBDE concentrations approach zero at a depth of eight centimeters, it is possible to deduce that PBDEs have been accumulating at this location in Lake Michigan since about 1985.



**Figure 1:** Concentrations of PBDEs and PCBs (totals and selected congeners) in sediment slices from a core retrieved from Lake Michigan.

### **Acknowledgement**

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