Polybrominated Diphenyl Ethers in the Sediments of Lake Superior

Wenlu Song, Justin C. Ford, An Li, William J. Mills, Dave R. Buckley, and Karl J. Rockne
University of Illinois at Chicago

Abstract
Sediment cores were obtained in Lake Superior at six locations away from lakeshores, and segmented. The year of sediment deposition was estimated using the ^{210}Pb dating technique. Samples were Soxhlet-extracted, cleaned up by silica gel fractionation, and the concentrations of 10 polybrominated diphenyl ethers (PBDEs) and 19 polychlorinated biphenyls (PCBs) were detected by GC-MS in SIM mode. In contrast to recent declining or level-off trends in PCB deposition rates, the sedimentary records of PBDEs generally show a significant increase in recent years. The surfacial ΣPBDE concentration ranged from 0.5 to 3 ng g^{-1}. The current ΣPBDEs flux was 8 to 31 pg cm^{-2} yr^{-1}, and was higher at the sampling location closest to Duluth, Minnesota. The concentrations of decabromodiphenyl ether (BDE209) was found about an order of magnitude higher than other congeners, and counts for about 90% of the total PBDE inventory in the sediments. Among the other 9 PBDEs detected, congeners 47 and 99 were the most abundant, and congeners 100, 153, 154 and 183 were also detected in all the cores. Congener analysis demonstrated that the pattern of PBDEs in Lake Superior sediments differs from those in air and fish, but resembles that of commercial products.

Introduction
Polybrominated diphenyl ethers (PBDEs) are a class of additive flame-retardants that are used in a wide range of consumer products including paints, plastics, textiles, and electronics. They are considered to be environmentally persistent due to their resistance to various degradation, and their high lipophilicity indicates a strong bioaccumulation potential [1,2]. Evidence of their toxic, carcinogenic, and hormone-disrupting effects is also mounting rapidly [3,4].

This research project was carried out to investigate the chronology of PBDE air deposition into the Great Lakes as recorded in the sediments. With the hypothesis that atmospheric deposition is a major source of PBDEs in the sediment of the Great Lakes, sedimentary records were retrieved from all five Great Lakes as well as three inland seepage lakes in the region to provide an estimated historical input of PBDEs during the past decades. Through this study, the temporal trend and spatial distribution of PBDEs in the sediments of these lakes will be revealed. To our knowledge, this work is the first comprehensive study examining the long term history of PBDE pollution in the Great Lakes. The results from Lake Superior are discussed here.

Methodology
Sediment sampling on Lake Superior was conducted in 2002 using a 0.084 m^3 box corer deployed from the US Environmental Protection Agency (EPA) Research Vessel *Lake Guardian*. Sampling locations are shown in Figure 1. Sediment samples were sectioned onboard and frozen for transport the the laboratory. 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. Sediment cores were dated using a ^{210}Pb radiological method.
The method was initially validated by analyzing a lake sediment sample with known ^{210}Pb activity, The results obtained with our method were within 15% of the reported result. Sediments for chemical analysis were extracted in a Soxhlet extractor for 20 hr with hexane:acetone mixture, concentrated on a Kuderna-Danish (K-D) concentrator, and cleaned-up by elution through g fully activated silica gel and again concentrated on the K-D concentrator to about 5 mL. The volumes of samples were further reduced to about 1 mL by a gentle stream of N_2, then brought up to exactly 2.0 mL by adding the solvent that was used to rinse the K-D tube.

Quantitative analyses of PCBs and PBDEs were performed on an HP 6890 gas chromatograph (GC) coupled with HP 5973 mass spectrometer (MS). Separate runs were made for PBDEs and PCBs. BDE209 was analyzed separately using a shorter column . Internal standard was added to each sample before GC injection. The internal standard PCB204 was used to normalize the peak areas in PBDE quantification, and PCB30 and PCB204 were used as internal standards for PCBs. For BDE209, BDE190 was chosen as the internal standard. The target PBDE analytes included tri- (BDE28), tetra- (BDE47 and -66), penta- (BDE85, -99, and -100), hexa- (BDE153 and -154), hepta- (BDE183), and deca (BDE209) bromodiphenyl ether congeners. These PBDE congeners were selected on the basis of their relatively high content in the commercial products [5], and are the most frequently detected congeners in the environment. For comparison purposes, PCB congeners with IUPAC No. 8, 18, 28, 52, 44, 66, 101, 77, 118, 153, 105, 137, 126, 187, 128, 180, 170, 195, and 206 were also analyzed for all the sediment samples. Further details on experimental procedures can be found elsewhere[6,7].

Results and Discussion

Concentrations of PBDEs and PCBs of 48 samples from 6 cores are quantitatively measured. The congener patterns observed (excluding BDE-209) are shown in Figure 2. The surface concentration and flux of BDE209 ranged from 81% to 93% and from 72% to 89% on mass and molar bases, respectively, of the total PBDEs. This finding agrees with the fact that BDE209 counts for >70% of the total PBDE production in North America [8]. The PBDE concentrations are illustrated in Figure 3 as a function of sediment depth. The ΣPBDEs (excluding BDE-209) concentrations in surfacial sediments are within the range of 0.49 to 3.1 ng g^{-1} dry weight, with an average of 1.4 ng g^{-1} dry weight and 11 to 44 ng g^{-1} OC for the four cores collected in 2002, with an average of 28 ng g^{-1} OC. For each core, the maximum concentrations generally appeared in the top layers of the sediment cores with the exception of SU16, which has the maximum concentration at the second uppermost segment. At all the sampling locations expect SU22, the highest concentration of BDE209 was found at the surfaial segment.

The ΣPCB concentrations in surfaial sediments of Lake Superior ranged from 2 to 27 ng g^{-1} dry weight, with an average of 3.6 ng g^{-1} dry weight. For the four cores taken in 2002, the average PCB concentration in surfacial segments ranged from 50 to 148 ng g^{-1} OC, averaged 102 ng g^{-1} OC.

While there is an obvious decrease in PCB concentrations in recent years from a PCB peak flux around 1985, the PBDE concentrations continues to increase at most locations. This indicates that, after the ban of production and limits on usage of PCBs in the late 1970s, an increasing trend had continued for less than a decade before PCB flux to the sediments of Lake Superior began to show a noticeable decrease.

Noticeable differences exist in congener distribution patterns observed for Lake Superior versus those collected in different regions of the world. For example, our results show that the ratio of BDE47 to BDE99 is > 1 in 62% of the samples, with an average of 1.5 and a median of 1.1, in Lake Superior sediments compared to a value of < 0.5 estimated from Dodder et al [9]. Another remarkable difference is the amount of BDE183, which is the marker congener for commercial mixtures of octa-BDE [10], its presence in the Great Lakes reflects the history of its manufacturing in North America.

It is well established that air deposition is the major pathway for persistent organic pollutants such as PCBs to enter Lake Superior [11]. This study shows evidence that this is also true for PBDEs. Compared with the commercial mixture DE-71, the higher fractions of BDE47 in the air, water, and fish of Lake Superior may attribute to the stronger "grass hopper effect" for BDE47 [12,13] than others. That is, more of BDE47 can be atmospherically transported to remote areas through a series of deposition / volatilization hops than heavier congeners can. To confirm this hypothesis, congener-specific air concentration data at the source regions and along the transport paths are needed. In addition, data regarding PBDE concentrations in the water column, both dissolved and particle-bound, must be obtained in order to estimate what is the percentage of the total atmospheric deposition that ends up in sediments. However, a reliable estimation cannot be made before more process parameters become available. The possibility of PBDE transformation during their transport can not be excluded by the results of this work.

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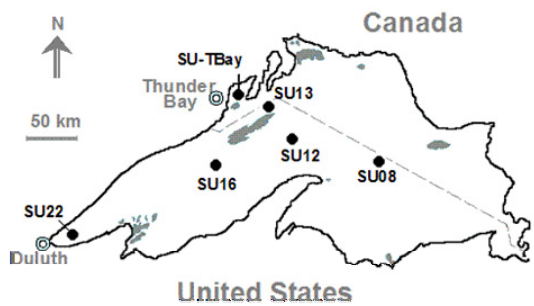

Figure 1: Sediment Sampling Locations for Lake Superior

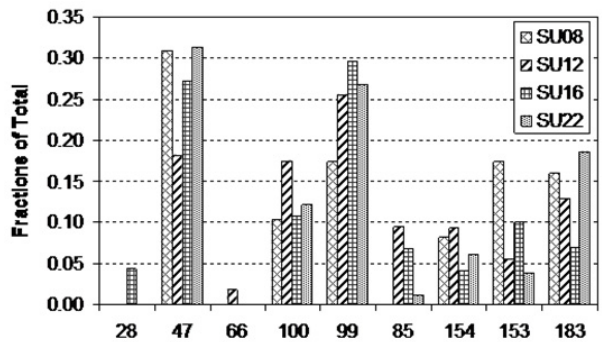

Figure 2: PBDE Congener Patterns for Lake Superior Cores

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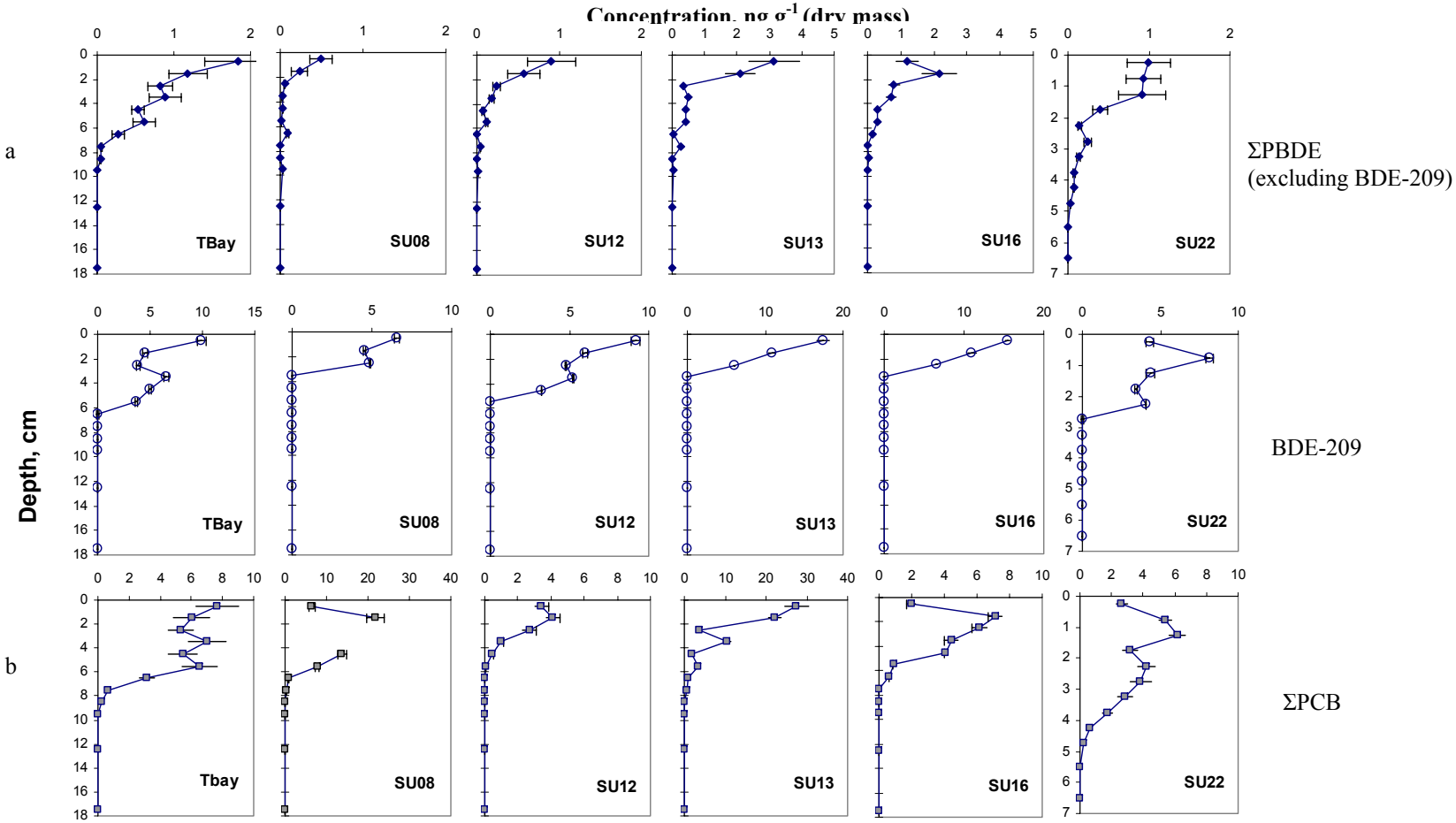

Figure 3. Total concentrations of (a) 9 PBDEs and (b) 19 PCBs versus depth in Lake Superior. Note that the y-scale for SU22 is different from others.