

## POLYBROMINATED DIPHENYL ETHERS IN LAKE HURON SEDIMENTS

Shen L<sup>1,2</sup>, Gewurtz S<sup>1,2</sup>, Kolic T<sup>1</sup>, MacPherson K<sup>1</sup>, Reiner E<sup>1</sup>, Helm P<sup>1</sup>, Brindle I<sup>2</sup>, Marvin C<sup>3</sup>

<sup>1</sup>Ontario Ministry of the Environment, 125 Resources Road, Toronto, Ontario, Canada M9P 3V6; <sup>2</sup>Faculty of Mathematics and Science, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario, Canada L2S 3A1; <sup>3</sup>Environment Canada, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

### Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardant additives that are used in a variety of commercial and household products in order to reduce their flammability.<sup>1</sup> Their concentrations in the environment are increasing over time, even in remote regions.<sup>2,3</sup> Although many studies on PBDEs focus on their occurrence in Great Lakes sediments,<sup>4-6</sup> reports on their concentrations in Lake Huron sediments are limited.<sup>7</sup> To assess the levels of PBDEs in Lake Huron sediments and to identify potential sources of PBDEs to the lake, a lake-wide sediment survey was conducted in 2002 by Environment Canada. In this paper, the results of the occurrence and spatial distribution of PBDEs are presented.

### Materials and Methods

Surficial sediment samples were collected from 30 stations throughout Lake Huron, including in Georgian Bay, aboard the Canadian Coast Guard Ship (CCGS) *Limnos* in 2002 using PONAR grab samplers. All samples were stored in solvent-washed sample jars at 4 °C until analysis. Methods for analysis of PBDEs are described elsewhere.<sup>7</sup> Briefly, surficial sediment samples were fortified with <sup>13</sup>C-labelled PBDE quantification standards with one congener for each homologue group and then Soxhlet extracted overnight in toluene for approximately 12-16 hours. Cleanup was performed using an acid/base/silver nitrate silica column. The PBDEs were eluted with 100 mL hexane followed by hexane/dichloromethane (50:50). Separation and quantification of the tri-BDEs to deca-BDE was performed using a GC-HRMS (HP 6890 gas chromatograph connected to Micromass Autospec-Ultima mass spectrometer) isotope dilution method. A DB-5HT column (15m x 0.25mm x 0.10 µm, J&W Scientific, USA) was used, and the GC-HRMS system was tuned to greater than 9000 RP. BDE extracts were analysed in splitless mode with He carrier gas at a linear velocity of 1.2 cm/s. Injector temperature and transfer line temperature were maintained at 270°C. The temperature program was: 110°C for 1 min; 110°C to 200°C at 40°C/min; 200°C to 330°C at 10°C/min; 300°C for 10 min.

### Results and Discussion

Sediment samples of Lake Huron were analyzed for BDE-17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -183, and -209. All sites had at least one PBDE congener detected, indicating diffuse sources of PBDEs to Lake Huron. The concentrations of BDE-47, -99, -100, -153, -154, and -209 represented the major PBDE burden on a mass basis (over 95% of total PBDEs) in Lake Huron sediments. Total concentrations, calculated as the sum of 17 individual congeners, ranged from 0.67 to 13 ng/g dry wt with a lake-wide average of 4.1 ng/g dry wt. The sampling sites and the corresponding total concentrations of PBDEs are presented in Figure 1 and Figure 2, respectively. Generally, PBDEs in sediments were observed at low-ppb levels. The highest concentrations in the lake were found at sites LH43 and LH100, which had levels of 3 ng/g dry weight and 8.5 ng/g dry weight, respectively. Site LH43 is located in a depositional region, whereas LH100 is located close to an industrialized area. The concentrations observed in this study are at the lower end of the range PBDE sediment concentrations reported in the literature, with concentrations similar to those found in Lake Superior, and slightly lower than those previously reported in Lake Huron.<sup>4,5,8</sup>

## Brominated Compounds - Sources and environmental levels

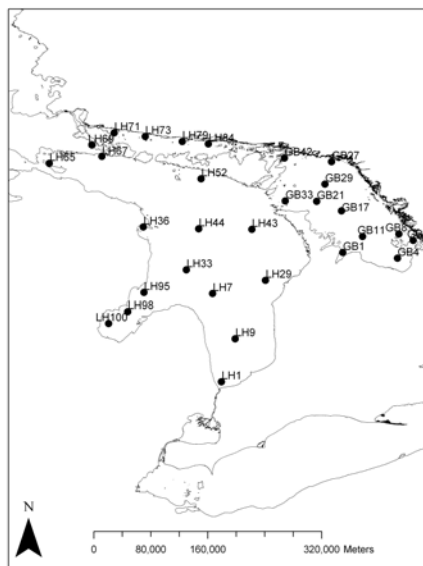


Figure 1: Map of Lake Huron showing sampling sites for the 2002 lake-wide sediment survey.

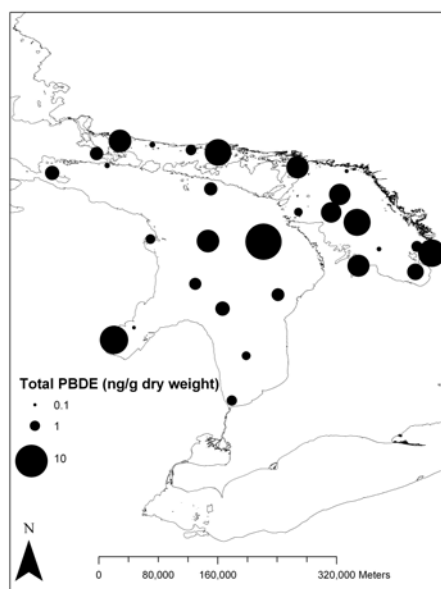


Figure 2: Total PBDE concentrations (ng/g dry weight) in Lake Huron sediment collected in 2002.

Of all the congeners, BDE-209 had the highest relative abundance in all samples except for one from Georgian Bay, and on average, represented 74% of total PBDE. The BDE-209 concentrations ranged from 0.11 to 12 ng/g dry weight. Among the other 16 PBDE congeners detected, in general, BDE-47 and -99 were most abundant, followed by BDE-100, -153 and -154. The congener profile at Site LH29 represented a typical congener-specific profile in Lake Huron sediment and is shown in Figure 3 (BDE-209 excluded). This typical Huron congener pattern was similar to most of the published sediment data in the literature, where BDE-47, -99, -100, and -209 were also dominant. For example, Song et al<sup>4,5,8</sup> found that BDE-209 was the most abundant congener in surficial sediments of Lakes Superior, Huron, Ontario and Erie. These results indicate that environment releases of PBDEs to Lake Huron are from the use of the penta- and/or deca-mixtures. North America accounted for 98% of the global demand for penta-BDE in 1999.<sup>9</sup> Dispersal of penta-containing foam is believed to be one mechanism by which PBDEs enter the environment.<sup>10</sup> Hale et al<sup>11</sup> also reported that the deca-BDE mixture accounts for greater than 70% of total PBDE production in North America. Compared with the commercial penta-mixture,<sup>12</sup> higher fractions of BDE-47 compared with BDE-99 were found in most samples, indicating that the atmosphere is a source of PBDEs to Lake Huron because BDE-47 can be more easily transported to remote areas in air through a series of deposition / volatilization compared with heavier congeners.

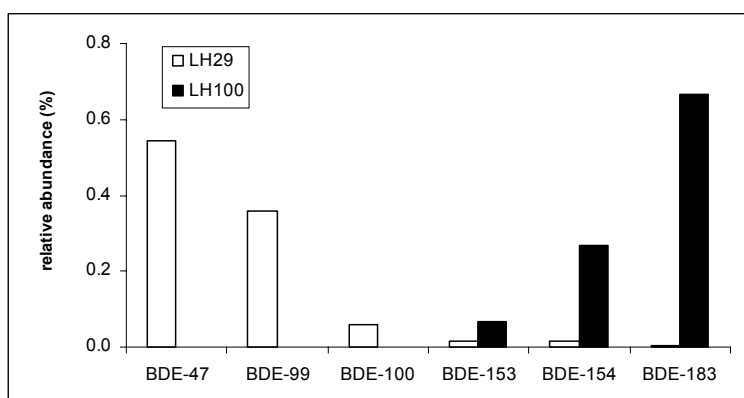


Figure 3: PBDE congener-specific profiles in Lake Huron surficial sediments, 2002. Data are shown for site LH29, a representative profile of most Lake Huron samples, and site LH100, a site which contained exceptionally high proportions of the heavier congeners.

The sample close to Saginaw Bay (site LH100) showed a different congener profile (Figure 2). BDE-209 still had the highest relative abundance, however unlike other samples, BDE-183 was the second most dominant congener, followed by BDE-153 and -154. The levels of BDE-47, -99, and -100 were lower than their detection limits. This suggests a different contaminant source to this site compared with the other locations. Lake Huron receives pollutants from the Saginaw River basin which is in proximity of heavily farmed and industrialized areas. BDE-183 is the marker compound for the octa-mixture, and therefore, the relatively high abundance of BDE-183 in this sample suggests that the octa-mixture is in use in this area.

To our knowledge, this study represents the most extensive lake-wide survey of PBDE concentrations in Lake Huron surficial sediments conducted to date. At most sites, PBDEs were detected at low-ppb concentrations and we suggest that atmospheric deposition is a major source of PBDE loadings to this lake. The relatively high concentrations at site LH100, as well as its distinct congener pattern, indicates localized point source inputs from agricultural and industrial activities to this area.

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