

## Environmental Chemistry

## PBDES AND METHOXYLATED ANALOGUES IN SEDIMENT CORES FROM TWO MICHIGAN, USA, INLAND LAKES

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**Abstract**—Polybrominated diphenyl ethers (PBDEs) have been widely studied in sediments from the North American Great Lakes; however, no studies have been conducted of occurrences of methoxylated (MeO-) PBDEs in abiotic compartments in this region. In the present study, 23 tri- to hepta-PBDEs and 12 MeO-PBDEs were analyzed in dated sediment cores collected from two inland lakes (White Lake and Muskegon Lake) in Michigan, USA. Concentrations of  $\Sigma_{23}$ PBDEs ranged from  $3.9 \times 10^{-1}$  to  $2.4 \times 10^0$  and from  $9.8 \times 10^{-1}$  to  $3.9 \times 10^0$  ng/g dry weight in White Lake and Muskegon Lake, respectively. The historical trends of tri- to hepta-PBDEs in the two lakes were different, possibly because of different input and remediation histories. The tri- to hepta-PBDE profiles were similar in the two lakes, with BDE-47 as the predominant congener, followed by BDE-99 and BDE-183. A different temporal trend for BDE-183 was found compared with other PBDEs, which is consistent with debromination of high-brominated PBDEs during sedimentation and aging. Methoxylated-PBDEs were detected only in Muskegon Lake ( $3.6 \times 10^{-3}$  to  $1.2 \times 10^{-1}$  ng/g dry wt). Methoxylated PBDEs showed different temporal trends compared with tri- to hepta-PBDEs. The differences in patterns of concentrations of MeO-PBDEs in the two lakes might be due to different aquatic communities in each lake. The occurrences of MeO-PBDEs could be the major source of hydroxylated-polybrominated diphenyl ethers (OH-PBDEs) observed in organisms collected in these freshwater systems. Environ. Toxicol. Chem. 2011;30:1236–1242. © 2011 SETAC

**Keywords**—PBDE Methoxylated PBDE Sedimentation rate Great Lakes Dating

## INTRODUCTION

Polybrominated diphenyl ethers (PBDEs), which have been used extensively as flame retardant additives, are ubiquitous pollutants in the environment. Polybrominated diphenyl ethers have been detected in sediments from many countries worldwide [1–3]. The North American Great Lakes are one of the aquatic areas contaminated with PBDEs [4–6]. It has been reported that concentrations of PBDEs range from 5 to 52 pg/m<sup>3</sup> in the air and from 117 to 434 ng/g lipid weight (lipid wt) in lake trout among the five Great Lakes [7]. From sediment cores it has been determined that tri- to deca-BDE congeners discharged 20 years ago are persistent in sediments of this region [4].

Methoxylated PBDEs (MeO-PBDEs) are structural analogues of PBDEs, which have been widely detected in wildlife with concentrations sometimes greater than those of PBDEs [8,9]. Because of their similar structures, MeO-PBDEs have been suggested to be biotransformation products of anthropogenic PBDEs. However, recent studies have demonstrated that two abundant MeO-PBDE congeners (6-MeO-BDE-47 and 2'-MeO-BDE-68) are natural products of marine organisms [8]. Furthermore, biotransformation of naturally occurring MeO-PBDEs is the more likely primary source of hydroxylated PBDEs (OH-PBDEs), which are the most toxic PBDE ana-

logues [10]. Hydroxylated PBDEs have also been detected in animals collected from the Great Lakes [11]. However, because no reports exist of synthesis of MeO-PBDEs in freshwater ecosystems, they have not been considered to be the precursor sources of OH-PBDEs in freshwater [11]. To explore further the occurrence of MeO-PBDEs in the freshwater environment and the relationships between PBDEs and MeO-PBDEs, a study was conducted in freshwater lakes connected to the North American Great Lakes.

Sediments can be a sink and a reservoir of various pollutants and can be used to study the historical input of persistent pollutants in aquatic environments [12]. In this study, sediment cores were collected from two inland lakes, White Lake and Muskegon Lake, in Michigan, USA. The project was conducted in conjunction with the Michigan Inland Lakes Sediment Trend Monitoring Program of the Michigan Department of Environmental Quality. Cores were dated by use of the <sup>210</sup>Pb radiological method and calibrated by use of <sup>137</sup>Cs. Twenty-three tri- to hepta-PBDE and twelve MeO-PBDE congeners were quantified. Historical trends of the two groups in the lakes were explored to determine input history, potential sources, influencing factors, and relationships of the target compounds in these freshwater ecosystems.

## MATERIALS AND METHODS

## Sample collection

Both lakes are located on the western coast of Michigan (Fig. 1). Muskegon Lake is a mesotrophic lake situated in Muskegon County. It has a surface area of 16.8 km<sup>2</sup> and a

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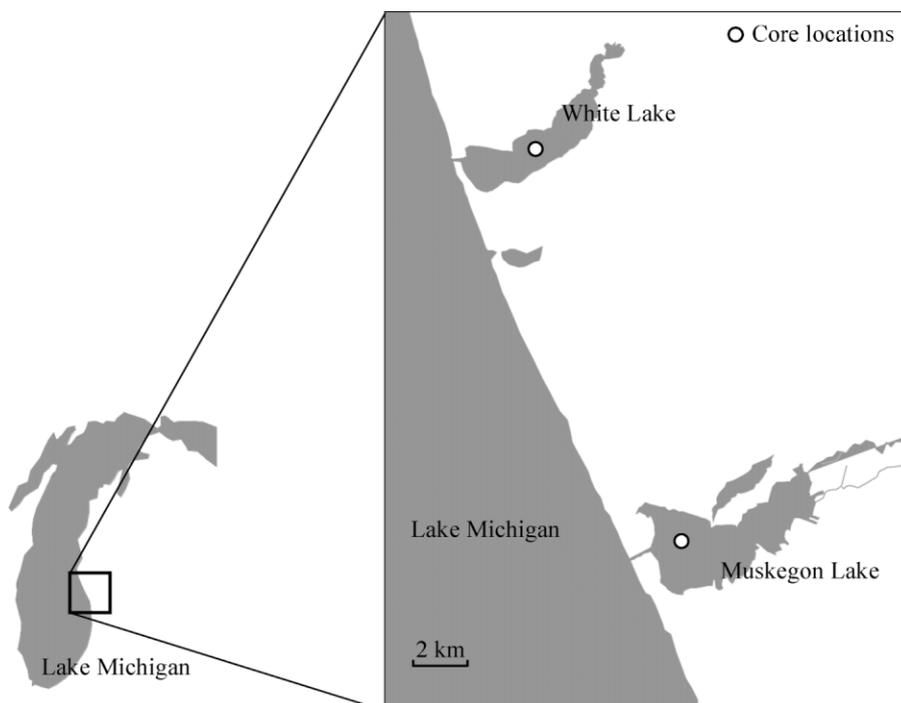


Fig. 1. Sampling locations of sediment cores in White Lake and Muskegon Lake, Michigan, USA.

maximum depth of approximately 15 m. It is within a watershed of approximately 53 km<sup>2</sup> and ultimately drains into Lake Michigan, which is approximately 1,000 m away. This lake is situated in an urban area and is subject to recreational use as well as input from upstream wastewater treatment facilities and various industrial sites along its shore. These include the Sappi Fine Paper plant and the Sealed Power manufacturing plant. White Lake is also a mesotrophic lake that is located in Muskegon County and has a surface area of 10.4 km<sup>2</sup> and a maximum depth of approximately 22 m. Its watershed is approximately 1,390 km<sup>2</sup>, some of which is rural. White Lake is classified as a drowned river mouth (freshwater estuary) and drains into Lake Michigan via a short outflow immediately west of the lake (Fig. 1). White Lake is less used for recreation than is Muskegon Lake.

Sediment cores were collected in 2006 by use of the monitoring vessel *Nibi*, equipped with an MC-400 Lake/Shelf Multi-Corer (Ocean Instruments). Coring was done in quadruplicate in a single sampling episode. Cores were collected from the deepest portion of the lake basin. The White Lake sampling site was located at 43°22.949'N and 86°22.902'W in 21.6 m of water. Remediation activities were initiated in White Lake prior to sediment sampling. However, dredging of sediment occurred at the Occidental Chemical outfall and in Tannery Bay, approximately 620 m and 2,900 m away from the core sampling station, respectively. The Muskegon Lake sampling site is located at 43°14.060'N and 86°16.996'W in 14.9 m of water. Once collected, core samples were transported to a temporary on-shore processing station for sectioning. All cores were sectioned at 0.5-cm intervals for the top eight centimeters and at 1.0-cm intervals thereafter. Sections were then individually stored in glass jars at -20°C until analysis.

#### Chemicals

Twenty-three tri- to hepta-PBDE congeners (BDE-28, BDE-17, BDE-30, BDE-71, BDE-49, BDE-47, BDE-66, BDE-77,

BDE-100, BDE-119, BDE-99, BDE-85, BDE-126, BDE-154, BDE-153, BDE-139, BDE-140, BDE-138, BDE-183, BDE-184, BDE-180, BDE-191, and BDE-171), and twelve MeO-PBDE congeners (6-MeO-BDE-17, 4-MeO-BDE-17, 2'-MeO-BDE-68, 6-MeO-BDE-47, 5-MeO-BDE-47, 4'-MeO-BDE-49, 5'-MeO-BDE-100, 4'-MeO-BDE-103, 5'-MeO-BDE-99, 4'-MeO-BDE-101, 6-MeO-BDE-90, and 6-MeO-BDE-85) were selected as target compounds; <sup>13</sup>C-PBDEs (<sup>13</sup>C-BDE-28, <sup>13</sup>C-BDE-47, <sup>13</sup>C-BDE-100, <sup>13</sup>C-BDE-99, <sup>13</sup>C-BDE-154, <sup>13</sup>C-BDE-153, and <sup>13</sup>C-BDE-183) were used as surrogate standards for tri- to hepta-PBDEs and MeO-PBDEs. The PBDEs, <sup>13</sup>C-PBDEs, and eight MeO-PBDEs standards were obtained from Wellington Laboratories. The 6-MeO-BDE-17, 4-MeO-BDE-17, 6-MeO-BDE-90, and 6-MeO-BDE-85 were synthesized in the Department of Biology and Chemistry, City University of Hong Kong. Purities of all standards were >98%. Pesticide residue-grade acetone was purchased from Honeywell Burdick and Jackson. Dichloromethane, *n*-hexane, and granular sodium sulfate were from EMD Chemicals—Merck KGaA. Silica gel was obtained from Supelco (100/200 mesh; Sigma Aldrich). Nonane was purchased from Fluka-Sigma Aldrich.

#### Sediment core dating

Cores chosen for dating were sent to the Freshwater Institute (Winnipeg, MB, Canada) for <sup>210</sup>Pb aging by use of methods described previously [13]. Briefly, 0.5 to 1 g of each core slice submitted for dating was digested in concentrated hydrochloric acid at 80°C. After digestion, excess <sup>210</sup>Pb was determined via <sup>210</sup>Po (daughter) activity by autoplating the polonium onto a silver disk in 1.5 N hydrochloric acid (HCl), counting activity with an alpha spectrometer, and subtracting <sup>226</sup>Ra activity. The resulting excess <sup>210</sup>Pb values were fitted into each of four sedimentation rate models, and the most appropriate model selection was confirmed using the peak <sup>137</sup>Cs value (mid-1960s) and stable Pb profile (anthropogenic mid-1970s peak).

### Organic matter and carbon determination

Carbon and organic matter content of strata were determined by the Soil and Plant Nutrient Laboratory, Michigan State University. Carbon content was determined using the chromic acid oxidation (external heat applied) method (<http://extension.missouri.edu/explorepdf/specialb/sb1001.pdf>). Briefly, a known mass of dried sediment, 10 ml of 0.167 M chromium potassium oxide ( $K_2Cr_2O_7$ ), and 200 ml concentrated sulfuric acid ( $H_2SO_4$ ) were added to a 500 ml Erlenmeyer flask and swirled gently to mix. The flask was heated for 30 min; the suspension was diluted with 200 ml water; 10 ml 85% phosphoric acid ( $H_3PO_4$ ), 0.2 g sodium fluoride (NaF), and 10 drops of ferroin indicator were added; and the solution was titrated with 0.5 M  $Fe^{2+}$  to a burgundy endpoint. Carbon content was calculated from the amount of  $Fe^{2+}$  solution used to titrate the sample. Organic matter content was determined via calculation, assuming that 58% of the organic matter is composed of carbon.

### Identification, quantification of PBDEs, MeO-PBDEs

Sample extraction and cleanup procedures followed the protocol outlined in U.S. Environmental Protection Agency (U.S. EPA) method 1614 [14]. To achieve sufficient mass for analysis, sediment strata were combined prior to extraction. For example, equal masses of the first two 1-cm aliquots from the Muskegon Lake sediment core generated during field processing were combined to create a pooled sample. This procedure was continued for all sample strata generated from the sediment core, reducing the total number of core samples to 40.

After compositing, 20 g of sample was weighed, mixed with granular sodium sulfate, and put into a Soxhlet extraction apparatus containing 3:1 dichloromethane in acetone. Each sample received 2 ng  $^{13}C$ -labeled PBDE mixtures while the laboratory control spike (LCS), matrix spike (MS), and matrix spike duplicate (MSD) also received 1.0 ml native PBDEs stock solution. Samples were refluxed overnight ( $18 \pm 2$  h).

After extraction, extracts were allowed to cool and then transferred to Turbovap concentration tubes (Caliper Life Sciences) and concentrated to approximately 1.0 ml. The extract was loaded onto the top of a silica gel column, which had been pre-eluted with 50 ml *n*-hexane. The column contained, from bottom to top, a glass wool plug, 1 g granular sodium sulfate, 1 g silica gel, 4 g basic silica gel, 1 g neutral silica gel, 8 g acidic silica gel, 2 g neutral silica gel, and 4 g granular sodium sulfate. Specific procedures for acidic and basic silica gel preparation can be found in the U.S. EPA method [14].

Extracts were first eluted from the column with 200 ml *n*-hexane. This first fraction contained all the tri- to hepta-PBDEs (confirmed during initial method evaluation). The second fraction containing the MeO-PBDEs was eluted with 1:1 dichloromethane in *n*-hexane. Both fractions were combined and concentrated to approximately 1 ml using the Turbovap and transferred to 1 ml amber chromatography vials. Crystal formation was observed during concentration, so activated copper granules were added to the extracts to remove sulfur. The extract/copper slurry was stored overnight. Determination of a final concentration of PBDEs and MeO-PBDEs was achieved by adding the extract to 10  $\mu$ l nonane in a wide-mouth low-volume vial insert and evaporating the mixture to 10  $\mu$ l using nitrogen evaporation.

### HRGC/HRMS analysis

All extracts received 2 ng  $^{13}C$ -labeled BDE-138 as an injection standard prior to analysis. Identification and quantification of all target compounds was performed using a Hewlett-Packard 5890 series II high-resolution gas chromatograph (HRGC) interfaced to a Micromass Autospec high-resolution mass spectrometer (HRMS; Micromass). Chromatographic separation of individual tri- to hepta-PBDEs and MeO-PBDEs was achieved by use of a DB-5MS fused silica capillary (30 m length, 0.25 mm ID, 0.1  $\mu$ m film thickness; Agilent), with helium used as carrier gas. The mass spectrometer was operated in selected ion-monitoring (SIM) mode. The resolution for all reference gas peaks in all time windows was more than 7,000. The injector and ion source were kept at 285°C. The electron ionization energy was 37 eV, and the ion current was 750  $\mu$ A. The GC temperature programs used for tri- to hepta-PBDEs was from 110°C (10 min) to 250°C at a rate of 25°C/min, then increased to 260°C at a rate of 1.5°C/min, and then to 325°C (15 min) at a rate of 25°C/min. For MeO-PBDEs, the temperature program was from 150°C (2 min) to 245°C (2 min) at a rate of 2°C/min and then increased to 320°C (2 min) at a rate of 30°C/min. Concentrations were determined by using a four-point calibration curve and referencing the labeled analog congener in each homolog group. Because no labeled MeO-PBDEs were available, quantification of MeO-PBDE was achieved by use of a five-point calibration curve and by referencing to  $^{13}C$ -labeled PBDEs.

### Quality assurance

Concentrations of all congeners were quantified by use of internal standard isotope-dilution methods using mean relative response factors determined from standard calibrations. Recoveries for the Muskegon Lake analyses for the MS, MSD, and LCS were 77 to 100%, 72 to 98%, and 89 to 119% respectively, whereas recoveries for White Lake were 82 to 101%, 82 to 313%, and 78 to 149% respectively. The greater recoveries for the White Lake quality-assurance data set were seen for two congeners, BDE47 and BDE99, and can be attributed to chromatographic interference observed during sample integration. A laboratory blank was incorporated in the analytical procedures for every batch of samples. The method detection limits (MDL) were defined as three times the standard deviation in the blank samples, in which BDE49, BDE47, BDE100, BDE99, BDE154, BDE153, and BDE138 were detected. The MDLs for the other compounds, which were not detected in blank samples, were set to the instrumental minimum detectable amounts. The detection limits were 1 pg/g dry weight for MeO-PBDEs, 3.3 pg/g dry weight for BDE49, 24.4 pg/g dry weight for BDE47, 3.5 pg/g dry weight for BDE100, 24.2 pg/g dry weight for BDE99, 3.0 pg/g dry weight for BDE154, 1.5 pg/g dry weight for BDE153, 7.1 pg/g dry weight for BDE183, and 1 pg/g dry weight for other tri- to hepta-PBDE congeners. For those results that were less than the MDL, a sensitivity analysis was conducted, and no statistically significant differences could be found by using different values ranging from 0 to the MDL. Thus, a value of 0 was assigned to avoid missing values in statistical analyses. Instrument performance was monitored by using a series of initial calibration verification injections. Each sequence contained at least one verification injection, and recoveries of native and labeled compounds ranged from 68 to 126% in all injections.

## RESULTS AND DISCUSSION

### *Sedimentation rates and core dating*

Dates of deposition were determined for a total of 52 sediment samples from White Lake and 51 sediment samples from Muskegon Lake. Detailed sedimentation rate data have been reported previously [13]. Sedimentation rates for each core sample were determined using one of four different models; constant flux:constant sedimentation (CF:CS), segmented CF:CS (SCF:CF), rapid steady-state mixing (RSSM), or constant rate of supply (CRS). The validity of model assignment was verified, if possible, using stable isotope abundance in the sample ( $^{210}\text{Pb}$ , excess Pb, and  $^{137}\text{Cs}$ ). The  $^{210}\text{Pb}$  isotope is formed by decay of  $^{222}\text{Rn}$  from atmospheric and water column sources. By knowing the rate of radioactive decay of  $^{210}\text{Pb}$  and assuming no additional sources of  $^{222}\text{Rn}$ , the date when the sediment was deposited can be calculated. In addition, the peak in excess (stable) Pb input (from use in leaded gasoline up to the early to mid-1970s) resulted in excess elemental lead that can be used as a confirmatory tool in selecting the most appropriate model for calculating the sedimentation rate.  $^{137}\text{Cs}$  was produced during thermonuclear weapons testing throughout the 1950s and 1960s with a peak fallout rate occurring in 1963. Detection of this peak in sediment cores may provide another means of calibrating the dates of each varve (annual layer) in sediment cores.

White Lake sediments were assigned deposition years from 2006 to older than 1901 (< 1901) based on averaged deposition dates of each 0.5-cm core section and using the SCF:CS sedimentation model. No  $^{137}\text{Cs}$  peak was observed. Stable Pb confirmation was not applicable in this case, because it has been postulated that sediment resuspension confounded the typical excess Pb curve, which is usually observed as a linear decrease in abundance from the upper sediment layers to the deeper layers. The appearance of excess Pb (stable) tends to support this choice, because excess Pb begins to appear at approximately 1900 using this model. The occurrence of sediment dredging in 2003 may explain the nondetections of pronounced Pb and Cs in upper layers as well as the reappearance of excess Pb in deeper layers around 1900. The SCF:CS model was assigned to White Lake based on the appearance of excess Pb at approximately 1900 and an unusually subtle peak at 1970. Muskegon Lake sediments were pooled in the same manner as White Lake sediments, and the CF:CS sedimentation rate model was the best fit for that data. Neither a clear excess Pb peak nor a  $^{137}\text{Cs}$  peak was observed in sediments from Lake Muskegon. Assignments of year of deposit in Muskegon Lake ranged from 2006 to 1966.

Sedimentation rates were calculated to be 1,607 and 977  $\text{g}/\text{m}^2/\text{year}$  for Muskegon Lake and White Lake, respectively. Consequently, sediment core strata taken from White Lake represent a greater temporal range, with the deepest strata ages estimated to be pre-1901. Ages of cores from Lake Muskegon range from the present back to 1966.

### *PBDEs in cores*

In total 22 sediment samples from White Lake and 21 sediment samples from Muskegon Lake were analyzed for 23 tri- to hepta-PBDEs. Total concentrations of the sum of all 23 tri- to hepta-PBDE congeners ( $\Sigma_{23}\text{PBDE}$ ) for both lakes were calculated. All congeners were detected at least once in White Lake sediments, and the concentration of  $\Sigma_{23}\text{PBDEs}$  ranged from  $3.9 \times 10^{-1}$  to  $2.4 \times 10^0$   $\text{ng}/\text{g}$  dry weight. In contrast, BDE-30, BDE-77, and BDE-126 were not detected in any

samples from Muskegon Lake. Concentrations of  $\Sigma_{23}\text{PBDEs}$  in Muskegon Lake ranged from  $9.8 \times 10^{-1}$  to  $3.9 \times 10^0$   $\text{ng}/\text{g}$  dry weight. Concentrations of  $\Sigma_{23}\text{PBDEs}$  in the surficial sediments in White Lake (2.1  $\text{ng}/\text{g}$  dry wt) and Muskegon Lake (2.1  $\text{ng}/\text{g}$  dry wt) were similar to those reported previously for Lake Michigan (1.7–4.0  $\text{ng}/\text{g}$  dry wt) [6]. Because BDE-209 was not quantified in the current study, the total tri- to hepta-PBDE concentrations were used in the comparisons with previous investigations. The  $\Sigma_{23}\text{PBDEs}$  concentrations measured in this study are greater than  $\Sigma_{10}\text{PBDEs}$  concentrations ( $5.1 \times 10^{-2}$ – $3.6 \times 10^0$   $\text{ng}/\text{g}$  dry wt) in surface sediment from Tokyo Bay, Japan [12] and the  $\Sigma_9\text{PBDEs}$  concentrations ( $1.9 \times 10^{-2}$ – $0.9 \times 10^0$   $\text{ng}/\text{g}$  dry wt) in sediments from the Beiji River, situated in an industrial region of China [2]. The  $\Sigma_{23}\text{PBDEs}$  concentrations in White and Muskegon Lakes were comparable to the  $\Sigma_7\text{PBDEs}$  concentrations (1.6  $\text{ng}/\text{g}$  dry wt) in Swiss lake sediment [1], but were less than those in sediments from the Clyde Estuary, Scotland, United Kingdom ( $\Sigma_{15}\text{PBDEs}$ : 1–307  $\text{ng}/\text{g}$  dry wt) [3].

In Muskegon Lake, concentrations of  $\Sigma_{23}\text{PBDEs}$  began to increase in 1974 and peaked in 1991 (Fig. 2, left). The historical profile was similar to profiles reported for the North American Great Lakes, in which the total concentrations of tri- to hepta-PBDEs start to increase in the period of 1960 to 1970 [4–6]. This is also consistent with the time (1960s) of production and usage of commercial PBDE products worldwide [15]. The historical trend for tri- to hepta-PBDEs was also compared with that of polycyclic aromatic hydrocarbons (PAHs) and some organochlorines in Muskegon Lake. Total concentrations of PAHs peaked in 1977, whereas concentrations of total polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane metabolite (*p,p'*-DDE) peaked in 1966 [16,17]. These trends are most likely a result of differences in annual peak production for the various compound classes. The  $\Sigma_{23}\text{PBDEs}$  concentrations in White Lake exhibit a somewhat different profile (Fig. 2, left). Concentrations peaked in 1999 at 2.4  $\text{ng}/\text{g}$  dry weight, with a second, smaller peak of 1.4  $\text{ng}/\text{g}$  dry weight observed in 1973. It is known that dredging of bottom sediment took place in October, 2003, so this may be an artifact caused by remediation activities in the basin near where the sediment core was sampled [18].

Comparisons of PBDE profiles (including eight major congeners: BDE-28, BDE-47, BDE-49, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183) from the two lakes indicated that present congener contributions to both lakes were similar (Fig. 3). The most prevalent congener is BDE-47 in all samples, followed by BDE-99 and BDE-183. Unfortunately, BDE-209 was not analyzed in the current study as a result of analytical limitations. However, the tri- to hepta-PBDE profile observed in the current study is consistent with that in previous investigations of sediments from all five Great Lakes, suggesting that PBDE contaminations have similar sources in this region and that BDE-209 is the predominant congener [4–6]. Concentrations of BDE-183 decreased with sedimentation age (depth in core), whereas concentrations of the other predominant PBDE congeners all increased with sediment age. A significant positive correlation was found between the ratio of concentrations of BDE-183 to those of  $\Sigma_8\text{PBDEs}$  and sedimentation age (Fig. 4). Specifically, the proportion of BDE-183 was less in younger sediments. The relatively great contributions of BDE-183 in samples could be due to the historical manufacturing of commercial mixtures of octa-BDE in the Great Lakes region [4]. If BDE-183 originated only from octa-BDE usage and production, the historical trend of this compound should be

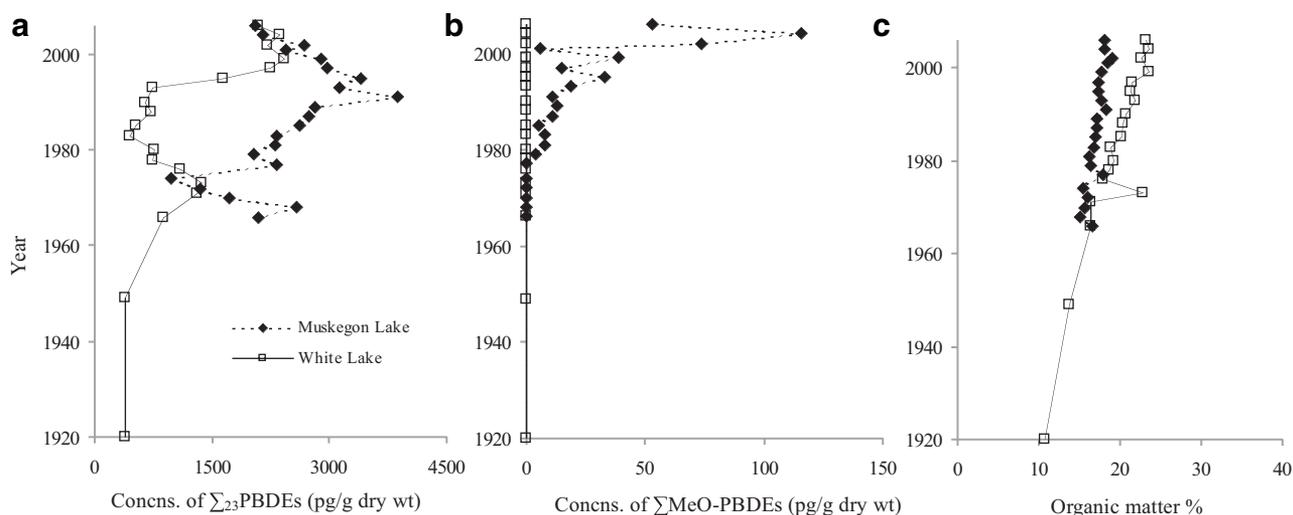


Fig. 2. Concentrations of  $\Sigma_{23}$ polybrominated diphenyl ethers (PBDEs; left),  $\Sigma$ methoxylated (MeO)-PBDEs (middle), and organic matter (%; right) versus sedimentation years in Muskegon Lake and White Lake, Michigan, USA. The method detection limits were 82 and 3 pg/g dry weight for  $\Sigma_{23}$ PBDEs and  $\Sigma$ MeO-PBDEs, respectively.

similar to that of other PBDE congeners. Thus, because it has been reported that BDE-209 has been the predominant PBDE congener throughout the sediment cores collected from all five Great Lakes [4–6] and hepta- and octa-BDEs can be produced through microbial reductive debromination of BDE-209 [19], the different temporal trends of BDE-183 could be due to reductive debromination of BDE-209 during diagenesis.

#### MeO-PBDEs in cores

In total, 22 sediment samples from White Lake and 21 sediment samples from Muskegon Lake were analyzed for 12 MeO-PBDEs. Previous studies have shown that MeO-PBDEs have a trophic magnification potential similar to that of PBDEs [20,21] and were detected in sediment samples [22]. A recent exposure study with Japanese medaka (*Oryzias latipes*) found that the biotransformation rate of 6-MeO-BDE-47 is only slightly less than that of BDE-47 [23], so the temporal trends of MeO-PBDEs could be reconstructed in sediment cores. In White Lake, the detected compounds were 6-MeO-BDE-47 ( $2.6 \times 10^{-3}$  ng/g dry wt in 1999) and 6-MeO-BDE-85 ( $9.9 \times 10^{-3}$  ng/g dry wt in 2006) in two sediment samples. In Muskegon Lake, 2'-MeO-BDE-68, 6-MeO-BDE-47, and 6-MeO-BDE-85 were detected in samples from 1979 to

2006. Total concentrations of MeO-PBDEs in samples ranged from  $3.6 \times 10^{-3}$  to  $1.2 \times 10^{-1}$  ng/g dry weight (Fig. 2, middle). The predominant MeO-BDE congener observed was 6-MeO-BDE-47. The profiles or relative concentrations of MeO-PBDEs were consistent with those reported in animals worldwide [8,10,24,25]. Using radiocarbon analysis, Teuten et al. [8] determined that 2'-MeO-BDE-68 and 6-MeO-BDE-47 found in the blubber of a True's beaked whale (*Mesoplodon mirus*) were not transformation products from synthetic PBDEs, and the pattern of stable isotopes in the two compounds was similar to that in the Pacific marine sponge (*Phyllospongia foliascens*).

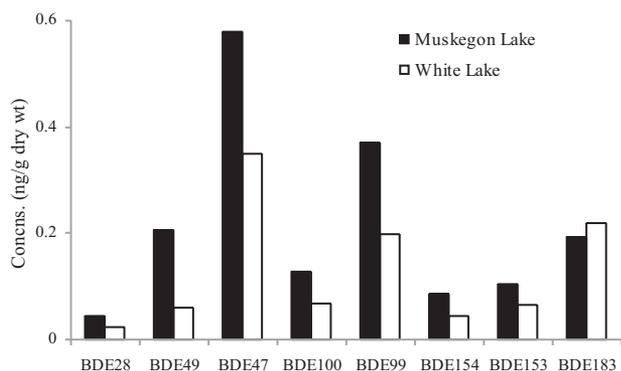


Fig. 3. Profiles of eight major polybrominated diphenyl ethers (PBDEs) in Muskegon Lake and White Lake, USA. The average concentrations in sediments from each lake were used because the profiles of the eight congeners were relatively constant in the sediment cores.

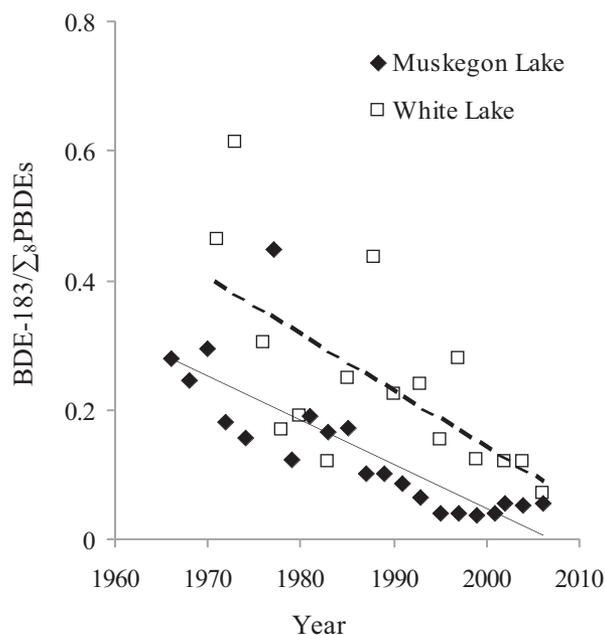


Fig. 4. Relationships between concentration ratios of brominated diphenyl ether (BDE)-183/ $\Sigma_8$  polybrominated diphenyl ethers (PBDEs) and sedimentation years in Muskegon Lake and White Lake, Michigan, USA. White Lake (dashed line).  $\Sigma_8$ PBDEs is the total concentrations of eight predominant congeners (BDE-28, BDE-47, BDE-49, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183); BDE-183/ $\Sigma_8$ PBDEs =  $-0.0088 \times \text{year} + 17.719$ ,  $r^2 = 0.4418$ ,  $p < 0.05$ ; Muskegon Lake (solid line), BDE-183/ $\Sigma_8$ PBDEs =  $-0.0068 \times \text{year} + 13.65$ ,  $r^2 = 0.6336$ ,  $p < 0.01$ .

The MeO-PBDEs detected in sediment from White Lake may have been generated by freshwater sponges, because approximately 30 species of freshwater sponge exist in North America. However, anthropogenic origins of these compounds should not be excluded, because humans ingest considerable amounts of marine derived seafood, so accumulated MeO-PBDEs may enter wastewater-processing facilities that discharge into freshwater systems such as the present inland lakes. Previous studies have shown that MeO-PBDEs could undergo trophic transfer in aquatic food webs [20,21]. Therefore, the MeO-PBDEs detected in the Great Lakes as well as in the present study could be the source of OH-PBDEs detected in animals collected in these freshwater environments (e.g., Great Lakes [11]) via demethylation as recently reported [10,23].

In Muskegon Lake, concentrations of  $\Sigma$ MeO-PBDEs began to appear in 1977, and increased to a maximum of  $1.2 \times 10^{-1}$  ng/g in 2004, followed by a decrease to approximately half this concentration in the uppermost stratum (Fig. 2, middle). The historical profile of  $\Sigma$ MeO-PBDEs concentrations in Muskegon Lake was different from that of  $\Sigma_{23}$ PBDEs (Fig. 2, middle). This result is consistent with temporal trends (1967–2000) reported for concentrations of PBDEs and MeO-PBDEs in pike collected from Swedish waters [24]. The greatest concentrations of the MeO-PBDEs were detected in fish collected before 1970, whereas concentrations of PBDEs showed increasing trends up to the mid-1980s [24]. These results further suggest the existence of different sources of PBDEs and MeO-PBDEs.

Concentrations of organic carbon (OC) were similar in the two lakes (Fig. 2, right), but MeO-PBDEs were detected only in Muskegon Lake, and concentrations of tri- to hepta-PBDEs were significantly correlated with organic carbon in the two lakes (Muskegon Lake:  $\Sigma_{23}$ PBDEs =  $0.0005 \times \text{OC} + 8.7$ ,  $r^2 = 0.30$ ,  $p = 0.01$ ; White Lake:  $\Sigma_{23}$ PBDEs =  $0.0018 \times \text{OC} + 9.2$ ,  $r^2 = 0.44$ ,  $p = 0.002$ ). This implies that accumulation of MeO-PBDEs, unlike PBDEs, is not dependant on the organic contents of the sediments. It is possible that MeO-PBDEs are natural byproducts of the pelagic or benthic fauna and that the activities of these organisms influence the concentrations of MeO-PBDEs in sediments. Similarly, the different aquatic communities in the two lakes could also explain why MeO-PBDEs were consistently detected in Muskegon Lake but not in White Lake.

### CONCLUSIONS

This study was conducted to determine concentrations of selected PBDE and MeO-PBDE congeners in dated sediment cores collected from two inland lakes in Michigan. Total PBDE concentrations in both lakes were comparable, but the temporal trends were different, possibly as a result of different input and remediation histories. Debromination of more-brominated PBDEs could occur during and after sedimentation and will contribute to variations in relative concentrations of PBDE in sediments. The present study demonstrated the detection of MeO-PBDEs in a freshwater ecosystem (e.g., the Great Lakes). However, MeO-PBDEs were detected only in Muskegon Lake. The detected MeO-PBDEs were naturally occurring compounds and exhibit different temporal trends and sedimentation rates compared with PBDEs. The different occurrences of MeO-PBDEs in the two lakes may be due to different aquatic communities in each lake. These results suggest that future studies in this region should not neglect contributions of MeO-PBDEs to the concentrations of OH-PBDEs in organisms and their contribution to toxic potency of halogenated phenolic compounds in this region.

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