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Spatial distributions of polychlorinated biphenyls, polybrominated diphenyl ethers, tetrabromobisphenol A and bisphenol A in Lake Erie sediment

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A B S T R A C T

Forty-seven polychlorinated biphenyls (PCBs), 9 polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA) and its mono-, di- and tri-bromo-analogs, and bisphenol A (BPA) were investigated in sediments (56 samples; collected in spring 2004) from the western, central and eastern basins of Lake Erie. Surficial (0–10 cm) sediment from the western basin contained significantly greater (p < 0.05) concentrations of PCBs, PBDEs and BPA than the other two basins. Σ47PCBs were 144 ± 141, 33 ± 34, and 13 ± 15 ng/g (mean ± standard deviation; d.w.) in the western, central, and eastern basins respectively. BDE-209 was the predominant PBDE congener in sediment samples, and was quantifiable in 56% of the samples with a concentration range of 0.3 to 12 ng/g (d.w.). BPA concentrations up to 6.1 ng/g (d.w.) were detected in 65% of the samples. For these chemicals, the Detroit River outflow is strongly suggested to be the major source/vector for Lake Erie. TBBPA was detectable in one sample (0.5 ng/g d.w.) from a site near the Detroit River, suggesting degradation and/or a low level deposition of polybrominated-BPAs to Lake Erie.

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Introduction

Many hazardous chemicals such as persistent organic pollutants (POPs) have been introduced to the Great Lakes of North America by human activities (Klečka et al., 2010). Some of these chemicals have low vapor pressures and high octanol–water partition coefficients (Kow) and thus they become associated with organic particles and have a tendency to accumulate in lake sediments (Warren et al., 2003). Lake Erie is the smallest (by volume), shallowest, warmest, and the most biologically productive lake among Great Lake, but it is the eleventh largest lake in the world by surface area (Conroy and Culver, 2005; Hartig et al., 2009). Lake Erie receives most of its water volume (> 80%) from the discharges of the Detroit River to the western basin and drains into Lake Ontario via the Niagara River from the eastern basin (Hartig et al., 2009). The average water depths for the western, central and eastern basins of Lake Erie are 7.3, 18.3 and 24.4 m respectively (http://www.lakeeriewaterkeeper.org/lake-erie/facts/). The sedimentation rate of Lake Erie has ranged from 0–7.4 mm yr−1, with the highest rates occurring in the western basin close to the mouth of Detroit River and at the deepest parts (up to 64 m) of the eastern basin (Kemp et al., 1977). Since the 1960s, this lake experienced significant eutrophication and species invasion, and consequently, food web stability disruption (Conroy and Culver, 2005; Dalouglu et al., 2012). Detroit, Michigan (USA) and Windsor, Ontario (Canada), and their environs, are the most highly urbanized and industrialized portion of the Lake Erie watershed, continually contributing chemical contaminants to the Detroit River from a variety of sources. Although many of these contaminants are known chemical stressors in the aquatic ecosystems, their

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lake wide spatial distribution and environmental fate, remain poorly understood, particularly for emerging POPs.

Polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA), as well as bisphenol A (BPA), are organic pollutants that continue to be of environmental concern. Although some of these pollutants have been banned (e.g., PCBs) or are restricted in use, they can still be found in the environment, particularly in lake sediments, because their chemical properties render them resistant to natural degradation. They can still be released to the environment from old products (e.g., in landfill sites). Because of their continued presence in the environment, we continue to monitor their spatial and temporal distributions. Such studies provide us with the empirical evidence that we need to understand historic and current uses of these chemicals and the risks posed by their presence in the environment (Klečka et al., 2010).

PCBs were widely used in dielectric fluids for transformers and capacitors, heat transfer fluids, hydraulic fluids, cutting oils and as additives in pesticides, plastics and even as flame retardant chemicals (Safe, 1994). PCBs can bioaccumulate in organisms through food chains and lead to many toxic effects (Safe, 1994). The production of PCBs has been banned since the mid-1970s, but they are still ubiquitous in the environment. Closed sources, building sealants and waste-handling facilities are the major current stocks of PCBs (Diamond et al., 2010). For example, about 437 tonnes of PCBs was the estimated stock amount in Toronto (Canada), and it was concluded this may be one of the major contamination sources of PCBs to the Great Lakes (Diamond et al., 2010). The annual load of total PCBs in the sediment of Lake Erie was reported to be about 1.49 ± 0.59 tonnes per year in 2002, and this load was greater than that for the other Great Lakes (0.13–0.71 tonnes per year) (Li et al., 2009), implying continuous, high contamination of PCBs in Lake Erie. Approximately 300 ± 50 tonnes of PCBs are estimated to have accumulated in the sediment of Great Lakes until 2002, which was >30% lower compared with the 1980s (Li et al., 2009). PCBs in re-suspended sediments from the Detroit River might be one source of these contaminants in Lake Erie (Marvin et al., 2006).

PBDEs are one type of BFR used as additives in a variety of household and industrial products (Wiseman et al., 2011). PentaBDE, OctaBDE, and DecaBDE are three commercial formulations of PBDEs. The PentaBDE and OctaBDE formulations have been listed as POPs in Stockholm Convention due to their high persistence, bioaccumulation and toxicity (PBT) properties (Stockholm Convention, 2009). Production and use of the PentaBDE and OctaBDE formulations were banned in Europe in 2004. The production of these two formulations was also ceased voluntarily in certain American states (Betts, 2008). The DecaBDE mixture is composed almost entirely (>92%) of 2,2′, 3,3′, 4,4′, 5,5′, and 6,6′-decabromodiphenyl ether (BDE-209) (La Guardia et al., 2006). DecaBDE was banned in Europe in 2008 (Betts, 2008). Major North American PBDE manufacturers discontinued the production, sale and importation of DecaBDE by the end of 2013 (Venier et al., 2014). However, it was estimated that over 1 million tonnes of PBDEs was produced in the last 30 years (Shaw and Kannan, 2009). In response to the phase out of PBDEs after 2004, it is important to investigate their temporal and spatial trends in order to assess the environmental quality and the effectiveness of regulations/treaty (such as the Stockholm Convention) on the production and use of these chemicals. Also, it is necessary to assess the global environments (Law et al., 2014), including the atmosphere (Ma et al., 2013), water (Streets et al., 2006), sediments (Song et al., 2004, 2005a,b; Zhu and Hites, 2005) and organisms (e.g., fish and birds) (Gauthier et al., 2008; Crimmins et al., 2012) of Great Lakes. PBDEs in the sediment cores of Lake Erie were studied previously (usually one or two sediment cores), which mainly focused on the vertical distribution of PBDEs (Song et al., 2005a; Zhu and Hites, 2005). However, lake-wide spatial distribution patterns of PBDEs have not been well investigated in Lake Erie. To our knowledge, the only other study reported in the scientific literature was by Gewurtz et al. (2009). In that study (Gewurtz et al., 2009), PBDE spatial distribution was investigated in sediment (top 3 cm) collected between 2002 and 2006, at approximately 220 sites at open water, nearshore, and at the mouth of tributary locations across the Great Lakes, including Lake Erie. Most sampling sites for Lake Erie had the sum (Σ) of PBDE concentrations of less than 20 ng/g dry weight.

TBBPA is currently the most extensively used BFR worldwide. In 2001, the global market of TBBPA was about 119,600 tonnes, representing more than 50% of the production of all BFRs (Birnbaum and Staskal, 2004). In contrast to PBDEs, in some products containing TBBPA, it is chemically bonded to polymers and thus less easily released to the environment (Wiseman et al., 2011). However, non-bonded TBBPA can be leached out of products and enter into the environment. TBBPA has been globally detected and reported in air, soil, sediment, indoor dust, bird, and human samples (Abdallah et al., 2008; Covaci et al., 2009; Shi et al., 2009; He et al., 2010).

BPA is widely used in the production of epoxy resins and polycarbonate plastics, which are used as food-contact surface coatings for consumer goods, including cans, metal jar lids, coatings, finishes, automobile parts and high-impact windows. The global demand of BPA was estimated as 5 million tonnes for 2010 (Huang et al., 2012). This chemical has been detected as a pollutant in different environmental compartments (Huang et al., 2012; Liao et al., 2012). Although BPA (log Kow = 3.3) is less hydrophobic than PCBs and PBDEs (log Kow = 4–10), a simple equilibrium model predicted that about 50% of BPA in the environment has the potential to accumulate in sediments or soils (Staples et al., 1998). In addition, TBBPA can be degraded to BPA in sediments (Voordockers et al., 2002). Therefore, sediment plays an important role in regulating the environmental fate of TBBPA and BPA. However, to our knowledge, there has been no reported study of the spatial distribution of TBBPA and BPA in Great Lakes sediments.

In 2003, the Binational Executive Committee of the Parties to the U.S.–Canada Great Lakes Water Quality Agreement (GLWQA) developed a plan to coordinate Great Lakes monitoring efforts. This entailed conducting lake-specific intensive, multiagency surveillance and sampling over a 5-year rotating basis (Matisoff and Ciborowski, 2005). Lake Erie was identified for investigation in 2004. In response to the GLWQA, the present study aims to examine and compare the spatial distribution patterns of PCBs, PBDEs, TBBPA and BPA in the sediment samples (collected in 2004) from representative sites throughout Lake Erie. To our knowledge, this is the first study for the lake-wide investigation of PBDEs, TBBPA and BPA in the sediment of Lake Erie.

Materials and methods

Sample collection

Sediment sampling was conducted on Lake Erie (283 stations) in May and June 2004 using 50 × 50 cm box corers deployed by numerous vessels, including those from Environment Canada, Ontario Ministry of the Environment, Ontario Ministry of Natural Resources, National Oceanic and Atmospheric Administration and the U.S. Geological Survey. On most vessels, core sediment samples were taken wherever the sediment was soft enough for the Ponor grab to be 80% full or more and where the sediment was cohesive enough to permit a 30 cm long × 8 cm ID polycarbonate, coring tube to extract an intact plug. Typically, the superficial 10 cm (0–10 cm) and the deeper 10 cm (20–30 cm) core were each put into Whirlpak plastic bags and frozen. Fifty-six sediment samples, including 46 superficial 0–10 cm sediments from the western basin sites W194, W122, W121, W219, W220, W221, W224, W228, W230, W237, W240, W248, W255, W259, W264, W267, W269, W272, W273, W275 and W280 (n = 20), the central basin sites C95, C97, C113, C122, C127, C131, C141, C152, C155, C158, C163, C167, C173, C174, C185 and
C198 \((n = 16)\) and the eastern basin sites E4, E18, E37, E93, E41, E61, E62, E72 and E88 \((n = 10)\) and 10 deeper sediment samples from 20–30 cm depth \((\text{sites E}29, \text{E}37, \text{C}131, \text{C}135, \text{C}141, \text{C}158, \text{C}167, \text{C}173, \text{W}200 \text{and W}264)\), were chosen as sub-samples for this survey of organic contaminants. Sample site numbers refer to the locations shown in Fig. 1. After collection, samples were stored at \(-20^\circ\text{C}\) before chemical analysis \((\text{carried out in 2004})\).

Reagents and chemicals

The 47 PCB and 9 PBDE congener \((\text{Table 1})\) analytical standards were purchased from Cambridge Isotope Laboratory \((\text{Andover, MA, USA})\) and AccuStandard \((\text{New Haven, CT, USA})\), respectively. TBBPA and BPA were obtained from Aldrich Chemical Co. \((\text{WI, USA})\) and were of minimum 97% purity. Ring-\(^{13}\text{C}_{12}\)-labeled TBBPA was obtained from Cambridge Isotope Laboratories Inc. and was of minimum 99% purity. Mono-BBPA and tri-BBPA were a kind gift from Drs. Goran Marsh and Åke Bergman \((\text{Department of Environmental Chemistry, Stockholm University, Sweden})\). 4,4’-Isopropylidenebis \((2\text{-bromophenol})\) (di-BBPA) was synthesized in our lab as described in Chu et al. \((2005)\).

Anhydrous sodium sulfate was purchased from VWR international Inc. \((\text{Mississauga, ON, Canada})\) and pretreated in a muffle furnace at \(650^\circ\text{C}\) for 12 h to remove any potential organic contamination. All other solvents \((\text{hexane, dichloromethane, methanol, acetone, tert-butyl methyl ether (MTBE)})\) were OMNISOLV® grade from VWR International Inc.

Sample extraction and clean-up

The moisture in the sediment samples was measured gravimetrically through the weight difference after heating the sub-samples at \(105^\circ\text{C}\) overnight. The analytical methods for PCBs and PBDEs were adapted with minor modifications from Covaci et al. \((2005)\). The analytical method for TBBPA and BPA is described in detail elsewhere \((\text{Chu et al., 2005})\). Briefly, the sediment samples were dried at room temperature for 48 h, and then a sample \((10\text{ g})\) of dry sediment was ground with 30 g anhydrous sodium sulfate in glass mortar. The mixture was then transferred to an extraction thimble and spiked with known amounts of internal standards: a solution of \(^{13}\text{C}_{12}\)-labeled CB-83 and CB-122 for PCB determination, BDE-71 for PBDEs and \(^{13}\text{C}_{12}\)-TBBPA for TBBPA, tri-BBPA, di-BBPA, mono-BBPA and BPA determination. TBBPA, tri-BBPA, di-BBPA and mono-BBPA are collectively referred to as BBPAs. The samples were Soxhlet extracted with MTBE for 12 h.

The Soxhlet extracts were concentrated and solvent exchanged to hexane. Neutral compounds \((\text{PCBs and PBDEs})\) and phenolic compounds \((\text{e.g. TBBPA and BPA})\) in the solution were separated by partitioning between hexane and sodium hydroxide \((1\text{ M})\). The organic phase from the hexane/sodium hydroxide partitioning separation contained PCBs and PBDEs. After the solution was dried with sodium sulfate, and concentrated to about 2 mL, sulfur precipitates were removed by adding activated granular copper. Clean-up was performed with a column packed with 6 g acid silica \((22\%\text{ sulfuric acid, w/w})\). PCBs and PBDEs were eluted with 50 mL of 50\% dichloromethane/hexane \((\text{v/v})\). The elutes were evaporated to dryness and reconstituted with 100 \(\mu\text{L}\) isooctane for gas chromatography/electron capture detector \((\text{GC/ECD})\) for PCBs and gas chromatography/mass spectrometry \((\text{GC/MS})\) for PBDE determination.

After acidification of the aqueous phase, the target analytes, BBPAs and BPA, were concentrated and isolated by solid phase extraction \((\text{SPE})\) using LC-C18 cartridges \((500 \text{ mg } \times 3 \text{ mL}; \text{Supelco, USA})\). The LC-Si SPE cartridges were first conditioned with 10 mL dichloromethane/hexane \((1:9\text{ v/v})\). After loading the SPE cartridge with sample, the
BBPs and BPA were then eluted by 10 mL of MTBE:dichloromethane (1:9 v/v). The elutes were concentrated to dryness under a gentle stream of nitrogen, and reconstituted with methanol to a concentration of 100 μg/L for high performance liquid chromatography–electrospray ionization (negative mode)–tandem mass spectrometry (HPLC–ESI(−)–MS/MS) analysis.

**Instrumental analysis**

An Agilent 6890 GC/ECD was used to determine PBPs in the final sediment fractions. The GC separation was performed on a capillary column (30 m × 0.22 mm, 0.25 μm film thickness J&W HP-5; Agilent Technologies, Mississauga, ON, Canada). The carrier and make-up gases were helium and argon/methane (95:5), respectively. The initial oven temperature was 90 °C, held for 1 min and then ramped to 200 °C at 15 °C/min, held for 2 min, ramped to 280 °C at 2.5 °C/min and held for 10 min. The injector and detector temperatures were 270 and 300 °C, respectively. Extracts (1 μL) were injected in splitless mode. PBDE determination, with exception of BDE-209, was performed on an Agilent 5973 Network mass spectrometer and equipped with a HP-5MS (30 m × 0.25 mm id.) capillary column. Extracts (1 μL) were injected into the GC–MS in splitless mode. Injection and interface temperatures were set to 280 °C. The oven temperature program was: 80 °C (hold for 1 min) ramped to 280 °C at 15 °C/min, held for 2 min, ramped to 300 °C at 20 °C/min and held for 10 min. The injector and detector temperatures were 270 °C and 600 °C, respectively. Extracts (1 μL) were injected in splitless mode. The MS/MS analysis was performed on an Agilent 6890 GC/ECD and equipped with an Agilent 5973 Mass Selective Detector (ionization mode (SIM)). Five ions (m/z 79, 81, 159, 161 and 163) were monitored. PBDE determination, with exception of BDE-209, was performed on an Agilent 5973 Network mass spectrometer and equipped with a HP-5MS (30 m × 0.25 mm id.) capillary column. Extracts (1 μL) were injected into the GC–MS in splitless mode. Injection and interface temperatures were set to 280 °C. The oven temperature program was: 80 °C (hold for 1 min) ramped to 280 °C at a rate of 2 °C/min, and held for 15 min. PBDE analysis was conducted with electron capture negative ionization (ECNI) in selection ion monitoring mode (SIM). Five ions (m/z 79, 81, 159, 161 and 163) were monitored. Quantification was carried out by comparison of signals with the standards. The results are reported as means of four replicates of 47 PCBs, 50 PBDEs and 10 CBs. The quantitation limit (QL) is 1 μg/L and the limit of detection (LOD) is 0.5 μg/L.
internal standard. For the determination of BDE-209, a J&W DB-5 capillary column (15 m × 0.25 mm i.d.; Agilent Technologies, Mississauga, ON, Canada) was used. The oven temperature program was: 80 °C held for 1 min, ramped from 80 to 215 °C at 10 °C/min, ramped from 215 °C to 270 °C at 3 °C/min, then ramped from 270 to 300 °C at 10 °C/min, held for 10 min.

As described in Chu et al. (2005), the determination of BBPAs and BPA was performed by HPLC–ESI(−)–MS/MS. HPLC separation was performed using a Genesis C18 120A column (150 mm × 2.1 mm i.d., 4 μm; Jones Chromatography Limited, Hengoed, UK) with a Phenomenex C18 guard column (4 mm length, 2.0 mm i.d., 4 μm particles; Phenomenex, CA, USA) operated at a solvent flow rate of 0.2 mL/min. Samples (20 μL) were injected by an autoinjector. Separation was performed using a mobile phase consisting of A: 25% methanol/75% water and B: 100% methanol. The solvent program was as follows: initial condition 100% A changed to 100% B upon injection, held constant for 15 min, and then decreased linearly to the initial condition (100% A) over a 5 min period, and held constant for 10 min. The target analytes were monitored in multiple reaction monitoring (MRM) mode. The transitions (parent → fragment; m/z) 272 → 212, 307 → 81, 385 → 81, 456 → 81, 543 → 81 and 555 → 81 were monitored to detect BPA, mono-BBPA, di-BBPA, tri-BBPA, TBBPA and their internal standard (13C12-TBBPA), respectively. Analyte identities were further confirmed based on their retention times. A six level calibration curve spanning the range of anticipated concentrations in the samples, along with internal standards, was used to quantify the analytes.

Quality control

Rigorous calibration and quality control measures were undertaken throughout the study. Quality control for the analysis was done by analyzing blanks and spiked samples for every batch of 10 sediment samples. Clean sand sample was put into a fresh Whirlpak bag to serve as a blank sample. With each batch of real sediment samples, a portion of this sand was included as the blank sample. All analytes under study were not found above their respective detection limits. Polycarbonate tubes were used for the original sample collection. However, it is not possible that the polycarbonate tubes were a source of e.g. BPA cross-contamination. First, sub-samples for the present contaminant analysis were taken for an inner portion of the sub-sample and thus not subject to contact with the polycarbonate tube or the Whirlpak bag. Second, if BPA cross-contamination was an issue, it is not possible that our results would show BPA in western basin sediment samples, and much lower or non-detectable levels in the central and eastern basin samples (see Results and discussion).

The method limits of quantification (MLOQs) (signal-to-noise ratio 10:1) were estimated on a congener-specific basis by measuring the background noise in the time interval wherein the analyte peak was expected. The MLOQs for all PCB and PBDE congeners ranged from 0.005 to 0.01 ng/g dry weight (d.w.). However, the exception was BDE-209 where the MLOQ was 0.3 ng/g (d.w.). The MLOQs for TBBPA, tri-BBPA, di-BBPA, mono-BBPA and BPA were 0.05, 0.04, 0.02, 0.02 and 0.15 ng/g (d.w.) respectively. Representing the PCB congeners, the percent recoveries of the 13C12-labeled CB-83 and CB-122 internal standards spiked to each sediment sample ranged from 67 to 107%. Representing the PBDE congeners, the percent recoveries of the BDE-71 internal standard spiked to each sediment samples ranged from 69 to 115%. For BPA, mono-BBPA, di-BBPA, tri-BBPA and TBBPA, the recoveries of the 13C12-TBBPA internal standard ranged from 71 and 102%. The concentrations of all quantifiable analytes were inherently recovery-corrected as relative response factors, and an internal standard quantification approach was used. All of the analyte concentrations presented are given on a dry weight (d.w.) basis.

Statistical analysis

Data was analyzed using GraphPad Prism 5.0 (La Jolla, CA, USA). The concentration data are reported as mean ± standard deviation (SD). The significance of differences in mean contaminant concentrations and the percentage of PCB homologs among the Lake Erie basins were tested using the nonparametric Kruskal–Wallis one-way analysis of variance on ranks and followed by Dunn’s post-hoc tests when the data did not consistently meet the normality assumption (D’Agostino–Pearson normality test), or one way ANOVA with Tukey’s post-hoc tests when the data was normally distributed. Student’s t-test and Mann–Whitney test were used for the data comparisons between two groups based on the normality of data distribution. Differences were considered significant at p < 0.05.

Results and discussion

PCBs

The spatial distributions of Σ47PCBs are illustrated in Fig. 2 and the concentrations for individual congeners are shown in Table 1. The dominant congeners in the sediment of Lake Erie were tetra-, penta-, hexa- and hepta-chlorinated PCBs and mainly included CB-52, -101, -110, -118, -138, -153 and -180 (Electronic Supplementary Material (ESM) Figs. S1 and S2). This is consistent with previous results by Marvin et al. (2004a,b). Western basin sediments (mean 144 ± 141 ng/g d.w.) contained statistically (p < 0.0001) greater Σ47PCB concentrations than sediments of the central basin (33 ± 34 ng/g d.w.) and the eastern basin (13 ± 15 ng/g d.w.). The spatial distribution patterns of individual PCB congeners were similar to total PCBs (ESM Fig. S1). This spatial distribution pattern of PCBs was consistent with the results of Lake Erie sediment surveys conducted in 1971 and 1997 (Frank et al., 1977; Marvin et al., 2004a,b). The percentage of tri-chlorinated PCBs in total PCBs was significantly greater (p = 0.0002) in the western basin than the percentage in the central and eastern basins (ESM Fig. S2). The western basin sediments also contained a greater (p = 0.01) percentage of hepta-chlorinated PCBs than the eastern basin (ESM Fig. S2). In contrast, the percentage of penta-chlorinated PCBs in the eastern basin was significantly greater (p = 0.004) than in the western basin (ESM Fig. S2). Partitioning and sediment resuspension, PCB transport as well as sources and degradation processes of the PCB homolog groups in different basins of Lake Erie, may contribute to and explain these PCB congener distribution patterns in sediment.

For the eastern and central basins, Σ47PCB concentrations in the southern sampling sites (sites E39, E62, C95, C141, C158 and C174; 27 ± 35 ng/g d.w.) tended to be greater than the concentrations in the north sites (sites E41, E72, C88, C127, C155 and C163: 6.4 ± 6.0 ng/g d.w.), but were not significantly different (Mann–Whitney test, two tailed, p = 0.24). The homolog distributions of PCBs from the southern and northern sampling sites were also similar (ESM Fig. S3). The relatively greater Σ47PCB concentrations around sites C95 (44 ng/g...
d.w.) and C158 (92 ng/g d.w.) were consistent with the surveys conducted in 1971 (Frank et al., 1977) and 1997 (Marvin et al., 2004a,b), indicating past contributions of historical discharges of PCBs in these areas (e.g., Cuyahoga River close to site C158). Sites C167, C173 and C198 (100, 80 and 72 ng/g d.w., respectively) in the central basin also contained relatively greater Σ47PCBs concentrations, which is likely due to the greater input of PCB contamination from the western basin. Song et al. (2005a) reported the concentration of 39 PCB congeners in the surface sediment collected from Lake Erie in 2002 of 23 and 28 ng/g d.w. for the eastern and central basins respectively, which were similar to our PCB data.

With respect to time point comparisons, the PCB levels in sediment were reported to have decreased by about 70% from 1971 (136 ng/g, 24 congeners) (Frank et al., 1977) to 1997 (98 ng/g, 103 congeners; 43 ng/g, 24 congeners) (Marvin et al., 2004a,b). The significant decrease of PCB concentrations in the surficial (0–3 cm) sediments during the period of 1971 to 1997 was mainly the result of restrictions on PCB manufacture and use in 1970s. It was reported that as of 1997, the number and magnitude of PCB sources to the Great Lakes had decreased about 20-fold since the 1970s (Froese et al., 1997). It is well established that the Detroit River outflow is the major contamination source/vector of organic pollutants, including for PCBs, into Lake Erie (Marvin et al., 2004a,b, 2013). The relatively stable concentrations of PCBs from 1997 to 2004 in the sediment of Lake Erie were consistent with the temporal trend of PCBs in the Detroit River from 1999 to 2009 (Szalinska et al., 2013).

In the present study, the mean concentration of Σ47PCBs in deeper bottom sediments (20–30 cm) below the surface, except for sites C135 and W200) was 50 ± 52 ng/g d.w., which was not significantly different from the PCB levels in surficial 0–10 cm sediment (68 ± 59 ng/g d.w.) of these sampling locations (paired t-test, two tailed, p = 0.41). However, different vertical distribution patterns of PCBs were observed where 0–10 cm and 20–30 cm sample pairs were available. For these sample pairs sites, Σ47PCBs were greater for the 20–30 cm sample for sites E29, E37 and C141 than the paired 0–10 cm sediments, whereas the Σ47PCB levels were lower for the 20–30 cm sample for sites C131, C158, C167, C173 and W264 when compared with the paired 0–10 cm sediments. Locations with greater concentrations in deeper (20–30 cm) or surficial (0–10 cm) sediments are not confined to one particular basin, and one possible reason for this distribution is the known variation in sedimentation rates (ranging from 0 to 7.4 mm per year) throughout Lake Erie (Kemp et al., 1977). The surficial (0–10 cm) and deeper (20–30 cm) sediments in different locations of the lake may represent different PCB contamination histories. There was no obvious change of the PCB congener pattern and homolog composition between the present surficial (0–10 cm) and deeper (20–30 cm) sediments (ESM Figs. S4 and S5).

The presence of PCBs in the sediment of Lake Erie can have adverse impacts on aquatic organisms, especially in the western basin. The concentration of PCBs in 70% of our western basin sediment samples (collected in 2004) exceeded the Canadian sediment quality threshold effect level (TEL, 34.1 ng/g d.w.) (Canadian Council of Ministers of the Environment, CCME, 1999) and the Ontario Provincial sediment quality lowest effect level (LEL, 70 ng/g d.w.) (Persaud et al., 1993). Σ47PCB concentrations for two sampling sites (site W259, 294 ng/g d.w.; site W273, 617 ng/g d.w.), and close to the downstream of the highly contaminated Detroit River and Trenton Channel (Furlong et al., 1988; Marvin et al., 2013) in the western basin, exceeded the Canadian sediment quality probable effect level (PEL, 277 ng/g d.w.) (Canadian Council of Ministers of the Environment, CCME, 1999), which is the guideline for the protection of aquatic biota for PCB exposure. In contrast, in the last lake-wide survey of PCB contamination in the sediment of Lake Erie in 1997–1998, there was no observation of exceeding the PEL based on more than 70 samples (Painter et al., 2001). In the central basin, 35% and 24% of the samples exceeded the TEL and LEL, respectively. Only one sample in the eastern basin exceeded the TEL. These results indicated that in 2004 there was a potential ecological risk associated with PCB exposure in the sediment of Lake Erie. For example, high concentrations (Σ47PCB, up to 1.50 × 10<sup>4</sup> ng/g lipid weight) of PCBs have been reported in the muscle of wild common carp (Cyprinus carpio) from the eastern basin of Lake Erie (Pérez-Fuentetaja et al., 2010). The dominant congeners in common carp were CB-138 and -153, which was consistent with the composition pattern of PCBs in the present Lake Erie sediment. The feeding ecology of carp mainly includes benthic prey, which may provide high probability for the fish to exposure to the PCBs in sediments (Pérez-Fuentetaja et al., 2010).

**PBDEs**

PBDEs were detected in all sediment samples from Lake Erie, but at varying concentrations. The spatial distribution of Σ8PBDEs (excluding BDE-209) in the sediment of Lake Erie is shown in Fig. 3, and the concentrations of individual BDE congeners are summarized in Table 1. Because high concentrations of BDE-209 were found in the samples, the results of less brominated congeners (BDE-28, -47, -99, -100, -138, -153, -154 and -183) and BDE-209 are discussed separately.

The total concentrations of less brominated PBDEs (Σ8PBDEs) were 1.35 ± 0.24, 0.19 ± 0.11 and 0.32 ± 0.38 ng/g d.w. for the western, central and eastern basins, respectively (Fig. 3a). BDE-47 and -99, the most common BDE congeners reported in exposed organisms (Watanabe and Sakai, 2003), were the predominant congeners of less brominated PBDEs in Lake Erie sediments (ESM Fig. S6). Based on the Canadian Federal Environmental Quality Guideline (FEQG) threshold levels for triBDEs (44 ng/g d.w.), tetraBDEs (39 ng/g d.w.), pentaBDEs (0.4 ng/g d.w.), hexaBDEs (440 ng/g d.w.), octaBDEs (5600 ng/g d.w.) and decaBDE (BDE-209; 15 ng/g d.w.), almost 100% of the PBDE congeners levels (Table 1) in our sediment samples (collected in 2004) and including the western basin, were below the respective FEQG threshold levels (Environment Canada, 2013). The lone exceptions were the concentrations of BDE-100 at sampling site W220 (0.86 ng/g d.w.) and BDE-99 at sites W220, W255, W269, W272, W273, W275 and E39 (0.43–5.8 ng/g d.w.), which were somewhat greater than the FEQG threshold level for pentBDEs of 0.4 ng/g d.w. These results indicated that in 2004...
there was a very low potential ecological risk associated with PBDE exposure in the sediment of Lake Erie.

Σ8PBDE concentrations in western basin sediment was significantly greater than the concentrations in the central and eastern basins (p < 0.0001), but there was no obvious difference in the concentrations between the central and eastern basins (Fig. 3a). However, relatively greater concentration of Σ8PBDEs (1.36 ng/g d.w.) was detected at site E39 from the eastern basin for reasons that are unclear. The greatest concentration of Σ8PBDEs was found at site W220 (12 ng/g d.w.), which is near the Detroit River inflow. In contrast, although very close to site W220, a very low level of Σ8PBDEs (0.11 ng/g d.w.) was measured at site W219. This result indicated that the spatial distribution of PBDEs in the sediment of Lake Erie was relatively heterogeneous in 2004. In addition, the spatial distribution of individual less brominated BDE congeners was similar to that of total PBDEs (ESM Fig. S6).

The levels of Σ8PBDEs in our 2004 study were lower than the data reported in sediment from Lake Ontario (Σ8PBDE = 5.59 ng/g d.w., 2002) and Lake Michigan (Σ9PBDE = 2.60 ng/g d.w., 2004) (Song et al., 2005a; Zhu and Hites, 2005). However, the Σ8PBDE concentrations in the western basin were similar to those in sediments collected from Lake Erie in 2002 (Σ8PBDE = 1.89 ng/g d.w.) and 2003 (Σ9PBDE = 1.10 ng/g d.w.), Lake Superior (Σ8PBDE = 1.40 ± 0.40 ng/g d.w., 2001–2002) and Lake Huron (Σ8PBDE = 1.51 ng/g d.w., 2002) (Song et al., 2004, 2005a,b; Zhu and Hites, 2005). The levels of Σ8PBDEs in the central and eastern basins of Lake Erie were comparable with the sediments of the watershed of Lake Huron (Σ8PBDE = 0.34–0.56 ng/g d.w., 2002–2004) (Yun et al., 2008), Gewurtz et al. (2009) also investigated the PBDE spatial distribution in sediment (top 3 cm) collected between 2002 and 2006, at sites at open water, nearshore, and at the mouth of tributary locations in Lake Erie. Most sampling sites for Lake Erie had Σ8PBDE concentrations (not including BDE–209) of less than 20 ng/g (d.w.), and BDE–209 levels that exceeded the other Σ8PBDE concentration, which was generally comparable to the mean Σ8PBDEs and separate BDE–209 concentrations found in the present sediment samples from 2004 (Table 1, Fig. 3).

Σ8PBDE concentrations in the surficial layer (0–10 cm) (0.34 ± 0.26 ng/g d.w.) of sediments from sites E29, E37, C131, C141, C158, C167, C173 and W264 were greater than the concentrations in the deeper layer (20–30 cm) (0.13 ± 0.07 ng/g d.w.), albeit not statistically significant (paired t test, two tailed, p = 0.07). BDE–28 and -183 were only detected in the 0–10 cm layer of sediment, but not in the deeper layer. There was no obvious difference of the pattern of other BDE congeners between the surficial and deeper sediments (ESM Fig. S7). The lower level of Σ8PBDEs in 20–30 cm sediment than in the 0–10 cm sediment was in agreement with former findings (Song et al., 2005a; Zhu and Hites, 2005).

BDE–209 was detected in 56% of the samples analyzed, with concentrations up to 12 ng/g (site C158), which as mentioned was lower than the Canadian EQG threshold level of 19 ng/g d.w. for BDE–209 (Environment Canada, 2013). BDE–209 accounted for 62% and 64% of the Σ8PBDEs in the eastern and central basins, respectively. These proportions were lower than those reported for Lake Erie and some European lakes, where the concentration of BDE–209 in sediment made up 95–99% of the Σ8PBDEs (de Boer et al., 2003; Song et al., 2005a; Zegers et al., 2003; Zhu and Hites, 2005). Interestingly, in the western basin, BDE–209 only contributed 29% of Σ8PBDEs, which might be due to the relatively greater inputs of other PBDEs from the Detroit River. The concentrations of BDE–209 detected in the present study were much lower compared with previous findings for Lake Erie (39.0–55.4 ng/g d.w.) (Song et al., 2005a; Zhu and Hites, 2005). One possible reason is that our tested sediments combined the surficial 0–10 cm of sediment as opposed to analyzing sediment layers at finer (i.e., 1 cm) intervals from the top of the sediment/water interface. Thus, our samples represented the average concentration of BDE–209 in the interval of 0–10 cm depth. Song et al. (2005a) took samples from a segmented core at 1 cm intervals and reported a remarkable decrease (from 55.4 ng/g to n.d.) of the BDE–209 concentration between the 0–10 cm depth stratum in Lake Erie (at a sampling location close to our site E37).

The distribution pattern of BDE–209 was different from that of the less brominated PBDEs (Fig. 3b). There was no significant difference among the BDE–209 concentrations in the three basins (p = 0.8). Relatively high levels of BDE–209 were found in the central and eastern basins (e.g., sites E29, E37 and C158), but the reasons are not clear. One possible explanation is that the eastern basin has the highest average sedimentation rate (e.g., ~ 6 mm/year close to sites E29 and E37) (Kemp et al., 1977) and water depth (about 50–60 m) of Lake Erie. These conditions make sediment re-suspension almost impossible. Thus, the surficial 10 cm depth sediment sample from 2004 reflected the more recent PBDE pollution period (e.g., 15 years before sampling, roughly estimated from the sedimentation rate) at which time BDE–209 and other PBDEs were heavily used. In addition, the concentration of BDE–209 in the 0–10 cm layer of sediment was significantly greater than the 20–30 cm layer (Mann–Whitney test, two tailed, p = 0.03) (ESM Fig. S8).

TBBA

TBBA was not detected in almost all sediment samples of Lake Erie (Fig. 4a). This contaminant was detected (S/N > 3) in the surficial and deeper sediment samples from site E29 in the eastern basin, but could not be quantified (S/N > 10; i.e., < 0.05 ng/g d.w.). TBBA was only quantifiable in the surficial (0–10 cm) sediment of site W269 in the western basin, where the concentration was 0.5 ng/g (d.w.) (Fig. 4a). In the same sample (site W269), tri-BBPA was also quantifiable with a concentration of 0.34 ng/g (d.w.). This result corroborates the findings of Quade et al. (2003) where low concentrations of TBBPA (0.3–1.6 ng/g d.w.) were reported in suspended sediment collected in July 2000 from eight stations in the Detroit River and Trenton Channel at the mouth into Lake Erie. The Quade et al. (2003) study is to our knowledge the only other report that exists on TBBPA in Great Lakes sediment samples. As a flame retardant, TBBA is ‘reactive’ and chemically bonded to polymers, and thus it is released into the environment with lower efficiency than non-bonded BFRs. This might be one reason for the low
concentrations of TBBA generally observed in the environment compared with PBDEs, which are additive flame retardants and blended with polymers. The degradation of TBBA to BPA under both methanogenic and sulfate-reducing conditions may be another possible factor affecting their concentrations in sediment (Voodeckers et al., 2002). The effluents of sewage treatment plants, municipal incinerators and factory flues are possible sources of TBBA and tri-BBPA for Lake Erie. For example, both TBBA and tri-BBPA were found in the final effluent (0.7 ± 0.3 ng/L TBBA and 2.1 ± 1.5 ng/L tri-BBPA) and sludge (36.3 ± 17.8 ng/g TBBA and 16.8 ± 8.6 ng/g tri-BBPA, d.w.) samples from wastewater treatment plants in Windsor, Ontario, Canada (McPhedran et al., 2013).

TBBA has been found in sediment samples world-wide (Watanabe and Sakai, 2003). Compared with other locations, the present Lake Erie sediment showed relatively low levels of TBBA contamination. Sellström and Jansson (1995) reported 270 ng/g d.w. of TBBA in the sediment close to a plastic manufacturing area. Morris et al. (2004) investigated the distribution of TBBA and other BFRs in North Sea estuaries. High concentrations of TBBA were reported in freshwater sediment samples (9.8 mg/kg) from the River Skerne, northeast England (Morris et al., 2004). TBBA was also detected in the sediment of the Pearl River Delta in southern China and ranged from 0.06 to 304 ng/g d.w. (Feng et al., 2012). Because the degradation of TBBA to BPA is a possible source of BPA contamination in sediment (Voodeckers et al., 2002), it is interesting to know the concentration of BPA in Lake Erie, as shown in the next BPA sub-section.

BPA

The concentrations of BPA in the sediment of Lake Erie are listed in Table 1. BPA was detected in 65% of the sediment samples analyzed, with a concentration up to 6.1 ng/g d.w. The mean BPA concentration for the western basin (1.3 ± 1.5 ng/g d.w.) was significantly greater (p < 0.0001) compared to the central (0.3 ± 0.3 ng/g d.w.) and eastern basins (0.1 ± 0.2 ng/g d.w.) (Fig. 4b). Most sediment samples with greater BPA contamination were found near the mouth of the Detroit River and the Trenton Channel (e.g., sites W273, W269 and W264), but the highest BPA contamination was found on site W212, with a concentration of 6.1 ng/g d.w. This distribution pattern implies that the Detroit River and Trenton Channel outflow were primary sources/vectors for BPA contamination in this area of Lake Erie. In a very recent study by Guerra et al. (2015), BPA was analyzed in 499 liquid and 347 solid samples collected from twenty-five wastewater treatment plants (WWTPs; including several in the Laurentian Great Lakes area) to investigate parameters affecting BPA occurrence, removal, and fate. Regardless of the season, median BPA concentrations in WWTP influent and final effluent were 400 ng/L and 150 ng/L, respectively, and the median removal efficiencies to biosolids ranged from 1 to 77%. The study indicated that substantial amounts of BPA can be discharged by WWTPs into receiving waters, and thus could end up with sediment in those receiving systems. Compared with PCBs and PBDEs, BPA has greater water solubility (120–300 mg/L). Therefore, water transport of BPA was likely an important factor affecting the transverse distribution of BPA in the central and eastern basins of Lake Erie. The solubility of BPA also facilitates its transport downward within the sediments. Indeed, BPA was uniformly and vertically distributed in the sediments. There was no significant difference in BPA levels between the 0–10 cm (0.3 ± 0.3 ng/g d.w.) and 20–30 cm sediment layers (0.2 ± 0.4 ng/g d.w.), at sites E29, E37, C131, C141, C158, C167, C173 and W264) (Mann–Whitney test, two tailed, p = 0.4).

The observed concentrations of BPA in the sediment samples from the western basin of Lake Erie were comparable to the concentrations in sediments of Massachusetts Bay, Boston, USA (1.5 to 5.0 ng/g d.w.) (Stuart et al., 2005). However, the contaminant level in the present 2004-collected sediment was lower than at most other sampling locations such as Masan Bay (Korea, 2.7–50 ng/g d.w.; 1998) (Khim et al., 1999), Tokyo Bay (Japan, 0.1–48 ng/g d.w.; 1998) (Hashimoto et al., 2005) and The Netherlands (<1.1–43 ng/g d.w.; 1999) (Vethaak et al., 2005).

Conclusions

This paper reports the spatial distributions of PCBs, PBDEs, TBBA and BPA in sediments of Lake Erie collected in 2004. Overall, at that time the contamination by legacy POPs such as PCBs was still a major component to the sediment pollution of Lake Erie, while the concentration of organic pollutants of emerging concern such as PBDEs, BBPAs and BPA at most sample sites of Lake Erie were comparable with or lower than concentrations at other sampling locations worldwide. The western basin showed a high level contamination of PCBs, less brominated PBDEs and BPA when compared with the central and eastern basins. This was similar to isomers of hexabromocyclododecane (HBCD) (where the γ-HBCD isomer was 56–100% of the ΣHBCD concentration) we reported in a sub-sample set of the present Lake Erie bottom sediment samples (Letcher et al., 2015). These patterns reinforce the interpretation of the Detroit River continuing to play a role as a major source/vector for these legacy sand emerging/emerged organic pollutants to Lake Erie. However, although PCB concentration has decreased dramatically since the 1970s, these pollutants may still pose risks of adverse effects to organisms in the western basin of Lake Erie. There was no clear spatial trend for the 2004 distribution of BDE-209 across the three basins, and the reasons for this require further and more recent investigation. TBBA was quantified in only one sediment sample, indicating low occurrence and accumulation of polybrominated-BPAs in Lake Erie.

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Appendix A. Supplementary data

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References


