

Levels and distributions of polybrominated diphenyl ethers, hexabromocyclododecane, and tetrabromobisphenol A in sediments from Taihu Lake, China

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Abstract The concentrations and distribution of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and tetrabromobisphenol A (TBBPA) were investigated in 28 sediment samples collected from Taihu Lake, Eastern China. The results showed that all three classes of compounds were detected in 28 sediment samples but that PBDEs were the main contaminants in the study area. The total PBDE concentrations ranged from 3.77 to 347 ng/g dry weight (dw) with a mean value of 72.8 ng/g dw, whereas the concentrations ranged from 0.168 to 2.66 and from 0.012 to 1.30 ng/g dw for HBCD and TBBPA, respectively. In all of the sediment samples, BDE-209 was the predominant congener, accounting for 95.9 to 98.6 % of the total PBDEs, which indicated that commercial mixtures of deca-BDEs were the main sources of PBDE contamination. Higher concentrations of PBDEs were found in samples collected from Meiliang Bay and Gonghu Bay near the inflow river, which suggested that inflow runoff might play an important role in the PBDE levels in Taihu Lake sediments.

Keywords Polybrominated diphenyl ethers · Hexabromocyclododecane · Tetrabromobisphenol A · Sediment · Taihu Lake

Introduction

Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBPA) are the three most commonly used brominated flame retardants (BFRs). These compounds are widely used in electronic equipment, plastics, upholstery textiles, building materials, foam, and other materials (Alaee et al. 2003). Their occurrence in the environment has been increasingly reported over the past several decades. However, the majority of environmental studies conducted to date have focused on PBDEs. PBDEs have been reported at different concentrations in various environmental media, including air (Law et al. 2014), sediments (Liu et al. 2014; Morris et al. 2004; Ramu et al. 2010), aquatic organisms (Kim et al. 2015), and in humans (Darnerud et al. 2015). The production and use of penta- and octa-BDE commercial formulations have been banned by the European Union and the USA, and the Stockholm Convention added penta- and octa-BDEs to Annex A (elimination of production and use of all intentionally produced persistent organic pollutants (POPs) in 2009 owing to their environmental persistence, bioaccumulation, and potential toxicity).

Like PBDEs, HBCD can also be released into the environment during their production and usage or via emissions. After penta- and octa-PBDEs were banned in Europe and the USA, HBCD concentrations were increasingly found in various environmental compartments, wildlife, and humans (Law et al. 2014). Currently, these compounds are considered to be ubiquitous contaminants, and they are under assessment for inclusion in the Stockholm Convention and in the UN-ECE Protocol on Persistent Organic Pollutants (POPRC 2010). The most

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commonly used BFR in the world, TBBPA, accounted for approximately 60 % of the global BFR demand in 2001, and is primarily used as a reactive flame retardant in the epoxy resins of printed circuit boards and electronic equipment, but it is also used as an additive flame retardant in polymers (Covaci et al. 2009). TBBPA has been found in air, soil, sediment, birds, and humans in a variety of places (Covaci et al. 2009; Feng et al. 2012). These contaminants have been on the fourth list of priority chemicals under the European Council (EC) Regulation No. 793/93 since 23 March, 1993. However, the EU risk assessment of TBBPA on human health (part II) concluded that they posed no human health hazards of concern and no risks were identified (EURAP 2006). As a result, there are still no regulations on the production or use of TBBPA and its derivatives.

Taihu Lake is the third largest freshwater lake in China and is located at the southern side of the Yangtze River delta, which is one of the most economically developed regions in China. Taihu Lake serves as a source of drinking water for more than 34 million residents around the lake watershed. The recent rapid industrialization and urbanization of the region have led to some severe environmental problem. For example, Taihu Lake has suffered from serious eutrophication due to nitrogen and phosphorus overloading. Recently, some contaminants such as perfluoroalkyl substances and chlorinated dioxins and organic phosphate flame retardants have been detected in this region (Chen et al. 2015; Cao et al. 2012; Zhou et al. 2012a, b). However, little information is available regarding the level and distribution of BFRs in environmental matrices in this region (Zhou et al. 2012a, b). Sediments are thought to be a major sink and long-term potential exposure source of hydrophobic organic contaminants commonly released into aquatic systems through direct/indirect discharge, runoff, or atmospheric deposition. Under appropriate conditions, these contaminants can be desorbed and reach the human body via drinking water. Therefore, this study collected 28 surface sediment samples from Taihu Lake to investigate the concentration and distribution of PBDEs, HBCD, and TBBPA and their debrominated products in the aquatic system. In addition, the congener profile and potential sources of these compounds were investigated.

Material and methods

Sample collection

A total of 28 surface sediment (0 to 5 cm) samples were collected from Taihu Lake in June, 2009. Briefly, nine composite sediment samples (ML-1 to ML-9) were collected from Meiliang Bay, ten (GH-1 to GH-10) from Gonghu bay, and seven (XK-1 to XK-7) from Xukou Bay. In addition, two samples were collected from the central section of the lake (HX-1 and HX-2). The samples were collected using grab

samplers (Ekmangrab, Wildlife Supply Company, Buffalo, NY, USA). All sampling locations were located with a global positioning system (Magellan, San Dimas, CA, USA) and are shown in Fig. 1. After collection, the samples were freeze dried and homogenized, sieved through an 80 mesh, and finally stored at -20°C until analysis. Detailed information regarding the study areas is available in our previous study (Cao et al. 2012).

Standards and materials

The PBDE reference materials (BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183, BDE-191, BDE-196, BDE-197, BDE-203, BDE-206, BDE-207, BDE-208, and BDE-209) were obtained from AccuStandard Inc. (New Haven, CT, USA), and ^{13}C -PCB141, ^{13}C -PCB208, ^{13}C -PCB209, native, d_{18} - and $^{13}\text{C}_{12}$ -labeled α -, β -, and γ -HBCD, ^{13}C -BPA, and ^{13}C -TBBPA were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Tri-BBPA, di-BBPA, and mono-BBPA were synthesized in our laboratory (purity $>98\%$). The ethyl acetate was from CNW Technologies GmbH (Düsseldorf, Germany), and HPLC-grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). The methyl *tert*-butyl ether (MTBE) was pesticide residue grade and was purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Oasis[®] HLB Extraction Cartridges (500 mg, 6 mL) were obtained from the Waters Corporation (Milford, MA, USA).

Extraction and cleanup

The samples (15 g) were spiked with ^{13}C -PCB209, ^{13}C -PCB141, $^{13}\text{C}_{12}$ -labeled α -, β -, and γ -HBCD, ^{13}C -BPA, and Soxhlet extracted for 48 h with 200-mL acetone/hexane mixture (1:1, *v/v*). Activated copper pieces were then added to remove the elemental sulfur. The extracts were concentrated and exchanged to hexane, and a basic aqueous solution (0.5 M KOH in 50 % ethanol) was added to isolate the neutral and polar fractions. The aqueous solution was extracted with hexane three times to separate the neutral compounds, and the remaining polar fractions were then acidified with 6 M hydrochloric acid (HCl).

The isolated neutral fractions were concentrated and then cleaned and fractionated on an acid/basic multilayer silica/alumina column with 70-mL hexane/dichloromethane (1:1, *v/v*). A detailed description of the cleaning and fractionation process is available in Gao et al. (2011). The eluate was concentrated to 200 μL under a gentle stream of nitrogen gas, and a specific amount of internal standard (^{13}C -PCB208) for PBDE analysis was added before instrumental analysis.

After finishing PBDE analysis by GC-MS, the solvent was exchanged to methanol, and d_{18} -labeled α -, β -, and γ -HBCDs

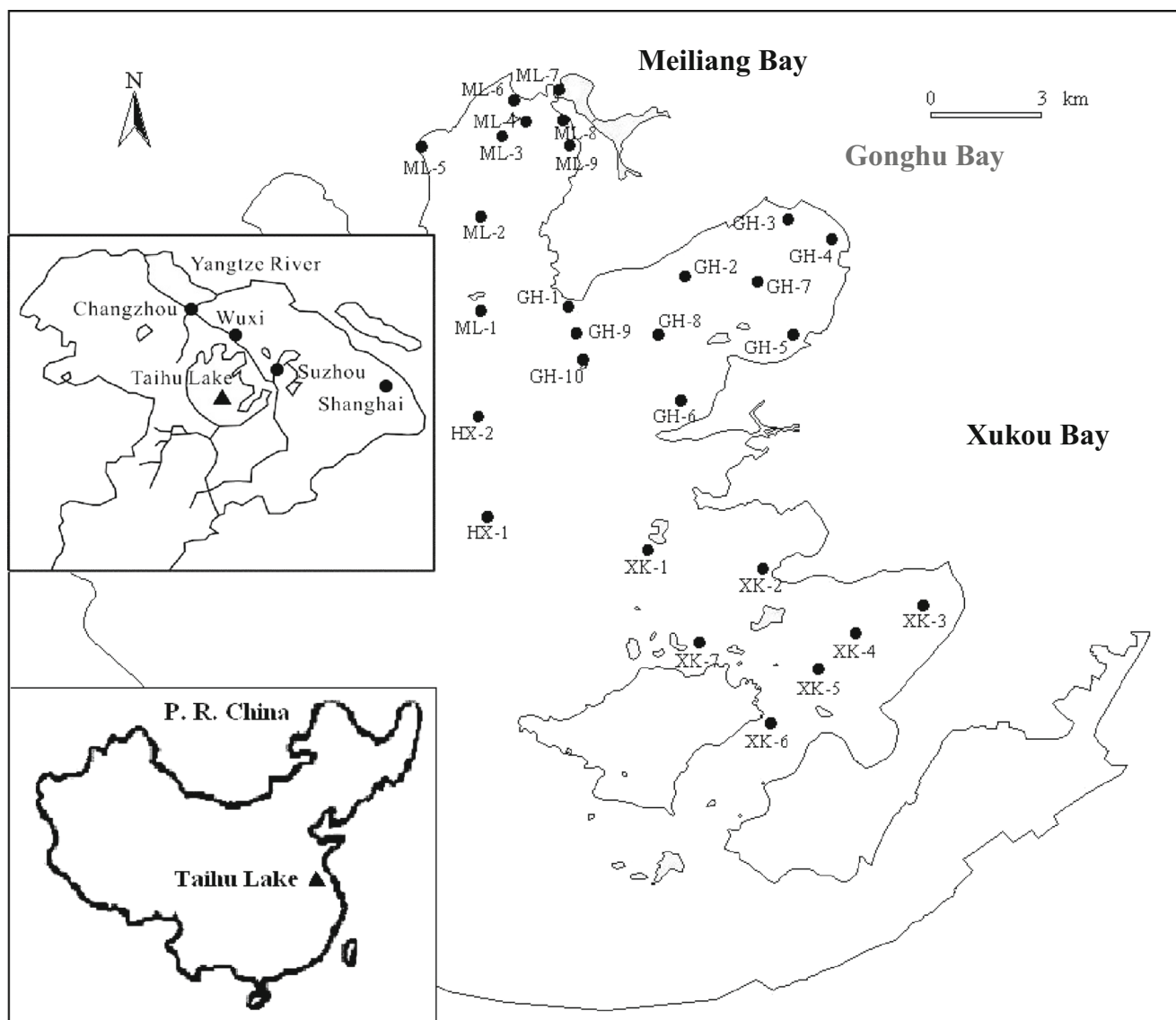


Fig. 1 The map of sampling sites in Taihu Lake

were added as internal standards for diastereoisomer determination of HBCD by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

The isolated polar fractions were extracted with hexane/MTBE (9:1, *v/v*). After exchanging the solvent to methanol/water (1:9, *v/v*), the enrichment and cleanup were performed using an OASIS®HLB (500 mg×6 mL) cartridge on a SPE Vacuum Manifold with methanol and ethyl acetate. The eluent was concentrated to dryness under a gentle steam of nitrogen gas and dissolved in 600 µL of methanol. Finally, a specific amount of ¹³C-TBBPA (1 µg/mL) was added as the internal standard prior to LC-MS/MS analysis for TBBPA.

Instrumental analysis

PBDE analysis was performed using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass

spectrometer in negative chemical ionization and selected ion monitoring mode. A HP-5MS (30 m×0.25 mm [i.d.], 0.25-µm film thickness; J&W Scientific) capillary column was used for determination of tri- to hepta-BDEs (BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-138, BDE-154, BDE-153, BDE-183, and BDE-191). The initial oven temperature was 110 °C (held for 1 min), after which it was ramped to 180 °C (held for 1 min) at a rate of 8 °C/min, then 240 °C (held for 5 min) at 2 °C/min, 280 °C (held for 15 min) at 2 °C/min, and finally to 300 °C (held for 12 min) at 10 °C/min. The temperatures of the injection port, transfer line, and ion source were 280, 300, and 200 °C, respectively. A DB-5-HT MS column (12.5 m×0.25 mm [i.d.], 0.1-µm film thickness; J&W Scientific) was used to determine the octa- to deca-BDEs. The initial oven temperature program was 110 °C (held for 5 min), after which it was increased to 200 °C (held for 4.5 min) at 8 °C/min, and

finally to 300 °C (held for 16 min) at 7.5 °C/min. The temperatures of the injection port, transfer line, and ion source were 260, 280, and 250 °C, respectively. The following ions were monitored: m/z 79 and 81 for PBDEs, m/z 486.7 and 488.7 for BDE-209, m/z 498.0 and 500.0 for PCB-209, m/z 372.0 and 374.0 for ^{13}C -PCB-141, and m/z 473.7 and 475.7 for ^{13}C -PCB-208, respectively.

For HBCD and TBBPA analysis, an Agilent 1100 series liquid chromatography (Agilent Technologies, Palo Alto, CA, USA) coupled to an Applied Biosystems API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) was used. A Zorbax SB-C18 reversed-phase column (4.6×250 mm, 5 μm , Agilent) was used to separate the HBCD diastereoisomers, TBBPA, and its debrominated compounds. For HBCD, the mobile phase consisted of methanol (*A*), acetonitrile (*B*), and water (*C*). The initial ratio of the mobile phase was 80:10:10 *A/B/C* (*v/v*), which was ramped to 50:40:10 *A/B/C* in 18 min, then to 30:70 *A/B* at 23 min, where it was held for 7 min, then returned to 80:10:10 *A/B/C* in 8 min. The injection volume was set at 10 μL and the flow rate was 0.5 mL/min. For TBBPA and its debrominated compounds, the mobile phase consisted of methanol (*A*), methyl cyanide (*B*), and water (*C*) with the following gradient: 70:15:15 *A/B/C* (*v/v*), which was held for 25 min, then changed to 70:30:0 *A/B/C* in 3 min, and finally ramped to 70:15:15 *A/B/C* in 4 min, where it was held for 12 min. The injection volume was 20 μL and the flow rate was 0.45 mL/min. The mass spectrometer was operated in electrospray ionization negative ion mode and multiple-reaction monitoring mode. The $[\text{M-H}]^- \rightarrow \text{Br}^-$ transitions at m/z 640.6→79, 652.6→79, and 658.6→79 were monitored for the three native and $^{13}\text{C}_{12}$ -labeled and d_{18} -labeled HBCD isomers, respectively. The m/z 542.8→78.8, 462.8→78.8, 384.9→78.8, 305.0→78.8, 226.9→211.9, 238.9→223.1, and 554.8→78.8 transitions were monitored for the TBBPA, tri-BBPA, di-BBPA, mono-BBPA, BPA, ^{13}C -BPA, and ^{13}C -TBBPA, respectively.

Quality control and quality assurance

One laboratory blank sample, one standard-spiked blank sample, and one standard-spiked matrix sample were analyzed in each batch of 12 samples for quality control. Five replicate samples were also analyzed in this study and the concentrations of target chemicals in replicate samples agreed well. The mean surrogate recoveries in all field and quality control samples were 88 ± 14 % for ^{13}C -PCB141; 94 ± 13 % for ^{13}C -PCB209; 84 ± 6 , 79 ± 5 , and 88 ± 10 % for $^{13}\text{C}_{12}$ -labeled α -, β -, and γ -HBCD, respectively; and 75 ± 7 % for ^{13}C -BPA. The limits of detection on the column, which were defined as a signal-to-noise (*S/N*) ratio of 3:1, were 0.005, 0.003, and 0.003 ng/g dry weight (dw) for α -, β -, and γ -HBCD; 0.05 and 0.002 ng/g dw for BDE-209 and other BDE

congeners; and 0.008, 0.005, 0.005, and 0.003 ng/g dw for TBBPA, tri-BBPA, di-BBPA, and mono-BBPA, respectively. Reported concentrations were not surrogate recovery corrected.

Results and discussion

Concentration levels and spatial distribution

Nineteen PBDE congeners (BDE-17, BDE-28, BDE-71, BDE-47, BDE-66, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-138, BDE-183, BDE-196, BDE-197, BDE-203, BDE-206, BDE-207, BDE-208, and BDE-209), three HBCD diastereoisomers (α -, β -, and γ -HBCD), and TBBPA and its three debromination compounds (mono-, di-, and tri-BBPA) were quantified in this study. Table 1 summarizes the concentration data of all 28 sediment samples. We defined $\Sigma^{18}\text{PBDEs}$ as the sum of 18 PBDE congeners, but did not include BDE-209, ΣHBCD as the total concentration of the three HBCD diastereoisomers, and ΣBBPAs as the sum of TBBPA and its three debromination compounds. As shown in Table 1, the concentrations of BDE-209 and $\Sigma^{18}\text{PBDEs}$ ranged from 3.61 to 342 (mean value 71.4 ng/g dw) and from 0.155 to 5.01 ng/g dw (mean value of 1.37 ng/g dw), respectively. The ΣHBCD concentrations ranged from 0.168 to 2.66 ng/g dw with a mean value of 0.734 ng/g dw, whereas the TBBPA and ΣBBPA concentrations ranged from 0.012 to 1.30 and from 0.027 to 2.57 ng/g dw, respectively. The PBDE concentrations in the sediments from Taihu Lake were significantly higher than the HBCD or TBBPA concentrations ($P < 0.05$), which indicated that PBDEs were the predominant contaminant in this area. Figure 2 shows that the sampling sites (ML-5, ML-6, ML-7, ML-8, and ML-9 and GH-3 and GH-4) with the highest PBDE concentrations were all located at Meiliang Bay and Gonghu Bay along the northeast edge of Taihu Lake, whereas no high concentrations of PBDEs were detected in Xukou Bay or the central portion of the lake.

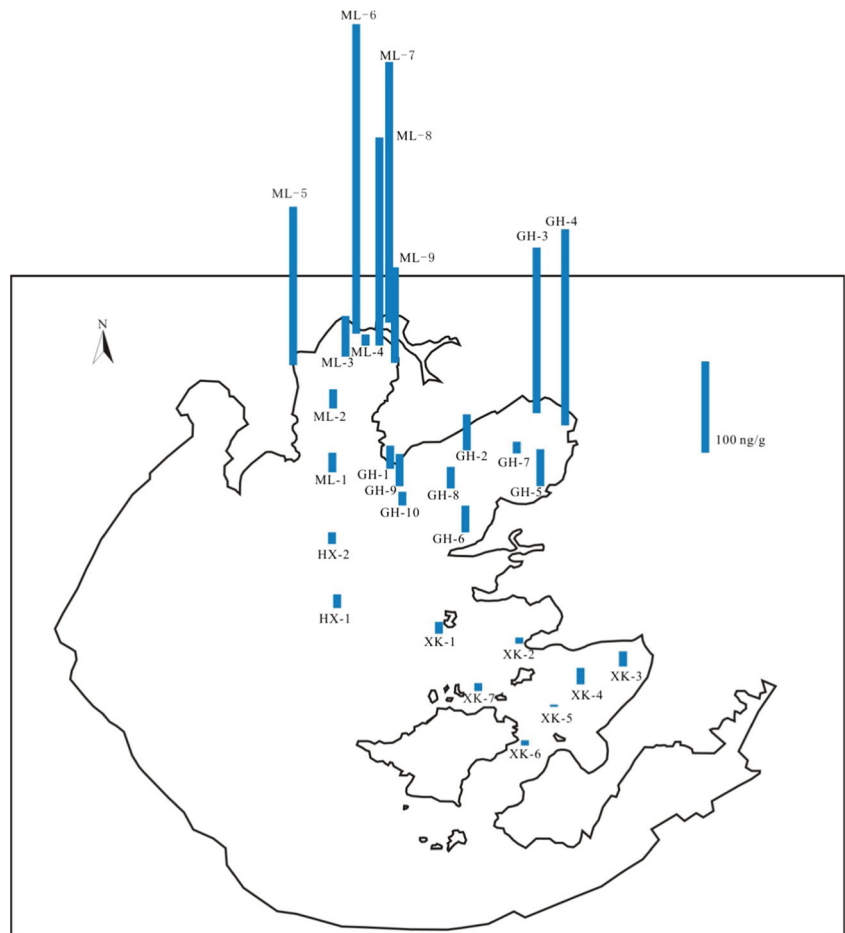
The total flow direction of Taihu Lake is from north-west to south-east and the PBDE levels were found to be in the order $\text{ML} > \text{GH} > \text{XK}$. These findings indicate that runoff might play an important role in the PBDE levels in the Taihu Lake sediments. Another notable observation is that the locations with higher PBDE concentrations were all near the inflow rivers around Meiliang and Xukou bays. These inflow rivers, which flow through some industrial cities, including Wuxi and Changzhou, as well as agricultural areas, contribute about 10 and 9 % of the total water intake of Taihu Lake, respectively. These findings confirm that there are inflow PBDE runoff sources in this region. Furthermore, Meiliang and Xukou are semi-closed U-shaped bays (Fig. 1), which may result in poor water exchange with the main lake. Therefore, sediments in the bays will be less disturbed by water flow, which will increase pollutant deposition and accumulation.

Table 1 Concentrations of PBDEs, HBCD, and TBBPAs in sediment of Taihu Lake (ng/g dw)

Congener	Meiliang Bay (n=9)		Gonghu Bay (n=10)		Xukou Bay (n=7)	
	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD
∑ ³⁻⁷ PBDEs	0.006–0.083	0.033±0.028	0.004–0.086	0.020±0.026	0.002–0.016	0.008±0.005
∑ ⁸⁻⁹ PBDEs	0.304–4.92	2.42±1.85	0.278–3.72	1.26±1.17	0.152–0.547	0.364±0.140
∑ ¹⁸ PBDEs	0.312–5.01	2.46±1.87	0.283–3.81	1.28±1.20	0.155–0.558	0.373±0.143
BDE-209	14.5–342	139±125	14.3–218	63.6±73.4	3.61–21.8	11.6±6.47
α-HBCD	0.032–0.149	0.091±0.046	0.044–0.365	0.178±0.120	0.040–0.092	0.066±0.020
β-HBCD	0.012–0.050	0.028±0.012	0.010–0.137	0.070±0.045	0.012–0.031	0.022±0.007
γ-HBCD	0.146–0.813	0.483±0.228	0.154–2.16	0.974±0.638	0.116–0.447	0.248±0.112
∑HBCD	0.193–1.01	0.602±0.283	0.210–2.66	1.22±0.779	0.168–0.570	0.336±0.125
TBBPA	0.045–0.465	0.223±0.130	0.086–1.30	0.634±0.376	0.012–0.471	0.207±0.169
Tri-BBPA	0.088–0.259	0.140±0.050	0.039–0.612	0.214±0.165	0.009–0.454	0.090±0.162
Di-BBPA	0.154–0.300	0.216±0.048	0.064–0.548	0.185±0.135	LQ-0.236	0.051±0.083
Mono-BBPA	0.005–0.020	0.011±0.005	0.037–0.111	0.056±0.023	LQ-0.032	0.016±0.013
∑BBPAs	0.324–0.930	0.590±0.200	0.228–2.57	1.09±0.658	0.027–1.19	0.365±0.394

n sample number; Mean arithmetic mean; SD standard deviation; ∑³⁻⁷PBDEs sum of BDE-17, BDE-28, BDE-71, BDE-47, BDE-66, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-138, and BDE-183; ∑⁸⁻⁹PBDEs sum of BDE-197, BDE-196, BDE-203, BDE-208, BDE-207, and BDE-206; ∑¹⁸PBDEs sum of BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-203, BDE-206, BDE-207, and BDE-208; ∑HBCD sum of α-, β-, and γ-HBCD isomers; ∑TBBPAs sum of TBBPA, tri-BBPA, di-BBPA, and mono-BBPA; LQ below the quantified limit; dw dry weight

Fig. 2 Concentration levels and spatial distributions of PBDEs in the sediment of Taihu Lake



The east Taihu Bays, including Xukou Bay and Gonghu Bay, are the major outflow areas and account for more than 70 % of the total outflow from Taihu Lake. XK is one of the major outflow areas of Taihu Lake, with tourism and fishery being the major industries in the surrounding area. Approximately 25 % of the total outflow water runs out of this bay annually. After the sedimentation of pollutants and self-purification of the main part of Taihu Lake, it is to be expected that the levels of PBDEs in XK Bay would be relatively lower than those in ML and GH.

Concentration comparison with other regions

The occurrence of PBDEs in sediments has been well documented in different regions around the world. However, we can only make a simple comparison between our data and other reports due to the inconsistencies in the congeners analyzed in other studies. As shown in Table 2, the mean PBDE concentrations (1.4 and 71.4 ng/g dw for Σ PBDEs and BDE-209, respectively) in the sediments from Taihu Lake in this study were one order of magnitude lower than those in sediments from e-waste recycling sites in east China (191 and 1839 ng/g dw, respectively) (Yang et al. 2009) and the Pearl River Delta, South China (9.9 and 465 ng/g dw, respectively) (Mai et al. 2005), but comparable to those reported in sediments from the Yangtze River Delta (Chen et al. 2006) and Baiyangdian Lake in North China (Hu et al. 2010). When our data were compared with those from other countries and regions, the concentrations of Σ PBDEs in sediments from Taihu Lake fell within the ranges of sediments from Japan (Minh et al. 2007), Korea (Ramu et al. 2010), and the Netherlands (Verslycke et al. 2005). However, the BDE-209 concentration was considerably lower than the concentrations in the Viskan river (Sellström et al. 1998) and the Scheldt estuary (Verslycke et al. 2005). Our sediment concentrations were comparable to those reported for sediments from the Great Lakes (Song et al. 2005) and Korea Bay (Moon et al. 2007), but somewhat higher than those in other sediments from Europe, North America, and Asia (Ramu et al. 2010; Minh et al. 2007; Eljarrat et al. 2005; Guzzella et al. 2008; Yun et al. 2008; Ilyas et al. 2011).

Compared to PBDEs, there is little literature available about the occurrence of HBCD and TBBPA in sediments. Additionally, most studies on HBCD have been conducted in Europe using different concentrations. High HBCD concentrations were reported in some sediments from Åsefjorden on the west coast of Norway (17,000 to 85,000 ng/g dw), the Cinca River, Spain (50 to 2658 ng/g dw), the River Viskan, Sweden (up to 1580 ng/g dw), and the River Skerne, UK (1680 ng/g dw), which had all been highly impacted by HBCD-processing factories near the sampling sites (Morris et al. 2004; Sellström et al. 1998; Haukås et al. 2010; Guerra et al. 2008). These findings are consistent with a technical report that most HBCD was

consumed in Europe (about 9500 of 16,700 tons in 2001) (BSEF 2005). Recently, a considerable level of HBCD (up to 1026 ng/g dw) was also detected in sediments collected from Laizhou Bay (Li et al. 2012), which was close to an area of HBCD production in China. However, significantly lower HBCD levels were observed in sediments collected in the present study and from industrial areas (Feng et al. 2012), which may indicate that HBCD is not the main BFR used in these regions, despite the production capacity of HBCD in China. The concentrations (0.012 to 1.30 ng/g dw) of TBBPA in the present study were comparable to or lower than those in sediments from rivers, estuaries (Verslycke et al. 2005), and lakes (Harrad et al. 2009b) in western Europe, except for one industrial area in the Pearl River Delta of China that had concentrations as high as 304 ng/g dw in the sediment (Feng et al. 2012). There were also estuarine and riverine sediments collected in England, which had a mean concentration of 450 ng/g dw (Morris et al. 2004).

Congener profiles and potential sources

BDE-209 was the predominant congener among the 19 PBDE congeners investigated in the present study and contributed 95.8 to 98.6 % of the total PBDEs in all sediments samples. In addition, octa- and nona-BDEs, including BDE-196, BDE-197, BDE-203, BDE-206, BDE-207, and BDE-208, accounted for 1.3 to 3.6 % of the total, whereas tri- to hepta-BDEs were only detected in 0.01 to 0.11 % of the sediment samples. Similar results have also been reported for sediment of the Pearl River Delta (Mai et al. 2005) and the Fuhe River and Baiyangdian Lake (Hu et al. 2010). These findings are consistent with the fact that deca-BDEs mixtures account for most of the total BFR production in China. Figure 3 shows the congener profiles of the sediments in this study, for two different commercial products available in the literature (La Guardia et al. 2007), and two Chinese deca-BDEs formulas collected from a market in China (Luo et al. 2009). As shown in Fig. 3, the congener profiles (octa- to deca-BDEs) in this study did not closely match the commercial deca-BDEs from North America (Saytex 102E) and Europe (Bromka 82-0DE) (La Guardia et al. 2007), but they were very similar to the pattern in a technical deca-formula (Deca-2) collected from a Chinese market. These findings suggested that the deca-BDE formulas could be a major commercial product used in the Taihu Lake study areas.

Figure 4 shows the diastereoisomer profiles of HBCD in sediment samples from Taihu Lake. It is clear that γ -HBCD, which accounted for 64.5 to 87.7 % of Σ HBCD in all sediment samples, was the predominant isomer. These findings are similar to the diastereoisomer profiles of commercial technical products (77 to 80 %) collected from Chinese markets and to those reported for soils near manufacturing plants in Belgium and Germany (78.1 %) (Covaci et al. 2006). β -HBCD levels were the smallest in all cases. However, when

Table 2 Comparison of PBDEs in sediments of the worldwide (ng/g dw)

Areas	Range (mean)		Reference
	ΣPBDEs	BDE-209	
Europe			
Swedish river, Sweden (<i>n</i> =9)	8–50 (NA)	68–7100 (NA)	(Sellström et al. 1998)
Scheldt estuary, Netherlands (<i>n</i> =3)	14–22 (19.3)	240–1650 (713)	(Verslycke et al. 2005)
Coast, Spain (<i>n</i> =13)	0.16–3.94 (1.2)	2.46–132.1 (23)	(Eljarrat et al. 2005)
Lake Maggiore, Italy (<i>n</i> =6)	0.2–3.3 (1.3)	1.6–15.3 (7.7)	(Guzzella et al. 2008)
North America			
Shiawassee and Saginaw River, USA (<i>n</i> =48)	0.03–3.57 (0.6)	0.15–49.4 (3.9)	(Yun et al. 2008)
Saginaw Bay, USA (<i>n</i> =5)	0.01–0.92 (0.3)	0.05–6.5 (2.3)	(Yun et al. 2008)
Lake Michigan and Huron, USA (<i>n</i> =6)	1.0–4 (2.2)	22–96 (46)	(Song et al. 2005)
Asia			
River bank, coast, Indonesia (<i>n</i> =33)	LD-8.5 (1.2)	LD-27 (4.7)	(Ilyas et al. 2011)
Coast, Korea (<i>n</i> =29)	0.04–32 (3.7)	0.40–98 (17.6)	(Ramu et al. 2010)
Korea Bay, Korea (<i>n</i> =111)	0.03–6.87 (2.2)	2.0–2248 (133)	(Moon et al. 2007)
Tokyo Bay, Japan (<i>n</i> =6)	0.05–0.78 (0.3)	0.89–18 (5.6)	(Minh et al. 2007)
China			
Pearl River Delta, China (<i>n</i> =66)	0.04–94.7 (9.9)	0.4–7341 (465)	(Mai et al. 2005)
Electronic waste recycling sites, China (<i>n</i> =4)	0.39–727 (191)	14.7–3510 (1839)	(Yang et al. 2009)
Yangtze River delta, China (<i>n</i> =32)	LD-0.55 (0.15)	0.16–94.6 (13.4)	(Chen et al. 2006)
Baiyangdian Lake, China (<i>n</i> =7)	2.59–9.97 (4.3)	4.35–19.3 (10.4)	(Hu et al. 2010)
Taihu Lake, China (<i>n</i> =28)	0.15–5.0 (1.4)	3.61–342 (71.4)	This study

ΣPBDEs the concentration of total PBDEs except BDE-209, *n* sample number, *NA* not available, *LD* below the detected limit

compared with the levels in commercial technical products, we found elevated relative abundances of α-HBCD (21.6 to 28.6 %) in eight of the 28 sediment samples, even though γ-HBCD was still the predominant isomer. Similar variations in isomer profiles have also been reported in sediments of rivers

around the North Sea (Morris et al. 2004) and suspended sediment samples from the Detroit River in Canada and the USA (Marvin et al. 2006). The ratio of HBCD diastereoisomers can be affected by thermal isomeric interconversion during the manufacturing process and incorporation of HBCD

Fig. 3 Congener profiles of octa- to deca-BDEs in the sediment of Taihu Lake and deca-BDE technical products

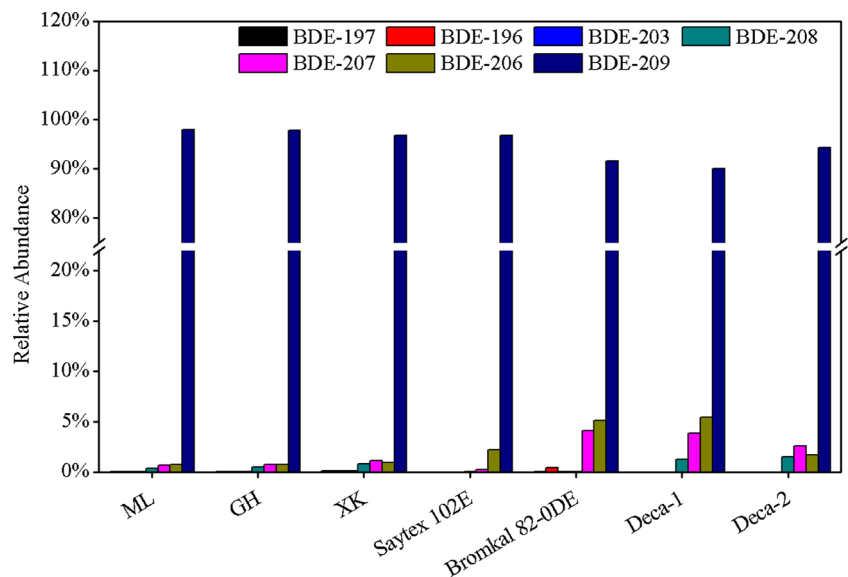
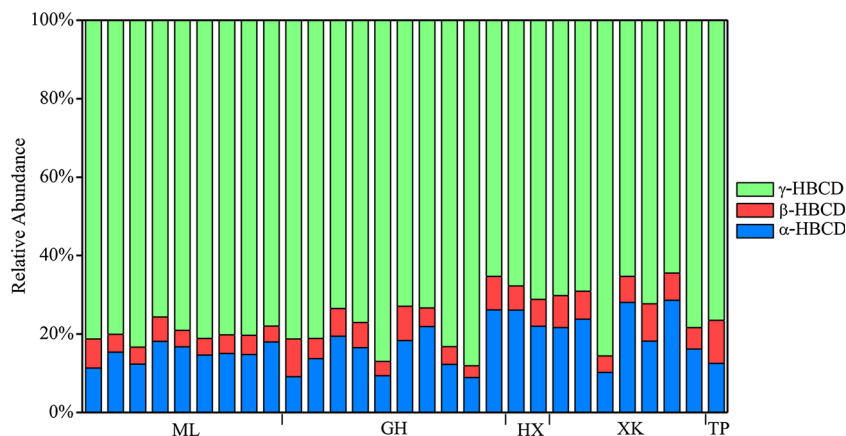


Fig. 4 Diastereoisomer profiles of HBCD in the sediment of Taihu Lake and technical product (TP)



into their products (Heeb et al. 2008), as well as abiotic/biotic transformations in environmental media (Harrad et al. 2009a, b; Davis et al. 2006). Unfortunately, we were not able to reveal the mechanism responsible for the apparent variations in isomer profiles in this study due to the wide range of factors that can affect HBCD diastereoisomer profiles.

Investigation of TBBPA and its debromination compounds, tri-BBPA, di-BBPA, and mono-BBPA, was conducted and quantified for all samples in this study, and they were found to vary between sampling sites. In Gonghu Bay, Xukou Bay, and the center of the lake, TBBPA and tri-BBPA were the predominant Σ BBPA fractions in most sediment samples, whereas higher proportions (28.1 to 57.4 %) of di-BBPA were present in sediments from Meiliang Bay. These results suggest that greater TBBPA debromination occurred in the Meiliang Bay sediment than at the other sampling sites. The debromination of TBBPA in environmental systems (e.g., sediment and sludge) has been reported as an important degradation path for TBBPA (Chu et al. 2005). In general, TBBPA debromination can be the consequence of thermal degradation processes, photolytic degradation, and anaerobic/aerobic microbial degradation processes in environmental media. Barontini et al. (2004) investigated the TBBPA thermal degradation process at a heating rate of 10 °C/min from ambient temperature to 600 °C, which possibly involved temperature runaway in industrial processes containing TBBPA. The results showed that mono- through tri-BBPA were all present in the main thermal decomposition products and suggested three possible decomposition processes (Barontini et al. 2004). Similar degradation processes were also proposed in a TBBPA degradation experiment where the heterogeneous UV/Fenton reaction was catalyzed by synthetic titanomagnetite (Zhong et al. 2012). In addition, TBBPA can be significantly degraded by microorganisms and has a mean half-life of about 2 months under both aerobic and anaerobic conditions (Ronen and Abeliovich 2000). However, the results of this study did not indicate whether the tri-BBPA, di-BBPA, and mono-BBPA originated from microbial

degradation in the sediment or from other abiotic debromination processes.

Conclusion

We detected PBDEs, HBCDs, and TBBPA in 28 sediment samples collected from Taihu Lake, which suggested that these three brominated flame retardants were widely used in this area. The predominant contaminants in this area were PBDEs and were present at significantly higher concentrations than HBCD or TBBPA. The contamination of Meiliang Bay and Gonghu Bay with PBDEs was more severe than that of Xukou Bay and the center of the lake. The congener profile and relative abundance of BDE-209 revealed that the deca-BDE formula may be the major brominated flame retardant used in the Taihu Lake study areas.

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