Polybrominated diphenyl ethers (PBDEs) in the surface sediments and suspended particulate matter (SPM) from Lake Chaohu, a large shallow Chinese lake

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HIGHLIGHTS

• PBDEs in the sediment were 2–3 orders of magnitude lower than those in the SPM.
• BDE 47 was the dominant PBDE congener in the surface sediment and in the SPM.
• Lower PBDE level in the sediments and higher level PBDEs in the SPM than those from references
• PBDE spatial distribution in the sediment and SPM influenced by local discharge and dredging
• A positive relationship between the PBDEs contents in the sediments and in the SPM was found.

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ABSTRACT

Suspended particulate matter (SPM) and surface sediment samples were collected from Lake Chaohu to investigate the residues, congener profile, and spatial distribution of polybrominated diphenyl ethers (PBDEs) in a large shadow lake in the middle of the Yangtze River Basin. The concentration of Σ_{13}BDEs (defined as the sum of 13 target congeners excluding BDE 209) and the concentration of BDE 209 ranged from 236.7 to 1373.4 pg/g dry weight (dw) and from 4.2 to 691.2 pg/g dw in the surface sediments, respectively, which were 2–3 orders of magnitude smaller than those found in the SPM. The congener composition was dominated by BDE 47 (50.8%) and BDE 209 (21.3%) in the sediment, while the proportion of BDE 47 to Σ_{14}BDEs in the SPM was slightly higher than that in the sediment. The concentration of Σ_{14}BDEs in the sediment from the drinking water source (WR) area in the eastern part of the lake was very low, with a mean value of 514.8 pg/g, whereas the mean concentration was 102.4 ng/g in the SPM. A cluster analysis (CA) was conducted to further illustrate the dominance of each congener and the similarity of each sampling site. Many factors, including resuspension, photodecomposition, microbial oxidation, local discharge, and dredging, influenced the distribution in the sediment and SPM for the PBDE congeners as well as the spatial distribution of PBDEs. A formula for the PBDE concentrations in the surface sediment and SPM was constructed to understand the potential relationship between sediment and SPM concentrations. Although the formula did not accurately predict specific PBDE congener concentrations in the sediment, it remains a practical and useful way to assess the overall pollution of PBDE in sediment in Lake Chaohu, as it depends only on the concentrations of PBDEs in the SPM.

1. Introduction

As an important class of brominated flame retardant (BFR) chemicals, polybrominated diphenyl ethers (PBDEs) are widely used in plastics, textiles, furniture, and electronic circuit boards. Their production has increased continuously between 1960 and 1990, and their estimated cumulative production is over 200 million tons (Rayne et al., 2003; Wiseman et al., 2011). BDE 209, also known as decabromodiphenyl ether, is the dominated component in commercial BFR like DE-83R produced by Chemtura (Great Lakes). The toxicity of BDE 209 is much less than its de-brominated congeners, but large detected concentration in media also denotes its great potential threat because of its toxic degradation products like tetra-, penta-, hexa-, and hepta-BDEs. Since BDE 209 was detected in sediment and soil downstream of a PBDE production plant in 1979 (de la Cal et al., 2003), PBDEs have been detected in various environmental media, including the air in the US and Norway (Jaward et al., 2004), water in San Francisco estuary (US), Hong Kong (China),

and Lake Ontario (Oros et al., 2005; Ueno et al., 2008; Wurl et al., 2006), in seabirds and marine mammals in the Baltic Sea, North Sea and Arctic Ocean (Jansson et al., 1987), in fish in the Visken River in Sweden (Andersson and Blomkvist, 1981), in fish, shellfish and sediments in the Pacific Coast (Watanabe et al., 1987), and in human adipose tissues (Stanley et al., 1991). Many studies have shown that PBDEs have typical characteristics of persistent organic pollutants (POPs): persistence, long-distance transport, bioaccumulation, and toxicity, which can interfere with human thyroid hormone balance, neurological development, and the endocrine and immune systems (Darnerud et al., 2007; He et al., 2008; Zhang et al., 2011). Due to the serious risks that PBDEs pose to eco-systems and human health, the EU completely banned the production and use of penta-and octa-BDEs in 2004. Major manufacturers voluntar-ily stopped producing them in North America. In May 2009, the United Nations Environment Programme (UNEP) listed tetra-, penta-, hexa-, and hepta-BDEs in the POPs Convention (SCPOP, 2009). However, deca-BDE, as a PBDE flame retardant chemical with high production and usage levels, remained in production and use. Many processes involving PBDEs, including their production, usage, waste incineration and recovery, will release PBDEs. Therefore, the study of the residual levels and distributions of PBDEs is important for understanding their environmental fates, toxic effects, and ecological risks.

The aquatic ecosystem is a major sink for contaminants (Doong et al., 2002; Feng et al., 1998). Because of their strong lipotropy and logKow value >4, PBDEs are more likely to be distributed in suspended particulate matter (SPM) and sediment, as indicated by the demonstration that 78% of PBDEs were present in SPM in San Francisco estuary (US) (Oros et al., 2005). Sediments represent an important sink, and PBDEs have been detected in sediments in lakes, rivers, and seas around the world (de la Cal et al., 2003; Eljarrat et al., 2004a; Ilyas et al., 2011; Li et al., 2010a; Mai et al., 2005; Minh et al., 2007; Nylund et al., 1992; Pan et al., 2010; Pan et al., 2011; Ramu et al., 2010; Sellstrom et al., 1998; Zarnadze and Rodenburg, 2008; Zhu and Hites, 2005). In China, most studies have focused on PBDEs in sediments in South China and coastal regions, such as the coastal region in Xiamen (Li et al., 2010a), the Pearl River Delta (Mai et al., 2005), the Bohai Bay (Pan et al., 2010), and Laizhou Bay (Pan et al., 2011). However, few studies of PBDEs in lake sediments and SPM in the middle of the Yangtze River have been performed. Lake Chaohu, which was our research subject, is located in the middle of the Yangtze River Delta; it has scenic beauty and high aquatic biodiversity. However, various persistent toxic substances have been detected in the

lake in recent years (Li et al., 2010b; Xu et al., 1999; Xu et al., 2001; Zhang et al., 2007). The objectives of the present study were (1) to study the residues, congener profiles, and spatial distributions of PBDEs in the surface sediment and SPM, (2) to explore the relationship between PBDEs in the sediment and those in SPM, and (3) to further understand the environmental fates and ecological risks of PBDEs in the aquatic ecosystem.

2. Materials and methods

2.1. Sampling and preprocessing

Fourteen SPM/sediment samples were collected from Lake Chaohu on August 8th and 9th, 2009, but two SPM samples were missing. The locations of the sampling sites are shown in Fig. 1. The sampling sites A1, A2, A3, and A4 are located in the eastern part of Lake Chaohu (ex-cluding the drinking water source (WR) area), while sites A6, B2, B3, B4, and B5 are located in the WR area, which supplies drinking water for the all residents of Chaohu City. The SPM and sediment samples from B6, C1, C2 and C4 were obtained from four inflow rivers located east of the lake, while D1 was located in the western part of the lake.

A stainless steel grab sampler and a cylinder sampler were used to collect surface sediment samples and water phase samples, respec-tively. At least three sub-samples were collected for every sample at every site. A composite sample, which was mixed thoroughly with the sub-samples, was used to decrease the possible random variation for later determination. After shaking and mixing, 1 L of water phase sam-ple was filtered through a glass fiber filter (which was baked at 450 °C for 4 h) to obtain the SPM by filtration devices, which consisted of a peristaltic pump (BT-001, Baoding Longer Precision Pump Co., Ltd., China) and a stainless steel filter plate with a diameter of 142 mm. The SPM was dried naturally and then packed with aluminum foil. The SPM and sediment samples were stored at −18 °C until the time of analysis.

2.2. Reagents and materials

Solvents, including analytical grade n-hexane (HEX), acetone (ACE) and dichloromethane (DCM) (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), were purified by distillation. A standard mixture stock of fourteen PBDEs, including BDEs 17, 28, 47, 66, 71, 85, 99,100,138, 153, 154, 183, 190, and 209, were purchased from AccuStandard Inc.
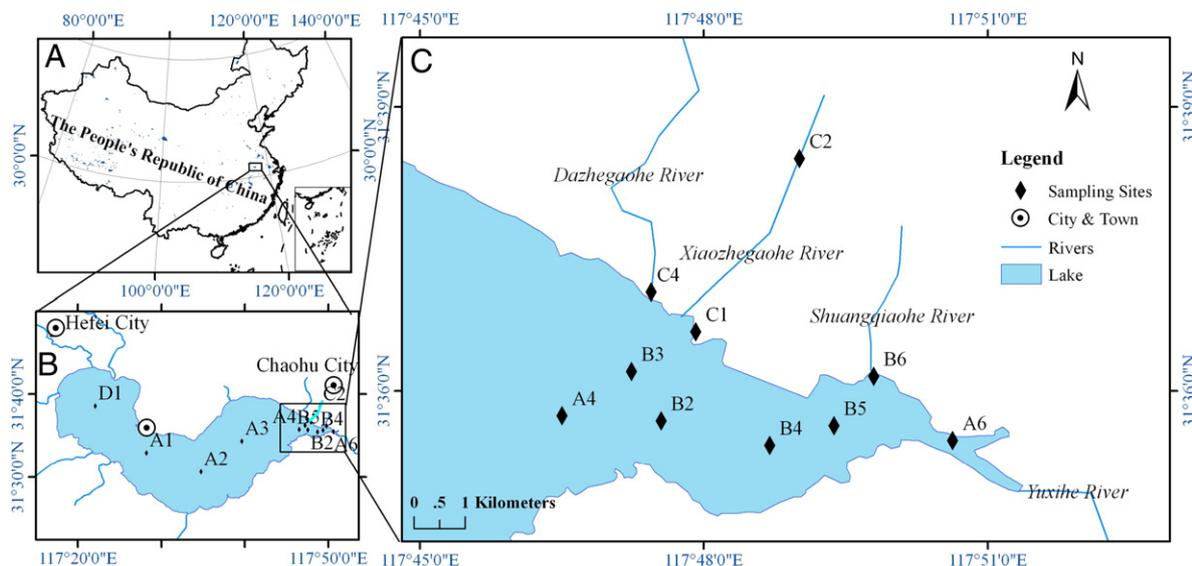

Fig. 1. Location of Lake Chaohu and the water sampling sites.

(New Haven, CT, US), and an internal standard (IS) of 2,2′,3,3′,4,5,5′,6,6′-nonachlorinated biphenyl (13C12, 99%, PCB-208-C13) and a surrogate standard (SS) of 2,2′,3,4,5,5′-hexachlorinated biphenyl (13C12, 99%, PCB-141-C13) were obtained from Cambridge Isotope Laboratories, Inc., MA, US. Granular anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was baked at 650 °C in a furnace for 6 h and then stored in a sealed desiccator until use. Silica gel (200–300 mesh) and alumina (100–200 mesh) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were baked at 450 °C for 6 h and then used to prepare neutral silica gel (NSG), acidic silica gel (AcSG), alkaline silica gel (AkSG), and neutral alumina (NAl). After allowing the baked silica gel and alumina to cool to ambient temperature, 3 g of ultrapure water was added into 100 g of silica gel or alumina to form neutral silica gel and alumina, and 33 g of 1 mol/L sodium hydroxide (NaOH, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and 44 g of concentrated sulfuric acid (H_2SO_4, 98%, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were added to 100 g of silica gel to form alkaline silica gel and acidic silica gel, respectively. The silica gel and alumina were shaken to a powder and then soaked in HEX overnight. All glassware was cleaned in an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument, China) and baked at 450 °C for 6 h.

2.3. Extraction and cleanup

The SPM and sediment samples were freeze-dried and weighed on an analytical balance. The sediment samples were ground and sieved through a 70-mesh sieve. All of the SPM on the same glass fiber membrane and 8 g homogenized sediment samples were microwave-extracted in a Teflon microware extract tank with 25 mL of the solvent mixture HEX:ACE (1:1 ratio). The tank was placed in the microwave-assisted extraction (MAE) system MARS 5 (CEM Corp., Matthews, NC, USA) with the following instrument conditions: working power 1200 W, temperature increase to 100 °C within 10 min, hold at 100 °C for 10 min, and decrease to ambient temperature within 30 min. The extracted solutions were concentrated to approximately 1 mL on a rotary evaporator at 35 °C and then transferred to the top of a glass column that was packed with 1 cm of anhydrous sodium sulfate, 6 cm of AcSG, 2 cm of NSG, 5 cm of AkSG, 2 cm of NSG, 6 cm of NAl and a litter pre-extracted absorbent cotton from top to bottom. A total of 70 mL of the solvent mixture HEX:DCM (1:1 ratio) was used to elute the column. The eluate was collected and concentrated to 1 mL before 50 ng IS was added. The cleanup component with IS was transported into a sampling vial, concentrated to 0.1 mL under a gentle stream of nitrogen and stored at −18 °C until GC-MS determination.

2.4. Instrument analysis

The samples were analyzed using an Agilent 7890 gas chromatograph that was equipped with an Agilent 5975C mass spectrometer (GC-MS) (Agilent Technologies, Avondale, PA, US) operating in negative chemical ionization (NCI) and selective ion monitoring (SIM) modes and an HP-5MS column (15 m × 0.25 mm internal diameter; 0.1 μm film thickness). The samples were injected by auto-sampling in splitless mode with a venting time of 1 min. The oven temperature was programmed to an initial temperature of 110 °C for 5 min and then increased at a rate of 20 °C/min to 200 °C, where the temperature was maintained for 5 min, increased at a rate of 10 °C/min to 280 °C, and finally increased at a rate of 20 °C/min to 305 °C, where the temperature was maintained for 10 min. Helium was used as both the carrier (2 mL/min) and the makeup gas (20 mL/min). The temperatures of the inlet, quadrupole, and ion source were 265 °C, 150 °C and 230 °C, respectively. The quantitative ion fragments m/z 79 or 81 were used for individual PBDEs, with the exception of BDE 209. The quantitative ion fragment of BDE 209 was m/z 487. Quantitation was performed using the internal calibration method based on a six-point calibration curve for individual PBDEs. The order of the PBDE congeners in the rest of the study followed the eluting sequence on the GC column. Total organic carbon (TOC) in the sediment was analyzed by TOC 5000A coupled with an SSM-5000A sampler (Shimadzu Corp., Japan).

Table 1
Summary of PBDE congener concentrations in surface sediments and SPM from Lake Chaohu.

Congeners	Sediment (N = 14, pg/g)			SPM (N = 12, ng/g)		
	DR[a], %	Mean ± SD[b]	Median (min–max)	DR, %	Mean ± SD	Median (min–max)
BDE 17	100	19.4 ± 13.6	14.7 (2.2–47.6)	92	1.1 ± 1.5	0.4 (0.2–5.0)
BDE 28	100	26.2 ± 15.7	28.6 (2.9–48.8)	100	14.2 ± 28.5	2.8 (0.5–100.0)
BDE 71	100	16.7 ± 23	10.5 (1.8–98)	17	1.4 ± 0.9	1.4 (0.5–2.4)
BDE 47	100	418.9 ± 280.6	397.5 (74.4–948)	100	152.9 ± 273.4	43.8 (1.6–1007.5)
BDE 66	93	5.9 ± 3.2	5.6 (2.5–12.7)	33	1.9 ± 1.8	1.1 (0.3–5.0)
BDE 100	93	6.7 ± 7.7	4 (2.5–32.5)	0	–	–
BDE 99	100	12.1 ± 9.2	9.5 (3.1–31.2)	92	2.0 ± 1.9	1.2 (0.3–7.5)
BDE 85	100	36 ± 18.6	36.4 (9.6–69.4)	17	1.4 ± 1.1	1.4 (0.3–2.5)
BDE 154	93	8.7 ± 4.2	7.4 (3.3–16.8)	17	0.8 ± 0.4	0.8 (0.3–1.2)
BDE 153	93	8.2 ± 5.9	5.8 (3.1–21.6)	42	0.4 ± 0.4	0.2 (0.1–1.0)
BDE 138	93	62.7 ± 53	48.8 (13.6–228.8)	100	28.7 ± 20.7	26.6 (1.7–72.5)
BDE 183	100	17.5 ± 22.5	7 (2.8–78.3)	75	3.0 ± 1.9	3.1 (0.4–7.5)
BDE 190	64	9.3 ± 6.3	8.8 (2.3–21.3)	50	3.5 ± 4.1	2.0 (0.6–12.5)
BDE 209	43	176.1 ± 235.3	82 (4.3–691.2)	50	56.7 ± 42.2	38.8 (12.6–125.6)
TriBDE[c]	100	45.6 ± 24.9	46.2 (6.8–82.8)	100	15.3 ± 30.0	3.3 (0.6–105.0)
TetraBDE[c]	100	441.2 ± 278.2	408.2 (91.8–970.4)	100	153.8 ± 274.6	44.3 (1.6–1012.5)
PentaBDE[c]	100	54.3 ± 23.5	48.4 (16.4–105.8)	92	2.3 ± 2.6	1.3 (0.3–10.0)
HexaBDE[c]	100	73.9 ± 61.8	58 (10.6–267.2)	100	29.0 ± 20.6	27.7 (1.8–72.5)
HeptaBDE[c]	100	23.4 ± 26.4	12.2 (3.8–99.6)	83	4.8 ± 5.4	3.3 (0.4–20.0)
DecaBDE[c]	43	176.1 ± 235.3	82 (4.3–691.2)	50	56.7 ± 42.2	38.8 (12.6–125.6)
Σ_{13}BDEs[c]	100	638.4 ± 307.6	666.3 (236.7–1197.4)	100	204.2 ± 323.9	91.4 (20.9–1220.0)
Σ_{14}BDEs[c]	100	713.8 ± 368.9	668.5 (236.7–1373.4)	100	232.5 ± 346.8	104.5 (20.9–1322.5)

[a] DR — detection ratio.
[b] SD — standard deviance.
[c] TriBDE includes BDEs 17 and 28. TetraBDE includes BDEs 47, 66, and 71; PentaBDE includes BDEs 85, 99, and 100; HexaBDE includes BDEs 138, 153, and 154; HeptaBDE includes BDEs 183 and 190; DecaBDE includes BDE 209; Σ_{13}BDEs is defined as sum of the target congeners except BDE 209; Σ_{14}BDEs includes all 14 BDE congeners.

2.5. QA/QC

A group of spiked extracted sediments with 50 ng PBDEs and extracted sediment without PBDEs was processed to determine the recovery and precision of the sediment analysis method, and a group of spiked baked glass fiber membranes with 50 ng PBDEs and baked glass fiber membranes without PBDEs was used to determine the recovery and precision of the SPM analysis method. The average recovery percentages were 84–106% for sediment and 76–103% for SPM. A total of 50 ng SS was added to each microware extract tank of 20% of the samples before extracting to evaluate the recoveries obtained by the procedure. The average recoveries were 62–102%. The limits of detection (LOD, 3 signal/noise) of individual PBDEs were 0.03–0.36 pg/g for 8 g of sediment and 0.24–28.8 pg/g for 0.1 g of SPM, and the limits of quantification (10 signal/noise) of individual PBDEs were 0.1–1.2 pg/g for 8 g of sediment and 8–96 pg/g for 0.1 g of SPM. Three procedural blank samples were analyzed for solvent and glassware contamination,

and the results indicated that contamination could be ignored. All samples were extracted and analyzed in triplicate. Thermal degradation of BDE 209 in the GC injector (265 °C) is likely to occur. Therefore, before determination of samples, we determined PBDE mixtures first to investigate the degradation of BDE 209. The samples will be run when the degradation of BDE 209 was less than 10%. The reported data in the present study was not corrected by SS because most samples' SS was under an acceptable scale (70–130%).

2.6. Statistical analysis and cluster analysis

Data compilation was performed using Microsoft Excel 2010, and statistical analysis, normal or logarithm normal distribution test, Pearson correlation analysis, linear regression analysis, and CA were carried out using SPSS v. 20. Significant value was assigned as 0.05. Because it was not clear enough to present multivariate data sets like multiple congener contributions to total PBDEs on conventional two- and
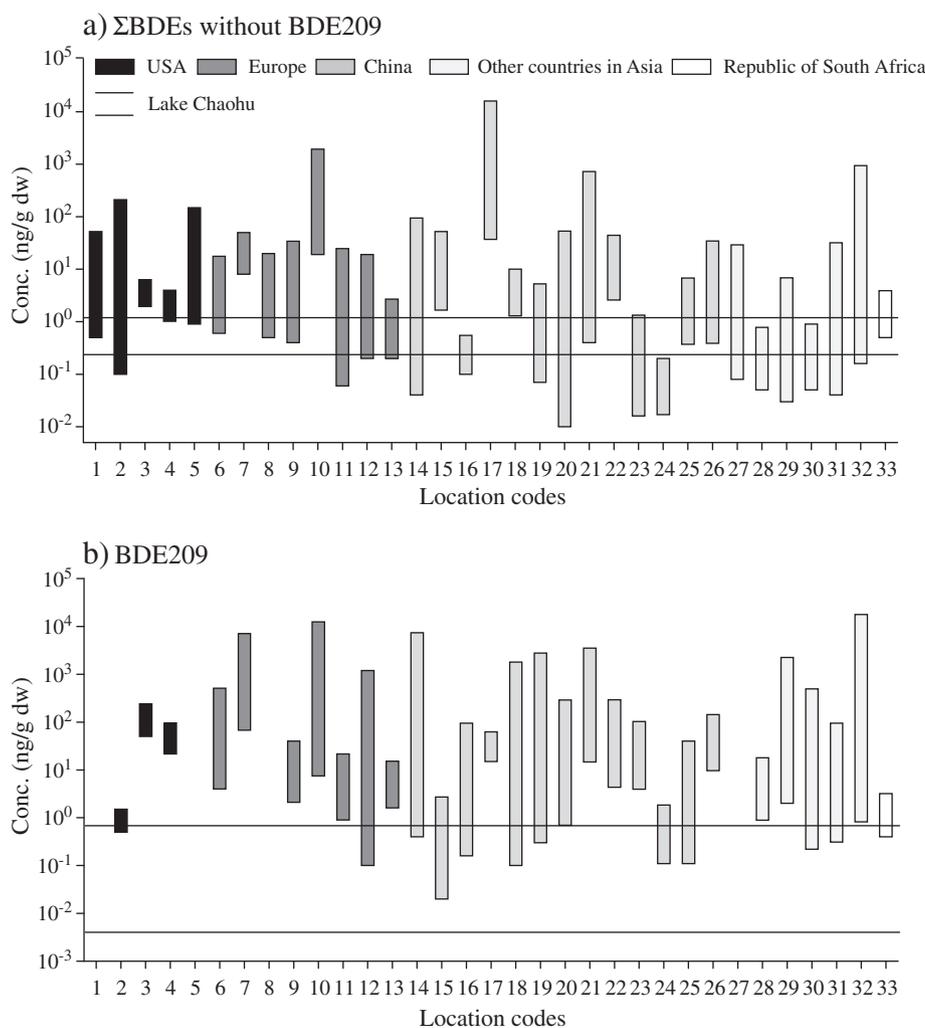

Fig. 2. Comparison with PBDE concentrations of sediments from rivers and coastal areas worldwide. a — Chart denotes sum of the concentrations of all BDEs excluding BDE 209; b — chart denotes BDE 209. The scale between the two black lines denotes the concentration range of BDEs in sediments from Lake Chaohu. Location codes 1 to 5 represent rivers or coastal areas from Virginia river watersheds (Ilyas et al., 2011), the San Francisco estuary (Oros et al., 2005), Lakes Erie and Ontario (Song et al., 2005a), Lakes Michigan and Huron (Song et al., 2005b), and the Niagara River (Samara et al., 2006) in the US. Location codes 6 to 13 represent rivers and estuaries in the Netherlands (Yu et al., 2009), rivers in Sweden (Sellstrom et al., 1998), the coast and a river in Portugal (Zarnadze and Rodenburg, 2008), Cinca River and Vero River in Spain (Eljarrat et al., 2004b; Eljarrat et al., 2007), the coast and rivers in Denmark (Streets et al., 2006), rivers and estuaries in Belgium (Voorspoels et al., 2004), and Lake Maggiore in Italy (Guzzella et al., 2008). Location codes 14 to 26 represent the Pearl River Delta (Mai et al., 2005), Hong Kong (Liu et al., 2005), the Yangtze River Delta (Chen et al., 2006), polluted rivers in Guiyu (Luo et al., 2007), Laizhou Bay (Jin et al., 2008), the coast of Bo Sea (Wang et al., 2009), Laizhou Bay (Pan et al., 2011), polluted rivers in Taizhou (Yang et al., 2009), Fuhe River and Lake Baiyangdian (Hu et al., 2010), the Dalian coast (Wang et al., 2011), the Daliao River and estuary (Zhao et al., 2011), 12 lakes (Wu et al., 2012), and Lake Taihu (Zhou et al., 2012) in China. Location codes 27 to 32 represent wetlands in India (Binelli et al., 2007), Tokyo Bay in Japan (Minh et al., 2007), rivers, estuaries (Moon et al., 2007a), coastal areas (Moon et al., 2007b; Ramu et al., 2010), and Lake Shihwa (Moon et al., 2012) in Korea. Location code 33 represents Jukskei River in South Africa (Olukunle et al., 2012).

three-dimensional graphs, the CA was used to further illustrate the similarities and differences among PBDE congeners and sampling sites. To meet the requirements of the CA, non-detected data were assigned as 1/2 LOD and the data was log-transformed to obey normal distribution. The similarity coefficient was set as the classification criterion.

3. Results and discussion

3.1. Residual levels of PBDEs in surface sediments and SPM

3.1.1. Surface sediments

In the surface sediments, the detection ratios (DRs) of 12 PBDE congeners were larger than 90%, with the exceptions of BDEs 190 and 209 (Table 1). The Σ_{13}BDEs is defined as the sum of the target congeners, excluding BDE 209. The concentrations of Σ_{13}BDEs and BDE 209 ranged from 236.7 to 1373.4 pg/g dry weight (dw), with a mean value of 638.4 pg/g dw, and 4.2–691.2 pg/g dw, with a mean value of 176.1 pg/g dw. BDE 47 was the major congener in all sediment samples, and its concentration ranged from 74.4 to 948 pg/g, which was one to two orders of magnitude higher than the levels of the other congeners.

To compare the residual levels of PBDEs in surface sediments from Lake Chaohu with those in the rest of the world, worldwide studies over the previous 10 years were summarized in Fig. 2. The range of ΣBDEs (excluding BDE 209) was widest in sediments from China, with a range of 10^{-2}-10^4 ng/g, followed by other countries in Asia, Europe, and the US, whereas the range for BDE 209 was similar in Europe and Asia. The levels of PBDEs in sediments from Lake Chaohu were at low levels relative to the rest of the world: the level of ΣBDEs excluding BDE 209 in Lake Chaohu was only higher than that of the Daliao River and estuary (Zhao et al., 2011); BDE 209 contamination was at the lowest recorded level in Lake Chaohu, even lower than that of Hong Kong (Liu et al., 2005). BDE 209 was not the dominant congener in the present study. However, it was the dominant congener in most locations, with the exceptions of the San Francisco estuary (Oros et al., 2005) in the US, sediments in Hong Kong (Liu et al., 2005), and polluted rivers in Guiyu, China (Luo et al., 2007).

3.1.2. SPM

The concentrations of PBDEs in the SPM were two to three orders of magnitude larger than those in the surface sediments (Table 1). The concentration of Σ_{13}BDEs and BDE 209 ranged from 20.9 to 1220.0 ng/g dry weight (dw), with a mean value of 204.2 ng/g dw, and from 12.6 to 125.6 ng/g dw, with a mean value of 56.7 ng/g dw, respectively. However, the DR values for individual BDEs were very low. The DR with values >80% appeared only for five congeners (BDEs 17, 28, 47, 99, and 138). Their concentrations were 1.1 ± 1.5, 14.2 ± 28.5, 152.9 ± 273.4, 2.0 ± 1.9, and 28.7 ± 20.7 ng/g dw, respectively. To our knowledge, there are few direct reports about SPM contents around the world. The residual level of ΣBDEs excluding BDE 209 in the SPM in Lake Chaohu was higher than those of Raritan Bay in the US (mean: 25 ng/g) and the Zhujiang River estuary in China (mean: 0.8 ng/g), The level of BDE 209 was lower than that of Raritan Bay (mean: 135 ng/g) and higher than that of the Zhujiang River estuary (mean: 32.7 ng/g) (Braekevelt et al., 2003; Luo et al., 2008). The level of BDE 209 was also much lower than water bodies in Netherland (mean: 272 ng/g) (de Boer et al., 2003).

3.2. Congener profile of PBDEs and possible source

3.2.1. Surface sediments

As shown in Fig. 3a, BDE 47 was the dominant PBDE congener in the surface sediment, and the relative abundance of BDE 47 ranged from 9.1% to 79.1%, with a mean value of 50.8%. The relative abundance of BDE 209 ranged from 0.6% to 50.3%, with a mean value of 21.3%. The ratio of BDE 209 to Σ_{13}BDEs varied from 0.1% to 1%, which did not agree with the fact that deca-BDE accounts for most of the total BFR production in China (Mai et al., 2005). The congener profile in Lake Chaohu was similar to that of the San Francisco estuary in the US and Guiyu, China, as indicated by the domination of BDE 47 (Luo et al., 2007; Oros et al., 2005). However, only five congeners were detected in San Francisco estuary, US. And the second most abundant congener was BDE 99. But BDE 138 was detected as the second dominated congers in Lake Chaohu. The similarity and differences indicated that BDE 47 widely existed and dominated BDE congeners in aquatic environments, but different aquatic environments would
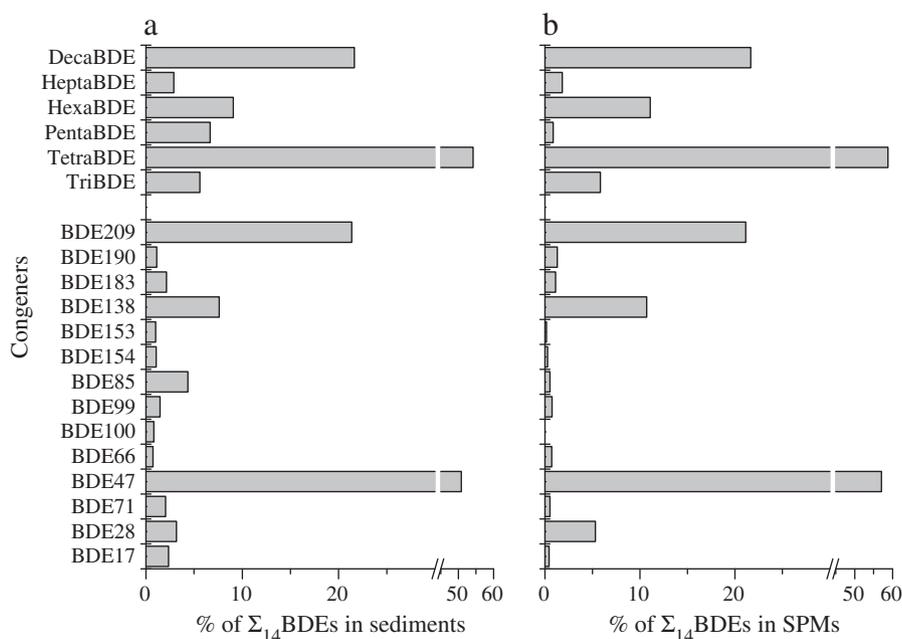

Fig. 3. Congener profile characteristics in the surface sediment and SPM from Lake Chaohu, China (charts a and b denote the relative abundance of individual congeners in the surface sediments and SPM, respectively).

result in the composition of BDE congeners without BDE 47. In some places, BDE 47 was also the dominant congener (excluding BDE 209) (Chen et al., 2006; Wang et al., 2009; Zarnadze and Rodenburg, 2008). Because the composition of a widely used flame retardant penta-BDE (Bromkal 70-5DE) is mainly BDE 47 and BDE 99 (Lacorte et al., 2003), the congener profile in the surface sediment also indicated that penta-BDE might be present in Lake Chaohu. By contrast, the low concentration and ratio of BDE 209 mean that deca-BDE was not widely used in

the past. Moreover, there was no electronic product factory or flame retardant (deca-BDE) industry near Lake Chaohu. Therefore, the possible source of PBDEs might be general electronic waste leachates from a solid waste landfill on the side of the lake near cities and towns. The ratio of BDE 47/99 is approximately 1.06 in penta-BDE Bromkal 70-5DE, whereas the ratio in Lake Chaohu ranged from 4.04 to 129.7, with a mean value of 49.9. These large values might result from the degradation of BDE 99 to BDE 47 by microorganisms in anaerobic
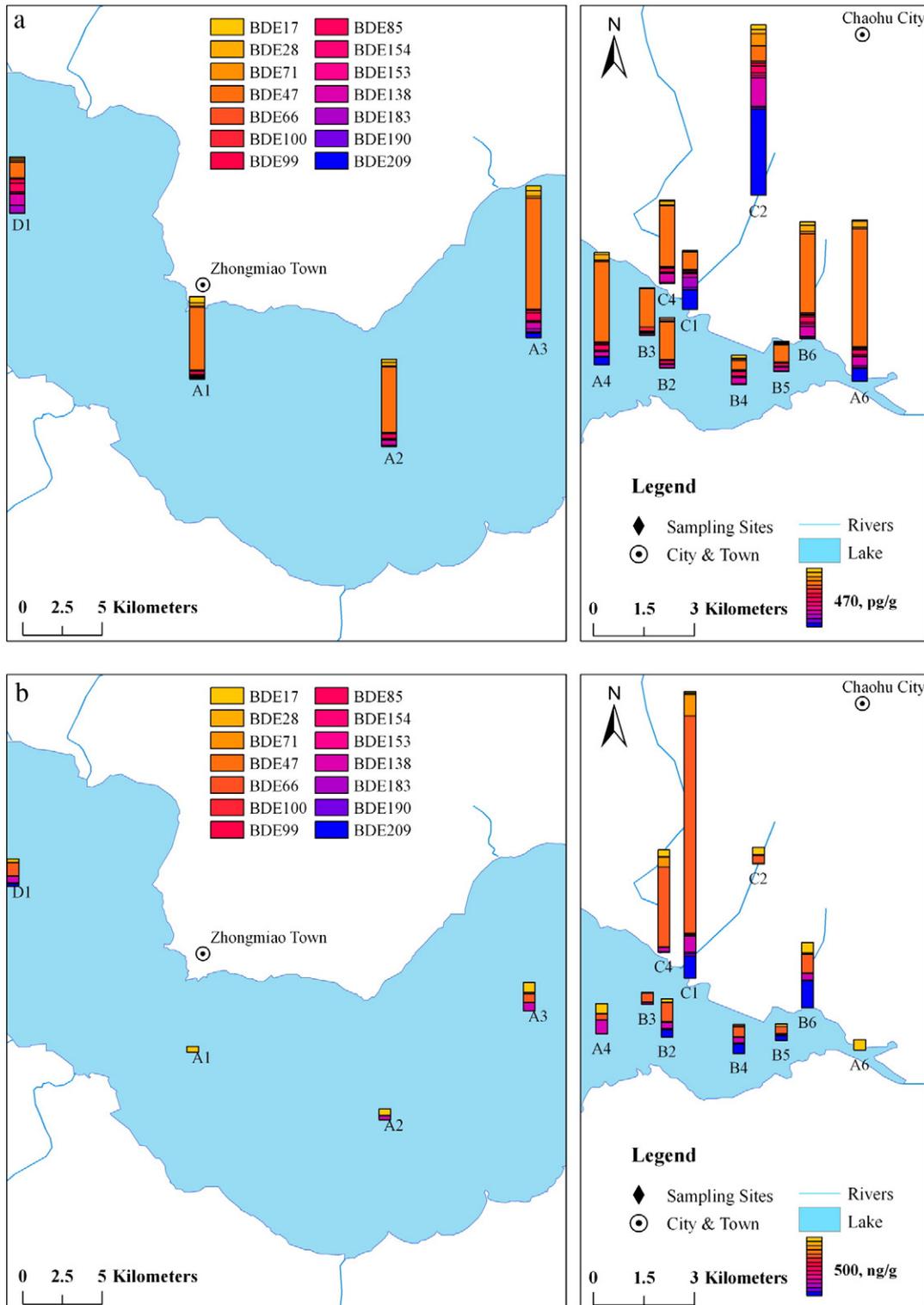

Fig. 4. Concentrations and geographic distributions of PBDEs in the surface sediments (a) and SPM (b) from Lake Chaohu.

sediments (He et al., 2006; Wurl et al., 2006). According to the number of bromines (Br), PBDE congeners were classified into six groups: tri-, tetra-, penta-, hexa-, hepta-, and deca-BDEs. Tetra-BDE was dominant among the six groups because of the high BDE 47 content. The relative abundance values of the six groups were 5.6%, 54.3%, 6.7%, 9.1%, 2.9%, and 21.6%, respectively.

3.2.2. SPM

The congener profile characteristics of PBDEs in the SPM were similar to those in the surface sediments (Fig. 3b), indicating that the resuspension of surface sediment might be a possible source of PBDEs in the SPM. However, the relative abundance values of most PBDE congeners (excluding BDEs 28, 47, 138, and 209) were very small, ranging from 0% to 1.3%. There were small differences between the SPM and the surface sediments with respect to the ratios of major congeners. The relative abundances of BDE 47 and BDE 28 varied from 7.7% to 86.1% (mean value of 57.0%) and from 1.0% to 10.4% (mean value of 5.4%), respectively. The relative increases in BDEs 28, 47, and 138 and decreases in the other congeners suggest that solar photodecomposition might occur in the surface water (de Boer et al., 2003). Tri-, tetra-, penta-, hexa-, hepta-, and deca-BDEs contributed 5.8%, 58.7%, 0.9%, 11.1%, 1.8%, and 21.7%, respectively. There were almost no changes in the ratios of tri- and deca- BDEs, whereas the ratios of both tetra- and hexa-BDEs increased, and the ratios of both penta- and hepta-BDEs decreased, indicating that photodecomposition

Fig. 5. The ratio of individual PBDE congeners to Σ_{14}BDEs and the relative abundance of PBDE congeners with different numbers of bromines (Br) in the surface sediment (a and b) and SPM (c and d) from various areas of Lake Chaohu. WB, the entire water body, including lake and river samples; EL, eastern Lake Chaohu, excluding the drinking-water source area; WR, the drinking-water source area in the eastern part of the lake; R, river samples; CW, the center of the western part of the lake.

and microbial oxidation in the surface water contribute to the degradation of penta- and hepta-BDEs to some extent. By contrast, darkness and a lack of oxygen slowed down the degradation process of PBDEs in the surface sediments, and many larger congeners would not thoroughly decompose into smaller congeners as they do under the condition of sunlight and microbial oxidation. Therefore, this circumstance in sediment might result in the maintenance of more PBDE congeners.

3.3. Spatial distributions of PBDEs

3.3.1. Surface sediment

The spatial distributions of PBDE congeners in the surface sediment from Lake Chaohu were determined using Arcgis 10 software and are shown in Fig. 4a. The concentration of Σ_{14}BDEs in eastern part (EL) of Lake Chaohu (excluding the WR area) was 875.7 ± 220.8 pg/g (ranging from 666.0 to 1224.1 pg/g). The concentration of Σ_{14}BDEs in the rivers of the eastern lake area was 865.6 ± 336.9 pg/g (ranging from 475.3 to 1373.4 pg/g), which approached the residual level of the sediments in the EL area. The concentration of Σ_{14}BDEs in the WR area in the eastern part of the lake was very low, with a mean value of 514.8 pg/g. The mean value in the WR area was 318.8 when sampling site A6 was excluded. We found that the sediments surrounding the WR area had more serious BDE pollution. The main reason for this difference was that the surface sediments have been desilted to create a shipping lane before our sampling occurred in this area. Dredging the sediments also reduced the pollution of PBDEs. By contrast, sampling site A6 is located very close to the main urban zone, and there is a navigation lock in this area. Pollution from Chaohu City and ships in this small area could increase the residual levels of PBDEs. The low PBDE levels in surface sediments of the WR area also reduced the stress of resuspending PBDEs into the water of the lake. The residual level of BDE 47 in the surface sediments from the Xiaozhegaohe River (including C1 and C2) was not dominant among PBDE congeners. However, there was a large amount of BDE 209 in this river. Sampling site C2, which is located close to a heat power station, had the highest BDE 209 level among the sampling sites. BDE 47 and BDE 138 dominated the BDE congeners in the estuaries of the Dazhegaohe River and Shuangqiaohe River.

As shown in Fig. 5a, tetra-BDE (mainly BDE 47) dominated the PBDE congeners in the EL area. Although BDE 47 and BDE 209 were the major components of PBDE congeners, the percentage of BDE 209 was lower than that of BDE 47. However, BDE 209 had the largest ratio in the river samples. In the core western lake area, the ratios of tri-BDE to Σ_{14}BDEs and deca-BDE to Σ_{14}BDEs were very low, whereas PBDE congeners with moderate levels of Br were the main components.

3.3.2. SPM

The SPM in rivers had the highest Σ_{14}BDEs, with a mean value of 516 ng/g (ranging from 43.6 to 1322.5 ng/g), followed by CW (112.7 ng/g), WR (mean value, 102.4 ng/g, ranging from 53.9 to 162.8 ng/g), and EL (mean value, 67.8 ng/g, ranging from 20.8 to 96.2 ng/g) (Fig. 4b). Lake Chaohu has a depth of 3–4 m, suggesting that resuspension effects resulted from wind-induced turbulence are significant; however, the hills on the northern and southern side of the WR area might reduce the wind speeds, resulting in a weak resuspension effect. In the WR area and some estuaries, there was little BDE 209 in the surface sediments but a large amount in the SPM, indicating that an important possible source of BDE 209 is very likely to be wastewater from the city. A wastewater treatment was built in Chaohu City many years ago; however, it was located near the Yuxi River, which was the only outflow river of Lake Chaohu. The wastewater treatment hardly satisfied the rapidly developing city. A large amount of wastewater without treatment or effective treatment was discharged directly into rivers, resulting in the higher detected PBDEs in rivers. Local government has noticed the lack of wastewater treatment plants and planned to expand the present plant.
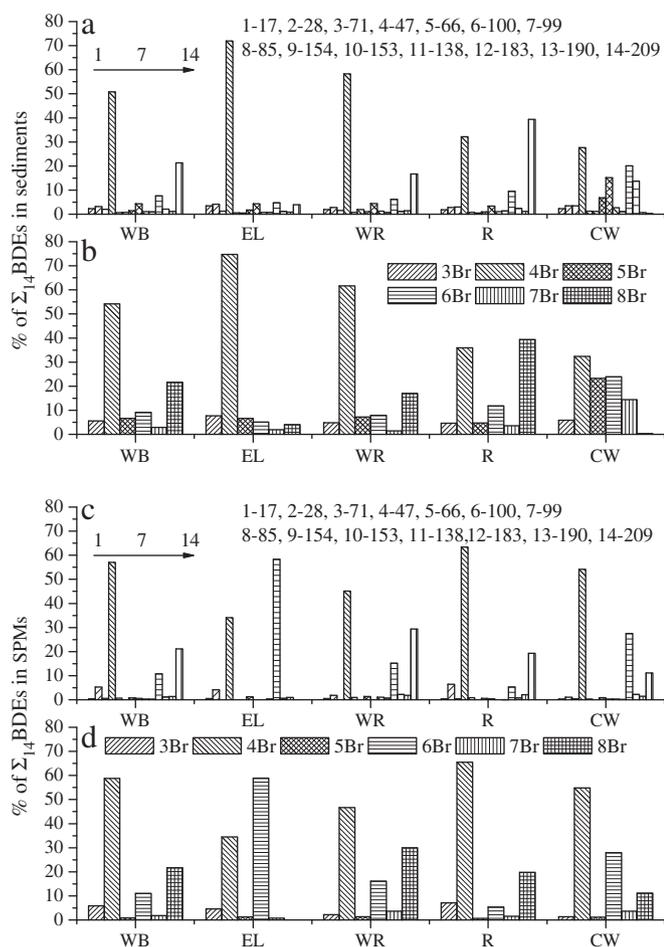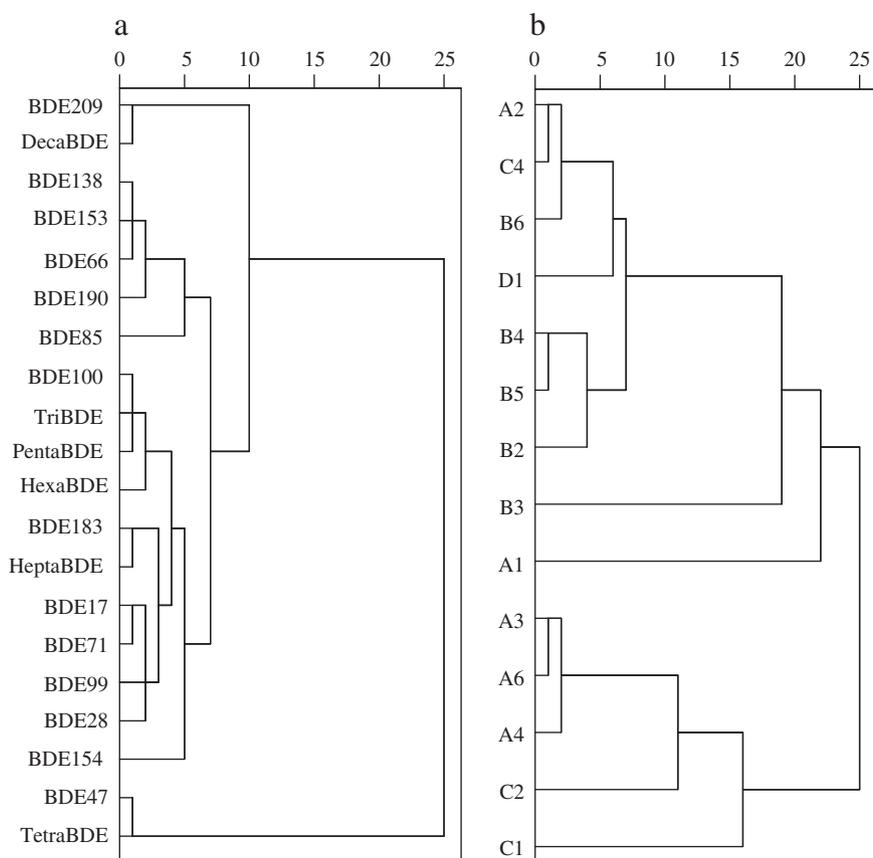
Fig. 6. Cluster analysis of individual PBDEs (a) and sampling sites (b).

As shown in Fig. 5b, in the EL area, BDE 138 dominated the PBDE congeners, followed by BDE 47. In the WR area, the main congeners were tetra-BDE (BDE 47), followed by deca-BDE (BDE 209) and hexa-BDE (BDE 138). In the rivers, BDE 47 accounted for over 60% of the Σ_{14}BDEs, followed by BDE 209. The main composition of PBDE congeners in the CW area was BDE 47, followed by BDE 138, and BDE 209. Unlike the composition of PBDE congeners in the sediments, the proportions of penta- and hepta-BDEs to Σ_{14}BDEs were very low in all parts of the lake.

3.4. Cluster analysis of PBDE congeners and sampling sites based on PBDEs in sediments

The PBDE congeners were divided into three clusters, as shown in Fig. 6a. The first cluster included BDE 47 and tetra-BDE and depended significantly on the highest concentration. The second cluster included BDE 209 and deca-BDE, as indicated by the second highest residual levels in the surface sediments. The rest of the PBDE congeners belong to the third cluster. The CA results were in accordance with composition

Table 2
Pearson correlation coefficients between different PBDE congeners and TOC.

	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 190	BDE 209	Σ_{13}BDEs	Σ_{14}BDEs
BDE 28	0.595[a]															
BDE 71	0.736[b]	0.616[a]														
BDE 47	0.232	0.649[a]	0.027													
BDE 66	0.432	0.558[a]	0.773[b]	0.170												
BDE 100	−0.182	−0.278	−0.129	0.277	0.647[a]											
BDE 99	0.563[a]	0.385	0.589[a]	0.181	0.386	0.266										
BDE 85	0.482	0.590[a]	0.730[b]	0.065	0.754[b]	−0.212	0.316									
BDE 154	0.118	0.4	0.611[a]	0.009	0.787[b]	0.593[a]	0.401	0.635[a]								
BDE 153	0.249	0.423	0.439	0.109	0.521	0.257	0.295	0.117	0.665[a]							
BDE 138	0.553[a]	0.619[a]	0.861[b]	−0.064	0.845[b]	−0.301	0.560[a]	0.737[b]	0.843[b]	0.606[a]						
BDE 183	−0.335	0.072	−0.122	−0.132	0.101	−0.197	0.071	0.292	0.472	0.176	0.241					
BDE 190	−0.053	−0.221	0.005	−0.132	−0.132	−0.328	−0.331	0.01	−0.331	0.081	0.477	0.113				
BDE 209	−0.346	−0.13	0.337	−0.572	0.617	−0.168	−0.383	0.466	0.844[a]	0.712	0.754	0.397	0.716			
Σ_{13}BDEs	0.446	0.854[a]	0.460	0.849[a]	0.540	0.17	0.483	0.41	0.426	0.417	0.433	0.072	−0.128	−0.162		
Σ_{14}BDEs	0.404	0.816[a]	0.555[b]	0.663[a]	0.601[b]	0.065	0.488	0.401	0.547	0.609[b]	0.579[b]	0.143	0.316	0.349	.936[a]	
TOC	0.780[b]	0.621[a]	0.963[b]	0.078	0.649[a]	−0.106	0.598[a]	0.663[b]	0.490	0.348	0.779[b]	−0.266	−0.113	0.136	0.431	0.466

[a] Correlation is significant at the 0.01 level.
[b] Correlation is significant at the 0.05 level.

analysis of PBDEs in Section 3.2.1. Although congener profile of PBDEs in sediment was identified in most studies, few researchers employed CA to obtain the dominated congeners. Rayne et al. (2003) have employed CA to identify the similarity and difference among various fishes based on PBDE congener patterns. We also did CA for sampling sites as shown in Fig. 6b. Eight clusters were employed. The first cluster contained A3, A4, and A6. The composition and quantity of congeners in this group were similar for all three sites. The second cluster included B2, B4 and B5. These sites were located in the WR area, and this group had low levels of PBDE contamination. The third cluster included A2, C4, and B6. The composition and quantity of congeners in this group were also similar. However, the residual level of PBDEs was lower in the third cluster than in the first cluster. Five other clusters contained only one sampling sites: C1, C2, A1, B3, and D1. After investigating the congener pattern at each site, we found that: The BDE 209 composition was higher at C1 than other sites. C2 had the highest concentrations of BDE 209 and BDE 138 among all of the sites. Many congeners were not detected at A1 and B3, and BDE 47 dominated the congener profile in the surface sediment. At D1, the detected congeners were present at similar concentrations (Fig. 4a). It was difficult to identify the similarities and differences among the sampling sites in Section 3.3.1 because multivariate data on conventional two- and three-dimensional graphs confused us easily. However, CA provided a useful approach for comprehensive classification. We could clearly distinguish which sampling sites belonged to one cluster.

3.5. Relationships between total organic carbon (TOC) and PBDEs in sediments

Before the Kolmogorov–Smirnov normal test, all data were log-transformed. The dataset obeyed a log-normal distribution. Pearson's correlation analysis was used to study the relationship between organic carbon and PBDE congeners in the sediments. As shown in Table 2, there was a positive correlation between TOC and congeners with small number of Br (BDE 17, BDE 28, BDE 71, BDE 66, BDE 99, BDE 85, and BDE 138). There was a weak correlation between TOC and BDE 47 ($r = 0.078$) and BDE 209 ($r = 0.136$), which resulted in a weak correlation between TOC and ΣPBDEs. These results were consistent with previous studies (Mai et al., 2005; Moon et al., 2007a). BDE 209 showed a correlation with BDE 154 only ($r = 0.844$), suggesting that most of the tri-to-hepta-BDEs did not result from the degradation of deca-BDE. BDE 183 and BDE 190 had very low correlations ($r = -0.335$–0.716) with other PBDE congeners, whereas BDE 138 showed significant positive correlations with BDE 71, BDE 66, BDE 154 and BDE 85. There was only a strong correlation between BDE 47 and BDE 28, indicating that

BDE 28 might originate from the decomposition of BDE 47. However, there was weak relationship between BDE 47 and other congeners, indicating that the source of BDE 47 was not the decomposition of congeners with larger numbers of Br. Combined with the results and discussion of PBDE distributions in the SPM and previous studies (Mai et al., 2005; Moon et al., 2007a), we believe that BDE 47 in the surface sediment originates from the SPM, which were imported by way of rainfall, runoff, and pollution discharge. It might be more meaningful to correlate particulate TOC with PBDEs. However, particulate TOC was not analyzed due to the limited SPM samples. We have been carrying out a further study of PBDEs' temporal distribution in SPM from Lake Chaohu, and correlation between particulate TOC with PBDEs will be considered in this study.

3.6. Relationship of PBDE distributions between the surface sediment and the SPM

According to the composition identification of BDE congeners in the surface sediment and the SPM, we assumed that there was a strong relationship between the two media for the distributions of PBDEs. The mean values of individual PBDE congeners in the sediments and SPM were log-transformed and normally tested. The two transformed datasets obeyed normal distributions. Pearson's correlation showed that there were significant positive correlations between PBDEs in the surface sediments and those in the SPM ($r = 0.877$, $p < 0.0001$). On the basis of this significant relationship, a linear relation formula (Eq. (1)) and nonlinear relation formula (Eq. (2)) were constructed for the concentrations of PBDEs in the surface sediments and SPM (Fig. 7a):

$$\mathrm{Log10}(C_{\mathrm{sediment}}) = -1.988 + 0.615\,\mathrm{Log10}(C_{\mathrm{SPM}}) \tag{1}$$

or

$$C_{\mathrm{sediment}} = 0.01\,C_{\mathrm{SPM}}^{0.615}, \tag{2}$$

where C_{sediment} and C_{SPM} are the concentrations of PBDEs in the surface sediments and the SPM, respectively.

The predicted values of PBDEs in the surface sediments were calculated using Eq. (1) or (2) and the detected values of PBDEs in the SPM at each sampling site. Both the determined and predicted values of PBDEs in the surface sediments are shown in Fig. 7b. According to the mean of relative deviance (MRD) between the determined and predicted values for each PBDE congener, the MRD ranged from 0.05 to 3.14. Using this formula, some PBDE congeners, including BDE 17, BDE 28, and BDE 47, were underestimated, while others, including BDE 66, BDE 99, BDE
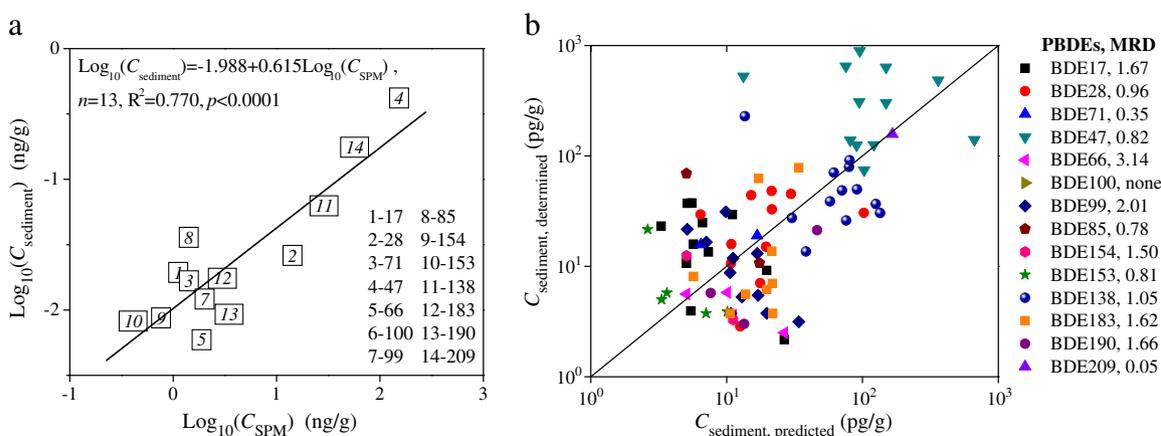

Fig. 7. PBDE congener distribution relationship between the surface sediments and the SPM (a) and mean relative deviance (MRD) between the determined and predicted data using the formula $\mathrm{Log}_{10}(C_{\mathrm{sediment}}) = -1.988 + 0.615 * \mathrm{Log}_{10}(C_{\mathrm{SPM}})$ and determined SPM data (b).

138, BDE 183, and BDE 190, were overestimated. Although the formula did not give an accurate prediction, the predicted and determined values were on the same order of magnitude. This method remains a practical and useful tool to estimate the overall level of PBDE pollution in sediments in Lake Chaohu, as it is only dependent on the PBDE concentration in the SPM. To our knowledge, de Boer et al. (2003) also determined PBDEs in SPM and sediment in water bodies in Netherlands. But there was weak correlation between SPM and sediment for PBDEs when outliers were excluded ($p = 0.158$). The reason is that samples were collected from different sites in Netherlands. Some places were seriously polluted by PBDEs (BDE 209 in SPM was up to 4600 ng/g), and some were natural environment with little pollution. Different aquatic environments might result in various correlations between PBDEs in SPM and in sediment. Therefore, it should cautiously used Eq. (1) in Lake Chaohu to predict PBDE pollution in sediments in other places.

4. Conclusions

The concentrations of Σ_{13}BDEs and BDE 209 ranged from 236.7 to 1373.4 pg/g dry weight (dw) and from 4.2 to 691.2 pg/g dw, respectively, in the surface sediments, which were two to three orders of magnitude lower than those of the SPM. The congener composition was dominated by BDE 47 (50.8%) and BDE 209 (21.3%) in the sediments, whereas the proportion of BDE 47 to Σ_{14}BDEs in the SPM was slightly larger than that in the sediments. The concentration of Σ_{14}BDEs in the sediments from the WR area in the eastern part of the lake was very low, with a mean value of 514.8 pg/g, whereas the value was 102.4 ng/g in the SPM. A cluster analysis (CA) was conducted to further illustrate the dominance of each congener and the similarities among sampling sites. Many factors, including resuspension photodecomposition, microbial oxidation, local discharge, and dredging, influence the distribution between the sediment and the SPM for PBDE congeners and the spatial distribution of PBDEs. A formula for the concentration of PBDEs in the surface sediments and the SPM was constructed to understand this potential relationship. Although it did not predict specific PBDE congeners in the sediment accurately, it remains a practical and useful way to assess the overall pollution of PBDE in sediments in Lake Chaohu, as it is only dependent on the concentration of PBDEs in the SPM. However, it should be cautiously used to predict PBDE pollution in sediments in other places.

Acknowledgments

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