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Baseline

Sediment records of polybrominated diphenyl ethers (PBDEs) in Yangtze River Delta of Yangtze River in China

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ABSTRACT

The spatial and temporal distributions of polybrominated diphenyl ethers (PBDEs) were investigated in five sediment cores from the Yangtze River Delta of Yangtze River in China. The surficial concentrations of nine tri-through hepta-BDE congeners (Σ_9BDEs) and BDE209 were highest at urban sites S3 and S2, followed by rural site S1 and estuary sites S5 and S4, respectively, based on dry sediment weight. Both BDE209 and Σ_9BDE concentrations exponentially increased between 1990 and 2008. Commercial deca-BDE, penta-BDE, and octa-BDE products were likely PBDE sources in the study area. The relative abundances of BDE209 were higher in sediment cores from estuary than those from urban and rural locations, ascribing to the atmospheric transport from the adjacent densely populated northern and eastern coastal regions. This conclusion was further confirmed by the higher ratios of BDE47/BDE99 and BDE100/BDE99 in cores from the estuary than those from other locations.

Polybrominated diphenyl ethers (PBDEs) have been extensively used in polymer matrices as fire retardants and dispersed in the global environment since the 1960s (Alonso et al., 2012; Song et al., 2004). According to the average degree of bromination, commercial PBDE mixtures mainly include penta-, octa-, and deca-BDEs (Betts, 2015). Penta- and octa-BDEs were mostly used as flexible polyurethane foam materials, while deca-BDEs were primarily used in various electrical and electronic products (Rahman et al., 2001). Existing production and usage inventory indicated that the cumulative global production of PBDE technical products was ca.1.5–1.7 million tons since the 1960s and reached a peak in 2003 (~75,000 tons) (Pietroń and Malagocki, 2017; van et al., 2016). The consumption of penta-, octa-, and deca-BDE mixtures peaked in 2003 (~12,000 tons), 1997 (~85,000 tons), and 2003 (~75,000 tons), respectively (Abbasi et al., 2015; Earnshaw et al., 2013; Prevedouros et al., 2004; Wang et al., 2007). As of 2018, the legacy stocks of commercial BDE209 and other five BDE mixtures (i.e., BDE28, BDE47, BDE99, BDE153, and BDE183) in the world were estimated to be ~38,000 and ~500,000 tons, respectively (Abbasi et al., 2019).

Exposure to PBDEs may cause developmental neurotoxicity, endocrine disruption, and thyroid toxicity (Kim et al., 2015; Zeng et al., 2014). Therefore, PBDEs were withdrawn from the penta-, octa-BDEs, and deca-BDEs markets in Europe and the US in 2004 and pre-2010s, respectively. In addition, penta-, octa-BDEs, and deca-BDEs were listed as persistent organic pollutants in the Stockholm Convention in 2009 and in 2017, respectively (Luo et al., 2020). China began to produce PBDEs (mainly deca-BDEs) in the 1980s and became the world's largest manufacturer and supplier in 2000 (Ni et al., 2013). Restrictions on penta- and octa-BDE mixtures in China began in 2004, whereas deca-BDE mixtures consisting of over 98% of BDE209 is still being produced and consumed without any regulatory restrictions. Considerable numbers of deca-BDE manufacturing facilities and electronic waste (e-waste) recycling factories located in Shandong, Jiangsu, Zhejiang, and Guangdong provinces in China (Bi et al., 2007; Tian et al., 2011; Wang et al., 2017; Yu et al., 2016). Therefore, PBDEs were widely present in various aquatic systems in different areas of China, such as coastal areas (e.g., the East China Sea, the Yellow Sea, and the South China Sea) (Sun et al., 2017; Zhu et al., 2019a), tributaries of large rivers (e.g., the Yellow River, the Yangtze River, and the Pearl River) (Wang et al., 2016b), and inland lacustrine deposits (e.g., the Taihu Lake and the

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Chaohu Lake) (Chen et al., 2018; Da et al., 2019a).

PBDEs can enter the aquatic environment in different ways, such as atmospheric deposition, surface/subsurface runoff, and accidental discharges (Chen et al., 2007; Lee et al., 2018). Due to the slow anaerobic debromination, sediments with anoxic and light-protected characteristics are an important sink for PBDEs (Ganci et al., 2019; Han et al., 2015). Thus, the past contamination of PBDEs could be investigated with well-dated and undisturbed sediment cores (Abbasi et al., 2015). The occurrence, distribution, and potential health risks of PBDEs have been examined in various aquatic systems in China (Chen et al., 2007; Mai et al., 2005; Wang et al., 2016a). Investigations of the sedimentary forms of PBDEs in China were mainly focused on the costal areas (i.e., the Bohai Sea, the Yellow Sea, the East Sea, and the South Sea) (Chen et al., 2007; Wu et al., 2017; Zhang et al., 2015). However, less attention has been paid to the sedimentary records of PBDEs in the inland river. Our previous studies conducted in the Chaohu Lake and Huaihe River in China suggested mixed contamination (industrial point sources and distant atmospheric transport) of PBDE technical products in response to the local and regional production and household usage (Da et al., 2019b,c). The current study further investigate the past changes of PBDEs in five sediment cores collected from the Yangtze River Delta (YRD) of the Yangtze River in China. The specific objectives include investigating historical PBDE input and contamination pathways, apportioning PBDE sources, and establishing correlations between the sedimentary histories of PBDEs and regional anthropogenic activities.

Yangtze River is the longest river in China and the third-longest river in the world in terms of water and sediment discharges. It is oriented from the Qinghai-Tibet Plateau and drains into the East China Sea, with a total distance of approximately 6400 km. The location of our study was targeted at the YRD section within the Yangtze River (Fig. 1). This district is one of the most industrialized and urbanized areas in China, with thousands of electrical, electronic, and plastic industries and imported e-waste recycling factories located in this area (Sun et al., 2016; Zhang et al., 2014). Coastal cities such as Nantong and Suzhou in Jiangsu province and Taizhou in Zhejiang province are the industrial center for deca-BDE production and e-waste import and recycling, respectively (Zhang and Lu, 2011). Expectable PBDE have emitted to air, soil and aqueous achieves due to the improper waste management in this district (Chen et al., 2017; Yu et al., 2016; Zhu et al., 2019b).

A series of five gravity sediment cores with 37–45 cm in length were collected using a gravity corer from May to July in 2018 (Fig. 1). Site S1 was located in rural area in Anhui Province and far from large cities. Sites S2 and S3 were located in Jiangsu Province and proximity to large cities (Nanjing and Changzhou, respectively). Sites S4 and S5 were located at the Yangtze River estuary in the nearshore area of Chongming Island in Shanghai (Core S4 and core S5 were in the Chongming island of the southern sector and northern sector, respectively). The morphometry, hydrology, biology, and geochemistry in this district have been well characterized in previous studies since 1980s (Hori and Saito, 2007; Wang et al., 2018; Yang, 1989). Cores were directly sliced at 1 cm intervals after coring. They were then wrapped in pre-baked aluminum foil, freeze-dried, pulverized to < 200 mesh, and stored in a brown glass bottle at −20 °C until analysis.

Hexane, acetone, and dichloromethane were HPLC grade and purchased from Fisher Scientific (Pittsburgh, PA). Silica gel and sodium sulfate were both analytical reagent grade and purchased from Fisher Chemical. Standard mixture of 40 PBDE congeners (i.e. 1, 2, 3, 10, 7, 11, 8, 13, 12, 15, 30, 32, 17, 25, 28, 33, 35, 37, 75, 49, 71, 47, 66, 77, 100, 119, 99, 118, 116, 85, 126, 155, 154, 153, 138, 166, 183, 181, 190, and 209) and internal standards PCB-204 and BDE 190 were from AccuStandard (New Haven, CT). Surrogate standards $^{13}C_{12}$-labeled BDE138 and BDE153 were from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). Copper strips were activated with dilute HCl, rinsed with Milli-Q water to neutral PH, and soak in hexane solution for water removal.

Samples were pretreated with 4 M hydrochloric acid to decompose inorganic carbon. Then the carbonate-free samples (ca. 5 mg dry sample) were analyzed for total organic carbon (TOC) content with a Vario EL-III Elemental Analyzer (Elementar Vario EL cube, Germany), and was calculated concerning the whole sediment dry weight. The precision of duplicate analysis of one sample (n = 5) was ± 0.03 wt%. The grain size of the sub-sectioned sediments was measured by sieving on mesh sizes in the range of 0.1 to 0.3 mm. The samples were suspended in water (ca.0.2 g for each sample) for 30 s prior to analysis. Three fractions were obtained according to their particle sizes: sand (< 0.1 mm), small gravel (0.1–0.3 mm), and gravel (> 0.3 mm).

The samples were analyzed for ^{210}Pb and ^{137}Cs activities with γ-spectrometry using Canbettra ultra-low-background germanium detectors. Precisely, ^{210}Pb, ^{226}Ra, and ^{137}Cs were measured from γ-peak at 46.5 keV, granddaughter ^{214}Pb (peaks at 295 and 352 keV), and the peak at 661 keV, respectively. The ages of the sediments yielded from a constant rate of supply dating model (Text S1) (Appleby, 2002). The ages and dating uncertainties are shown in Fig. S1 and statistical errors were better than ± 3%. Information on the five cores including the sediment lengths and calculated ages, deposition rates, sedimentary fluxes, and focusing factors, are shown in Table 1. The estimation methods of focusing factors and sedimentary fluxes are described in Text S2.

PBDEs were extracted following the procedures described in our previous studies (Da et al., 2019b,c). Approximately 5 g of freeze-dried segmented sediment from individual sediment intervals were spiked with $^{13}C_{12}$-labeled BDE138 and BDE153 as surrogate standards and Soxhlet extracted with a mixture of n-hexane, dichloromethane and acetone (2:2:1 in volume). Activate copper strips were added to the extraction flasks to remove elemental sulfur from the extracts. Each extract was concentrated to approximately 1 mL with a rotary evaporator (RV-10, IKA, Germany). The concentrated extracts were purified on a silica gel column (i.d. = 1.0 cm) packed with 6 cm neutral silica (3% H_2O deactivated), 12 cm sulfuric acid silica (44% sulfuric acid, w/w) and 2 cm anhydrous sodium sulfate from bottom to top. The columns were eluted with 30 mL of hexane, then rinsed with 70 mL of hexane and dichloromethane mixture (1:1, v/v). The second fraction containing PBDEs was then concentrated to 100 μL in hexane and spiked with internal standards (PCB204 and BDE190) prior to GC–MS analysis.

Concentrations of nine PBDE congeners (28, 37, 47, 85, 99, 100, 153, 154, and 183) in freeze-dried sediment were determined using an Agilent 7890 Series gas chromatograph (GC) interfaced with an Agilent 5975C mass spectrometer (MS) in selected ion mode. A DB-5MS capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness) was used for chromatographic separation, with temperature program increasing from 60 °C (held for 2 min) to 200 °C at 10 °C min^{-1}, then rising at 20 °C min^{-1} to 300 °C (held for 10 min). Ultra-purity helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. BDE209 was analyzed on a Thermo Trace Ultra gas chromatography and DSQ II mass spectrometer, and separated on a DB-5HT capillary column (15 m × 0.25 mm i.d. with 0.1 μm film thickness), with temperature program increasing from 120 °C (held for 2 min) and increasing at 20 °C min^{-1} to 300 °C (held for 12 min). Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1}. Ion source and interface line temperatures were 150 and 280 °C, respectively. Ion fragment monitored for BDE209, $^{13}C_{12}$-labeled BDE138 and BDE153, PCB204, BDE190 and other PBDE congeners were reported in our previous studies (Da et al., 2019b,c; Yuan et al., 2016).

Laboratory quality control was conducted with procedural blank, spiked blank, and spiked matrix samples. All glassware was pre-cleaned with distilled water, acetone, and methanol, and then was baked at 450 °C for 5 h before use. One duplicate sample was analyzed for every five samples were conducted to check for the repeatability of the analysis. The relative standard deviation, limits of detection, and recoveries of individual PBDE congeners were shown in Table S1. Quantification

Fig. 1. Sampling locations of the sediment cores in Yangtze River of Yangtze River Delta section.

Table 1
Sampling locations, age, deposition rate, sedimentary flux, and focusing factor.

Cores	Length	Latitude	Longitude	Age	Deposition rate	Sedimentary flux	Focusing factor
	(cm)	(N)	(E)		(cm yr^{-1})	(g cm^{-2} yr^{-1})	
S1	44	30°44′3.99″	117°25′15.34″	1959–2017	0.75	0.052	2.85
S2	45	32°08′9.98″	118°45′33.49″	1961–2016	0.80	0.039	2.02
S3	42	31°57′59.00″	120°03′22.40″	1964–2017	0.78	0.064	2.10
S4	37	31°24′14.26″	121°49′28.79″	1965–2016	0.71	0.061	2.64
S5	39	31°37′0.30″	121°50′26.74″	1966–2017	0.75	0.048	2.21

was made according to internal calibration curves deriving from standard solutions at seven concentrations with correlation coefficient (R^2) value at 0.999 or above. The recoveries of the surrogate standards and field samples ranged from 67.3% to 117.6% and 62.1% to 113.5%, respectively. The relative standard deviation of the duplicate samples ranged from 0.8% to 7.9%. Instrumental detection limits (defined as a

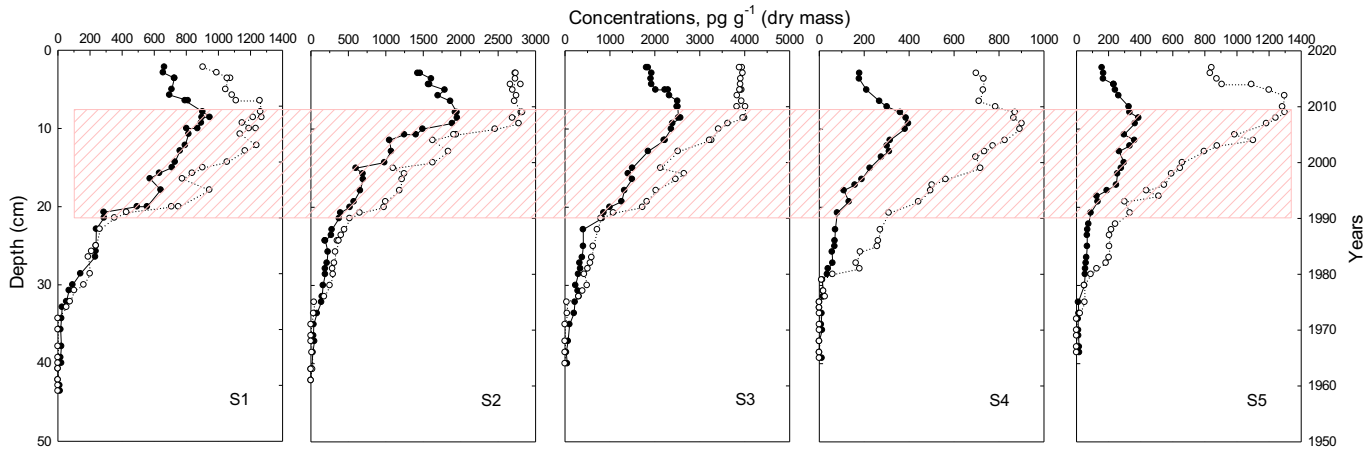

Fig. 2. PBDE concentrations versus deposition year in five cores: empty circle, BDE209; black circle, other BDE congeners (Σ_9BDEs).

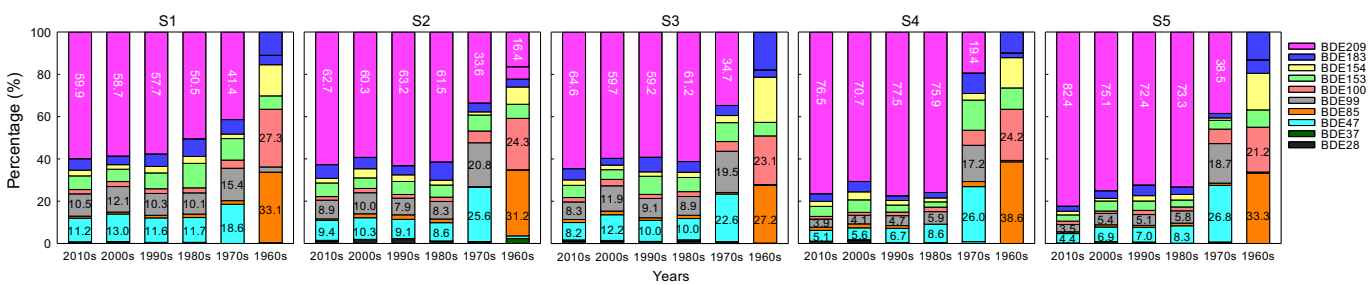

Fig. 3. PBDE congener ratios in different time periods across the five cores.

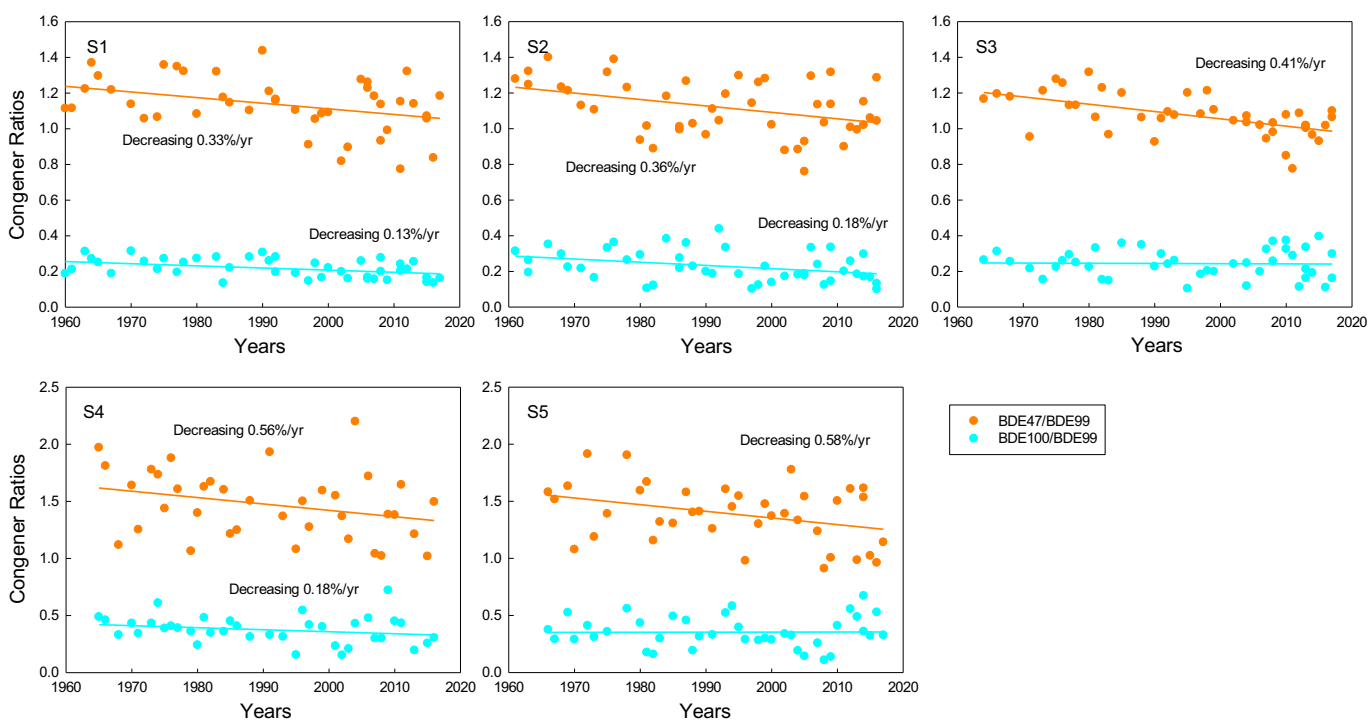

Fig. 4. Congener ratio trends of BDE47/BDE99 and BDE100/BDE99 in five cores.

signal-to-noise ratio of 3), which was determined according to the U.S. EPA method (U.S. EPA, 2016), ranged from 2.0 pg g^{-1} to 18 pg g^{-1}.

Statistical analysis of the data was conducted using SPSS 16.0 (Chicago, IL, USA). The potential differences in PBDE concentrations among different sites were checked by the *t*-test method. The level of significance was set at $p = 0.05$. PBDE concentrations were calculated as pg g^{-1} dry weight (dw).

The total concentrations of BDE209 and other BDE congeners (denoted as Σ_9BDEs) in surface sediments from different locations followed the order: S3 (3942 and 1813 pg g^{-1} dw) > S2 (2726 and 1427 pg g^{-1} dw) > S1 (903 and 663 pg g^{-1} dw) > S5 (842 and 159 pg g^{-1} dw) > S4 (699 and 179 pg g^{-1} dw) (Table S2). The total

concentrations of PBDEs were higher at S3 and S2 than those at other locations were probably because these two locations are near urbanized and highly populated cities, thus were probably more contaminated by local domestic sewage and industrial effluent. In addition, the surface sediments from locations S2 and S3 contained higher contents of total organic carbon (5.1% and 4.3%, respectively) and percentages of small particles (< 1 mm) (87.1% and 79.5%, respectively) comparing to those from other locations (2.6%, 2.6%, and 2.0% for the total organic carbon, and 71.1%, 69.8%, and 70.4% for percentages of small particles from locations S1, S2, and S3, respectively). These were another influencing factors which resulted in higher PBDE concentrations in surface sediments from locations S2 and S3. Moreover, sites S4 and S5 locating at the estuary are frequently impacted by the seawater turbulence with the influx of saline water, which can lead to flocculation and aggregation of cohesive suspended sediment and consequent formation of large particulates (Droppo and Ongley, 1994; Eisma et al., 1991). This is probably why the surface sediments from locations S4 and S5 had the lowest PBDE concentrations.

The literature values of PBDE concentrations in surface sediments from Chinese lakes, rivers, river estuaries and marines were summarized in Table S3. PBDE concentrations in the present study were significantly higher than those in marine sediments from Bays of Yellow river (Zhen et al., 2016) and lake sediments from Chaohu Lake (He et al., 2013), and were comparable to those in marine/river sediments from East China Sea (Liu et al., 2015), Yangtze River Delta (Zhu et al., 2013), East China Sea (Li et al., 2012), Yellow river (Pei et al., 2018), and Yellow River estuary (Yuan et al., 2016), but much lower than those in lake sediments from Taihu Lake (Chen et al., 2018; Wang et al., 2016a; Yin et al., 2017; Zhou et al., 2012), marine sediments from city river in Qingdao (Wang et al., 2019), and river sediment from Yangtze River Delta (Zhu et al., 2013) and Dongjiang River in Pearl River Delta (Mai et al., 2005) (Table S3).

The total concentrations of BDE congeners excluding BDE209 (denoted as Σ_9BDEs) were detected at low levels in the deep sediment layers dated back to the mid-1960s (ca.1964–1966) (Table S2). The initial detectable time of BDE209 was ca.10 years later (starting from 1973 to 1976) than those of Σ_9BDEs, coinciding with the beginning of production and usage of commercial penta-, octa-, and deca-BDE products (Abdallah and Harrad, 2014). Some trace level congeners (e.g., BDE28, BDE37, and BDE85) were detected in the cores prior to the initial industrial production of PBDEs (Table S2), which was consistent with our previous studies (Da et al., 2019b,c). This could be caused by the down-core diffusion of chemicals deriving from resuspension and bioturbation, and unavoidable sedimentary vertical mixing (Yang et al., 2016), as reflected by the ^{210}Pb concentration profiles against the cumulative dry mass of the sediments (Fig. S1).

The variations in Σ_9BDE concentrations across five cores were first randomly from the mid-1960s to the mid-1970s, followed by a slow increase from the mid-1970s to the post-1980s (Fig. 2). Thereafter, Σ_9BDE concentrations increased dramatically, with trends ranging from 13.5% to 29.3% per year in the period of ca. 1990–2008, consistent with the historical booming period of national production and consumption of household appliances and electronics (Chen et al., 2007; Li et al., 2016). The time at which sedimentary PBDE concentrations (ca. 1990) began to exponentially increase is consistent with that at Pearl River estuary in China (early 1990s) (Chen et al., 2007) and Sydney estuary in Australia (early 1990s) (Drage et al., 2015), and earlier than that at Bohai, Yellow Sea, and East China Sea in China (post-1990s) (Fan et al., 2017; Li et al., 2016; Wang et al., 2016a, 2017), but much later than that at upper Great Lakes (i.e., Lakes Michigan, Superior, and Huron) in the US (early-1970s) (Song et al., 2005; Zhu and Hites, 2005), seven English lakes in England (mid-1970s) (Yang et al., 2016), Svalbard in Norway (late 1970s) (Hermanson et al., 2010), and at Seine River basin of Paris Megacity in France (mid-1980s) (Lorgeoux et al., 2016).

The concentrations of Σ_9BDEs across five cores continued to increase until ca. 2007–2010, and significantly decreased toward the top layers of the sediment (Fig. 2), ascribing to the voluntary and regulatory phase-out of production and/or usage of penta- and octa-BDEs products in China since 2004. BDE209 depositions from the mid-1970s to post-1980s paralleled the temporal variations of Σ_9BDEs. Still, they increased faster than the latter ones during the period of ca.1990–2008 (Fig. 2), ascribing to the more widespread use of deca-BDE technical products than penta- and octa-BDEs (La Guardia et al., 2006). The continual increase in Σ_9BDE concentrations in the period of ca.2004–2008 after restrictions of commercial penta- and octa-BDE technical products in China suggested the culminated input of Σ_9BDEs deriving from the usage and circulation of legacy PBDE products (Fig. 2). The following declines of BDE209 and Σ_9BDE concentrations can be associated with the decreasing use of legacy commercial PBDE mixtures in recent years (de Wit et al., 2010).

The gradual decline of PBDE concentrations in sediment cores since the mid-1990s from developed countries/regions such as Europe, Japan, and the US was recorded by previous studies (Minh et al., 2007; Yun et al., 2008). However, the annual global consumption of PBDE technical products, particularly for deca-BDE mixtures, continually increased during the same period (Abbasi et al., 2019). Therefore, the increasing trends of both BDE209 and Σ_9BDEs during the 1990s and 2000s largely reflected the transferring of PBDE contamination sources from the developed countries to China.

BDE209 was dominant in the five cores with dated years after the 1970s, contributing to 45.0 ± 23.9%–65.3 ± 26.3% of the total PBDEs (Fig. 3). This is because BDE209 was extensively used in deca-BDE products (over 97%) (La Guardia et al., 2006), and was still being manufactured in China. Sites S4 and S5 are located at the estuary of the Yangtze River, frequently influenced by the seasonal variability of East Asian monsoons, thus receiving a large amount of aerosol bounded organic contaminants (Guo et al., 2006; Zhang et al., 1992). Therefore, the contributions of BDE209 in cores S4 (56.7 ± 31.2%) and S5 (65.3 ± 26.3%) were significantly higher than those in other cores (45.0 ± 23.9%–52.6 ± 20.8%) (Fig. 3). Moreover, the adjacent northern and eastern coastal regions of locations S4 and S5 have long been the brominated flame retardant manufacturing and e-waste recycling center (Zhang and Lu, 2011), which also result in PBDEs input through atmospheric transport and sediment disperse to ocean.

The other dominated BDE congeners in the five cores included BDE47, BDE99, and BDE153, with relative contributions of 11.3 ± 9.6%–16.2 ± 7.9%, 8.0 ± 6.3%–14.1 ± 6.1%, and 6.1 ± 3.9%–9.4 ± 5.7%, respectively (Fig. 3). This is consistent with the compositions of commercial BDE mixtures, which were consisted of 80% of BDE47, BDE99, and BDE153 for penta-BDEs, 30% of BDE153 and BDE183 for octa-BDEs, respectively (Abbasi et al., 2019). Other BDE congeners included BDE28, BDE37, BDE85, BDE100, and BDE154, most of which were the constitutes of penta- and octa-BDE mixtures (Sjödin et al., 1998), with concentrations following the order: BDE154 > BDE100 > BDE85 > BDE28 > BDE37 (Fig. 3). The temporal variations of BDE47/BDE99 and BDE100/BDE99 tend to decrease from bottom to top layers across five cores with two exceptional cases of BDE100/BDE99 in cores S3 and S5 (Fig. 4). They were generally higher than those in penta-BDE mixtures Bromkal 70-5DE (0.96 and 0.18, respectively) and DE-71 (0.79 and 0.27, respectively) (La Guardia et al., 2006). This is ascribed to the stability differences of individual BDE congeners in the environment, which follows the order: BDE100 > BDE47 > BDE99 (Wania and Dugani, 2003). Moreover, the ratios of BDE47/BDE99 and BDE100/BDE99 in cores S4 (1.47 ± 0.29 and 0.37 ± 0.12) and S5 (1.39 ± 0.26 and 0.35 ± 0.14) were generally higher than those in cores S1 (1.14 ± 0.15 and 0.22 ± 0.05), S2 (1.12 ± 0.16 and 0.23 ± 0.09), and S3 (1.07 ± 0.11 and 0.24 ± 0.08) (Fig. 4). This result further confirmed the significant influence of atmospheric deposition and/or sediment transport at the estuary of the Yangtze River.

To conclude, the distribution of surficial PBDE concentration

profiles largely reflected the local urban emissions and inputs. The dramatic increase of Σ_9BDE and BDE209 concentrations in both cores in the period of ca. 1990–2008 is consistent with the booming period of regional and national production and consumption of household appliances and electronics. Following declines in BDE209 and Σ_9BDE concentrations can be associated with the deceasing use of legacy commercial PBDE mixtures. Moreover, the increasing trends of both BDE209 and Σ_9BDEs during the 1990s and 2000s largely reflected the transferring of PBDE contamination sources from the developed countries to China. Higher ratios of BDE209, BDE47/BDE99, and BDE100/BDE99 in cores S4 and S5 than other ones confirmed the significant influence of atmospheric deposition and/or sediment transport at Yangtze River estuary.

CRediT authorship contribution statement

Ruwei Wang designed research; Chunnian Da, Linlin Xia, and Jiawei Cai performed research; Chunnian Da, Jiawei Cai, and Feixuan Cai contributed sample sampling and sampling map; Ruwei Wang, Qing Huang, and Chongjing Gao analyzed data; and Ruwei Wang, Chunnian Da, and Linlin Xia wrote the paper.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111714.

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