



Time trends of polybrominated diphenyl ethers in East China Seas: Response to the booming of PBDE pollution industry in China



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ABSTRACT

The East China Seas (ECSs) are the receptors of the land-based persistent organic pollutants (POPs), such as polybrominated diphenyl ethers (PBDEs) mainly from China through atmospheric deposition driven by the East Asian winter monsoon and fluvial discharge (e.g., Yangtze River and Yellow River), making the offshore sediments to be a good proxy to reconstruct history of those pollutants in China. In this work, four well-placed sediment cores were extracted from the mud areas in the ECSs, and the ²¹⁰Pb-dated cores were analyzed to yield historical concentration profiles of PBDEs in the area. The results showed that there was a persistent increase from 1970s and almost no clear sign in the decline of PBDEs until recently in China. More importantly, there was a faster increase of PBDEs from 1990s in China; while this period was just shown as gradually leveling off or even declining trends in developed countries. The persistently increasing trend of PBDEs in China since 1990s could be largely due to the booming of the manufacturing industry and unexpectedly transfer of PBDE pollution from developed countries to China. Besides, the relative high concentrations and fluxes of PBDEs in the core from coastal ECS located near a well-known electrical/electronic waste (e-waste) recycling area suggests an important contribution of PBDE emissions from recycling centers of e-waste in China. Although efforts in environmental monitoring of PBDE contamination have been substantially increased over the last decade, China is still lagging behind in terms of nationwide regulation of PBDE usage and treatment of disposal PBDE-containing products.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as additives in many electrical and electronic products, textiles, plastics, building materials and furnishings to reduce flammability. PBDEs dissolve in the polymers and can therefore easily escape from these products during their production, usage and disposal (de Wit, 2002; Rahman et al., 2001). Generally, PBDEs are commercially available in three technical mixtures as penta-, octa- and deca-BDE mixtures (Siddiqi et al., 2003). The industrialized countries started to use PBDEs and the usage increased from the early 1970s. In 1992, the global production of PBDEs was ~40,000 t, but in 1999 this increased to close 70,000 t (Renner, 2000). High levels of PBDEs in the environment (including water, soil, atmosphere and various organism bodies) have been documented in the USA and Western European countries (Minh et al., 2007; Song et al., 2004, 2005a, 2005b; Zegers et al., 2003). The penta- and octa-BDE mixtures were banned in Europe and United States in 2004 largely due to environmental and public health concerns. In May 2009, two

kinds of PBDEs were listed on the Stockholm Convention. Shortly afterwards, restrictions have been imposed on the production and use of deca-BDE in Europe and United States. As PBDEs were banned in those developed nations, lots of manufacturing capacities were moved to the less developed nations such as China, India, Indonesia, Malaysia, the Philippines, Thailand and Vietnam (Hale et al., 2003; Kwan et al., 2014). Especially in China and India, as the manufacturing industry has been increasing considerably, there has been a heavy demand for PBDEs in recent decades (Chen et al., 2007). The production of deca-BDE technical mixture, the predominant commercial PBDE product, increased from 10,000 t to about 30,000 t from 2000 to 2005 in China (Chen et al., 2007). More importantly, as Asian countries, China, India and Pakistan have long been suspected of receiving and disposing the bulk of the world's obsolete electronic goods so-called "e-waste" (Martin et al., 2004). Because no definite regulations have been imposed on PBDE production and usage, it could be expected that the environmental levels of PBDEs will continue to increase in some Asian countries.

PBDEs have been found in various environmental media and gradually become a critical problem in China in recent decades (Kang et al., 2011; Li et al., 2012; Mai et al., 2005; Wang et al., 2011, 2012). However,

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continuous data about the pollution status of these pollutants was extremely scarce in China. In most cases, the market demand of these PBDE compounds is not fully known and there is an absence of production and usage data, thus making it difficult to track the time trend and evaluate the recent pollution situation of these chemicals. PBDEs preserved in undisturbed and well-dated sediment cores could be an effective means to reconstruct the historical record of these chemicals.

The East China Marginal Seas (including Bohai Sea (BS), Yellow Sea (YS) and East China Sea (ECS)) (Fig. 1) adjoin the famous industrial districts in China. Adjacent four provinces (including Shandong, Hebei, Jiangsu and Zhejiang) and three municipalities under the direct jurisdiction of the Central Government (including Beijing, Tianjin and Shanghai) supported almost 40% of the national GDP in the past twenty years (<http://www.stats.gov.cn>). These developed areas could be considered to account large demand and emission of PBDEs in China. The

continental shelves of the East China Marginal Seas are in the pathway of Asian continental outflow to the northwest Pacific Ocean driven by the East Asian monsoon (Lang et al., 2008; Lin et al., 2011; Primbs et al., 2007; Zhang et al., 1992). Besides, the East China Marginal Seas receive discharge from two dominate rivers (Yellow River and Yangtze River) in China. They are thus the receptors of the land-based POPs through atmospheric deposition and fluvial discharge (Lin et al., 2011, 2013). The coastal ECS is a major sink of the Yangtze River-derived sediments and associated pollutants into the sea (Li et al., 2012; Liu et al., 2006). The mud deposits from the central BS, YS and distal ECS contain airborne contaminants transported from the upwind region, Mainland China, therefore, they can memory the PBDE pollution in North and East China (Guo et al., 2006, 2007). In the previous studies, the historical records of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in these areas were well documented to coincide

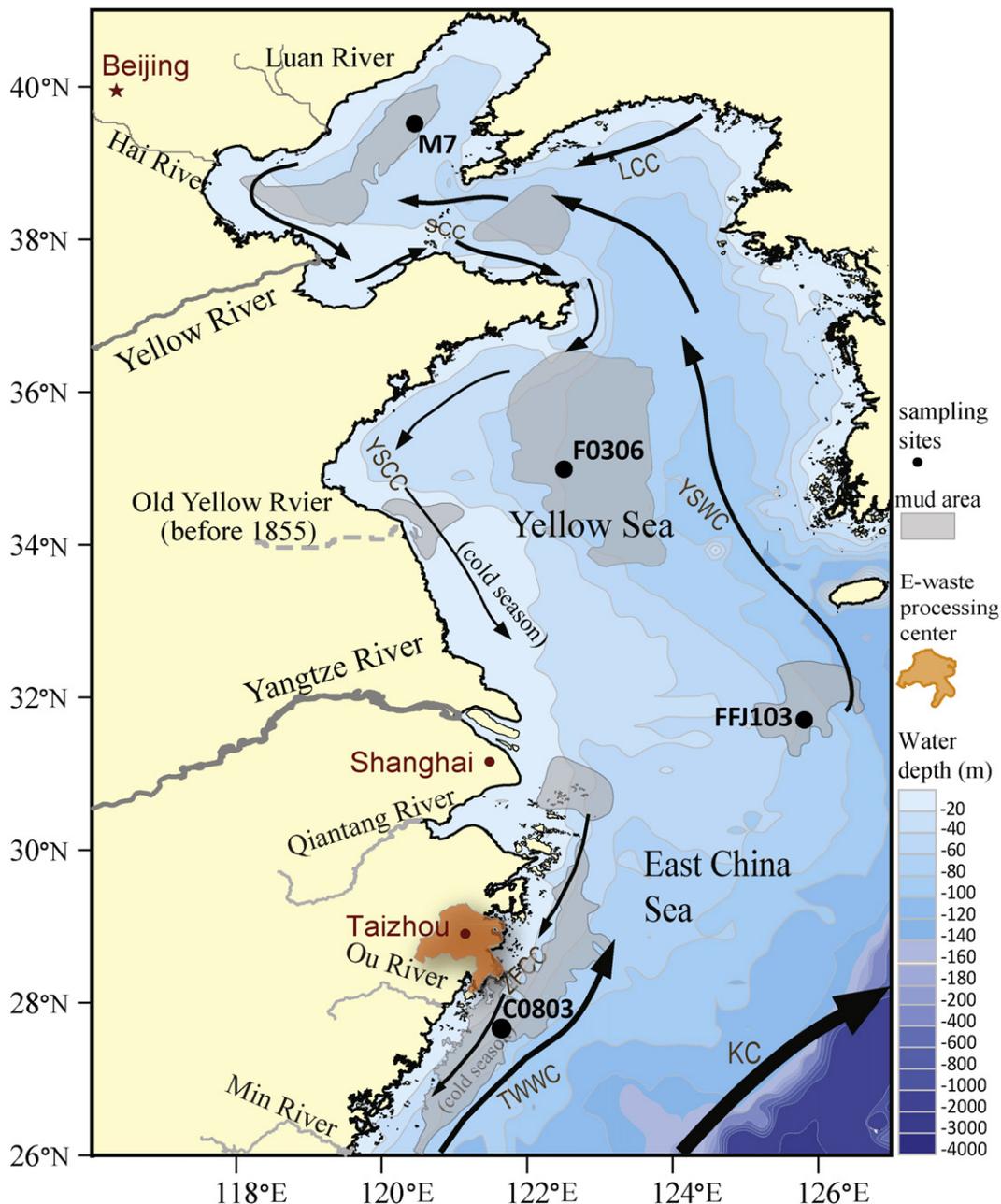


Fig. 1. Study areas and locations of sampling sites in BS, YS and ECS. KC: Kuroshio Current; TWWC: Taiwan Warm Current; ZFCC: Zhejiang-Fujian Coastal Current; YSCC: Yellow Sea Coastal Current; YSWC: Yellow Sea Warm Current; SCC: Shandong Coast Current; LCC: Liaonan Coast Current. Circulations and mud areas are modified from Hu et al. (2011).

with the emission or usage of these pollutants in China (Guo et al., 2006; Lin et al., 2016). In this study, four well-placed ^{210}Pb dated sediment cores collected from the different mud areas in the central BS, central YS, coastal ECS and central ECS were analyzed in order to identify their possible sources and provide a better understanding of the long-term trends of PBDE pollution in China.

2. Materials and methods

2.1. Sample collection

Core M7 (39°32'N, 120°27'E) was collected from the central BS in 2013 using a box corer with the water depth of 29 m and the core length of 53 cm. Core F0306 (34°59'N, 122°30'E) was collected from the central mud in the south YS in 2007 using a box corer with the water depth of 65 m and the core length of 37 cm. Core C0803 (27°38'N, 121°39'E) was collected from the inner shelf mud in ECS in 2009 using a gravity corer with the water depth of 50 m and the core length of 189 cm, and core FFJ103 (31°40'N, 125°52'E) was collected from the distal mud southwest to Cheju Island in the central ECS in 2007 using a box corer with the water depth of 65 m and the core length of 46 cm (Fig. 1). The four cores were stored at 4 °C in the ship. In the laboratory, the cores were cut into 1 cm sub-samples using a stainless steel cutter, then packed in Al foil and stored at –20 °C until analysis.

2.2. ^{210}Pb dating

The ^{210}Pb dating of sediment cores F0306, FFJ103 and C0803 was measured at Nanjing Institute of Geography and Limnology; and the core M7 was analyzed for ^{210}Pb at Institute of Earth Science, Academia Sinica, Taiwan. The measurement of ^{210}Pb was based on the method according to Guo et al. (2007). Briefly, ^{210}Pb and ^{226}Ra activities were measured using an Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detector. ^{210}Pb was determined by gamma emissions at 46.5 keV, and ^{226}Ra by 295 keV and 352 keV gamma rays emitted by the daughter isotope ^{214}Pb following 3 weeks of storage in sealed containers to allow radioactive equilibration. $^{210}\text{Pb}_{\text{ex}}$ was calculated by subtracting ^{226}Ra activities from the total ^{210}Pb activities. The relative error for this method was < 10%. The ^{210}Pb dated sedimentary rates of sediment cores M7, F0306, FFJ103 and C0803 were 0.64 cm/year, 0.53 cm/year, 0.33 cm/year and 1.05 cm/year, respectively (Fig. 2).

2.3. Measurements of the sediment grain size and dry density

The grain size composition of the sediment samples was determined using a laser Particle Size Analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). The particle sizes were <4 μm for clay, 4–63 μm for silt and >63 μm for sand. The relative error of the duplicate samples was <3%. The four cores were all dominated by clay and silt, with a smaller fraction of sand (Fig. S1). The vertical profiles of grain composition showed a slight variety in the four cores, indicating a stable dynamic sedimentary environment in the mud areas. A pre-cleaned and pre-weighted stainless steel specimen ring (59.96 cm³, 2 cm in height, and 6.18 cm in diameter) was used to collect samples from the wet sediment cores for dry density measurement. After weighing the total wet sample, about one eighth of the wet sample was dried in a 110 °C oven for 24 h for dry weight measurement.

2.4. Analysis of PBDEs

According to the ^{210}Pb dating of four sediment cores (Fig. 2), only a portion of individual cores was used to do PBDE analysis in this work which were 0–40 cm from the top of core M7 (about years 1968–2012), 0–27 cm from the top of core F0306 (about years 1956–2007), 0–40 cm from the top of core C0803 (about years 1969–2009) and 0–15 cm from the top of core FFJ103 (about years 1962–2007),

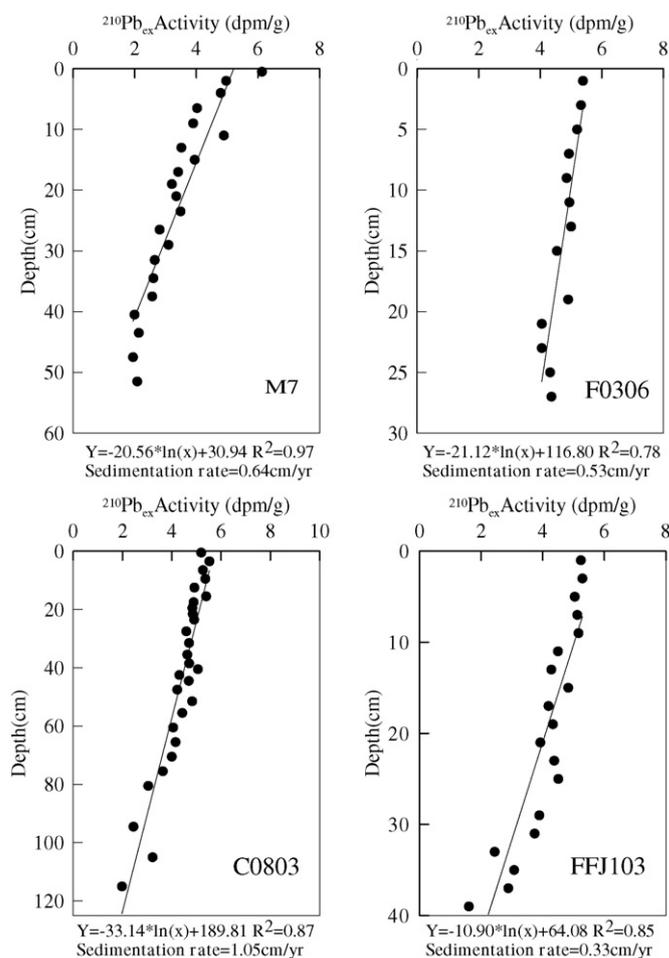


Fig. 2. ^{210}Pb dating of the cores M7, F0306, FFJ103 and C0803.

respectively. A standard mixture of BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190 and a single standard of BDE-209 which were both purchased from AccuStandard, Inc. (USA) were used for quantification. PCB-209 was added as surrogate and BDE-77 was used as an internal standard. The neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were Soxhlet extracted with dichloromethane for 72 h, and sodium sulfate was baked at 450 °C and stored in sealed containers. The determination of PBDEs was based on the method by Li et al. (2012). Briefly, about 10 g samples (freeze-dried, pulverized, and sieved through 80-mesh stainless steel) were spiked with PCB-209 and extracted with dichloromethane in a Soxhlet apparatus for 48 h. Activated copper was added to remove the sulfur in the samples. After extraction, the extracts were concentrated and solvent-exchanged to *n*-hexane using a rotary evaporator. Concentrated extracts were cleaned and fractionated using an 8 mm i.d. alumina/silica column packed with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), sulfuric acid silica (2 cm, 50% on a weight basis), and anhydrous sodium sulfate (1 cm) from the bottom to top. The PBDE fractions were eluted with 50 mL of dichloromethane/*n*-hexane (1:1), and solvent-exchanged to *n*-hexane and concentrated to 0.5 mL under a gentle nitrogen stream. A known quantity of BDE-77 was added as an internal standard prior to instrumental analysis. GC-MS (Agilent GC7890 coupled with 5975C MSD) with negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode was used to measure PBDEs. A DB-5MS capillary column (9 m × 0.25 mm × 0.1 μm) and a longer one (30 m × 0.25 mm × 0.25 μm) were used for BDE-209 and other PBDE congeners, respectively. For BDE-209, the oven temperature was programmed from 130 to 300 °C at a rate of 10 °C/min (hold for 12 min). For other PBDE congeners, the oven temperature set at

130 °C for 1 min, ramped to 155 °C at 12 °C/min, to 215 °C at 4 °C/min, then up to 300 °C at 3 °C/min and hold for 10 min. Injector temperature was 290 °C. 1 μ L sample with split-less injection was performed with a 5 min solvent delay time. Ion fragments m/z 79 and 81 were monitored for tri- to hepta-BDEs, m/z 79, 81, 486.7 and 488.7 for BDE-209, and PCB-209 was monitored using m/z 496, 498 and 500. For each batch of 10 samples, a procedural blank (solvent with a filter paper identical to that used to wrap the sediments) and a spiked blank (14 PBDE congeners spiked into solvent with the filter paper) were processed for quality assurance and control. The detection limits were 50 pg/g for BDE-209 and 0.5 pg/g for other individual PBDE congeners. No target compounds were detected in procedural blanks. The average recoveries for spiked blanks were $88.0 \pm 8.5\%$; and the average surrogate recoveries were $86.7 \pm 9.7\%$.

3. Results

3.1. Concentrations and deposition fluxes of PBDEs

The four cores (M7, F0306, FFJ103 and C0803) were measured for the following 9 PBDE congeners: BDE-28, -47, -99, -100, -138, -153, -154, -183 and -209, and their concentrations are shown in Tables S1–S4. These congeners have also been reported in abundance and high detection frequencies in the coastal air, soils, sediments and water in China (Han et al., 2009; Li et al., 2012; Qiu et al., 2010; Wang et al., 2011). BDE-209 in the environment has been reported to originate only from deca-BDE technical mixtures, and is generally in much higher concentrations than the other lower brominated PBDE congeners, therefore, BDE-209 has been discussed separately from the other PBDEs in most studies (Cai et al., 2008; Li et al., 2012; Darnerud et al., 2001). In this work, \sum_8 PBDEs is defined as the sum of the PBDE congeners minus BDE-209. Overall, the highest concentrations of BDE-209 and \sum_8 PBDEs occurred at the surface or subsurface segments of these cores, having values of 34.2 and 631.2 pg/g in core M7; 141.5 and 625.4 pg/g in core F0306; 49.1 and 229.0 pg/g in core FFJ103; and 140.8 and 842.0 pg/g in core C0803 (Tables S1–S4), respectively. These concentrations were significantly lower than those in coastal or inland locations, such as in sediment cores from the Pearl River Estuary (China), the Great Lakes (USA) and Western Europe countries (Chen et al., 2007; Zegers et al., 2003; Zhu and Hites, 2005). Core C0803 had the highest fluxes of BDE-209 and \sum_8 PBDEs, followed by core F0306 and M7. The deposition fluxes of BDE-209 and \sum_8 PBDEs in C0803 surface sediment layer (about year 2009) were estimated to be 744.5 pg/cm²/year and 124.5 pg/cm²/year, respectively. This higher abundance of PBDEs could be due to the influence of coastal e-waste dismantling/recycling industry in the nearby Taizhou city of Zhejiang Province (Fig. 1) and the higher sediment discharge from the Yangtze River (Chen et al., 2006; Li et al., 2012). The deposition fluxes of BDE-209 and \sum_8 PBDEs in cores M7 were nd (not detected)-294.9 pg/cm²/year and 2.0–16.0 pg/cm²/year and in core F0306 were nd-284.6 pg/cm²/year and 2.4–64.4 pg/cm²/year. Core FFJ103 located far away from the mainland China had the lowest fluxes with the value of nd-48.2 pg/cm²/year and 1.0–10.3 pg/cm²/year. The observed one-order of decrease in PBDE fluxes in these cores with distance from the coast (e.g., from C0803 to FFJ103) further support that the major contribution of these compounds is from the Mainland China.

3.2. Temporal trends of PBDEs

The vertical variations of \sum_8 PBDEs and BDE-209 concentrations in the four sediment cores were shown in Fig. 3. It can be observed that \sum_8 PBDEs were first detected in the sediment layers in the 1960s while BDE-209 in the 1980s. This lag in time in the appearance of these two groups of compounds in the cores coincided with the fact that the deca-BDE technical mixture was used as commercial product 20 years later than the penta- and octa-BDE technical mixtures (Chen

et al., 2006). There were significant increases in both BDE-209 and \sum_8 PBDE concentrations since the post-1990s period with one accord in BS, YS and ECS. The concentrations of BDE-209 in cores M7, F0306, C0803 and FFJ103 increased about 5, 9, 10 and 3 folds from 1990s to the year corresponding the surface or subsurface segments of these cores, respectively; while the concentrations of \sum_8 PBDEs increased only about 2, 3, 6 and 3 folds, respectively. Overall, BDE-209 increased faster than \sum_8 PBDEs since the post-1990s, implying that deca-BDE technical mixture was more widely used than penta- and octa-BDE technical mixtures in China. The latter were in the phase out legislation due to the growing environmental and human health concerns globally and they were banned in 2007 in China (Cai et al., 2008; Mark et al., 2006).

More importantly, on the basis of a comparison of historical surface sediment concentration data, there is almost no clear sign of declining trend in concentrations of PBDEs following their increase from the post-1990s, indicating that the continuous source emission of PBDEs still exist and even increase in the current environment of China. As a typical group of anthropogenic brominated flame retardants (BFRs), PBDEs are still added in industrial and commercial products (Rahman et al., 2001). Prior to the end of production in 2004, ~95% of penta-BDE was used as an additive flame retardant in flexible polyurethane foam materials; while deca-BDE was mostly added in various electrical and electronic products (Rahman et al., 2001). Until now, PBDEs were detected in many products which largely exceeded the residual concentration detected in environment media (e.g. soil, water, and sediments) in China. Chen et al. (2009b) reported that \sum_{16} PBDEs were detected with a median concentration of 53,000 ng/g; while BDE-209 had the highest concentration of 4,232,000 ng/g and a median value of 34,300 ng/g in the various hard plastic toys in China. Huang et al. (2010) reported that the median concentrations of BDE-209 and \sum_9 PBDEs were 71,820 ng/g and 313.4 ng/g in TV dust; while 61,255 ng/g and 146.3 ng/g in computer dust (Table S5). PBDE concentrations in indoor dust were higher than that in outdoor dust which might suggest the off-gassing of PBDEs from the housing of electrical and electronic equipment (Huang et al., 2010). This implies that a link might exist between the major emission sources of PBDEs and the household products during their life cycle. Time relationships of BDE-209 and \sum_8 PBDE concentrations in cores M7, F0306, FFJ103 and C0803 with the production of some electrical and electronic products in China were shown in Fig. 4. In fact, China experienced a rapid growth of manufacturing activities, and became the global processing factory from the 1990s, especially for electronic and telecommunication equipment, such as household appliance, computer and phone. From 1990 to 2013, the household consumption expenditure (HCE) of China increased about 18 times, from US\$135 to US\$2542 (<http://www.stats.gov.cn>). The production of household appliance (including color TV, refrigerator and washing machine) increased about 13 times, from 20 to 300 (million unit) from 1990 to 2013. Due to the popularity of computer and mobile phone from 1990s, the productions sharply increased about 70 and 120 folds from 1998 to 2013 respectively, and about 80% of mobile phones might export to other countries in recent years. BDE-209 was dominant used PBDEs added in various electronic equipments, so that the relationships of fluxes of BDE-209 with the production of household appliance, computer and mobile phone in China were examined for the period of 1990–2013. Good correlation for BDE-209 concentrations of core M7, F0306, FFJ103 and C0803 with the production of household appliance (R^2 was 0.62, 0.84, 0.71 and 0.65 in sequence) and the sum of computer and mobile phone (R^2 was 0.42, 0.96, 0.73 and 0.67 in sequence) ($p < 0.01$) were conducted, showing a good synchronous increase between them since the post-1990s. This result suggests that the release of PBDEs occurred in the production and processing of those products would be a major source for PBDEs in the environment of China. Therefore, the rapid increase of PBDEs from the 1990s in sediment cores in China could be chiefly attributed to the booming of the manufacturing activities in China.

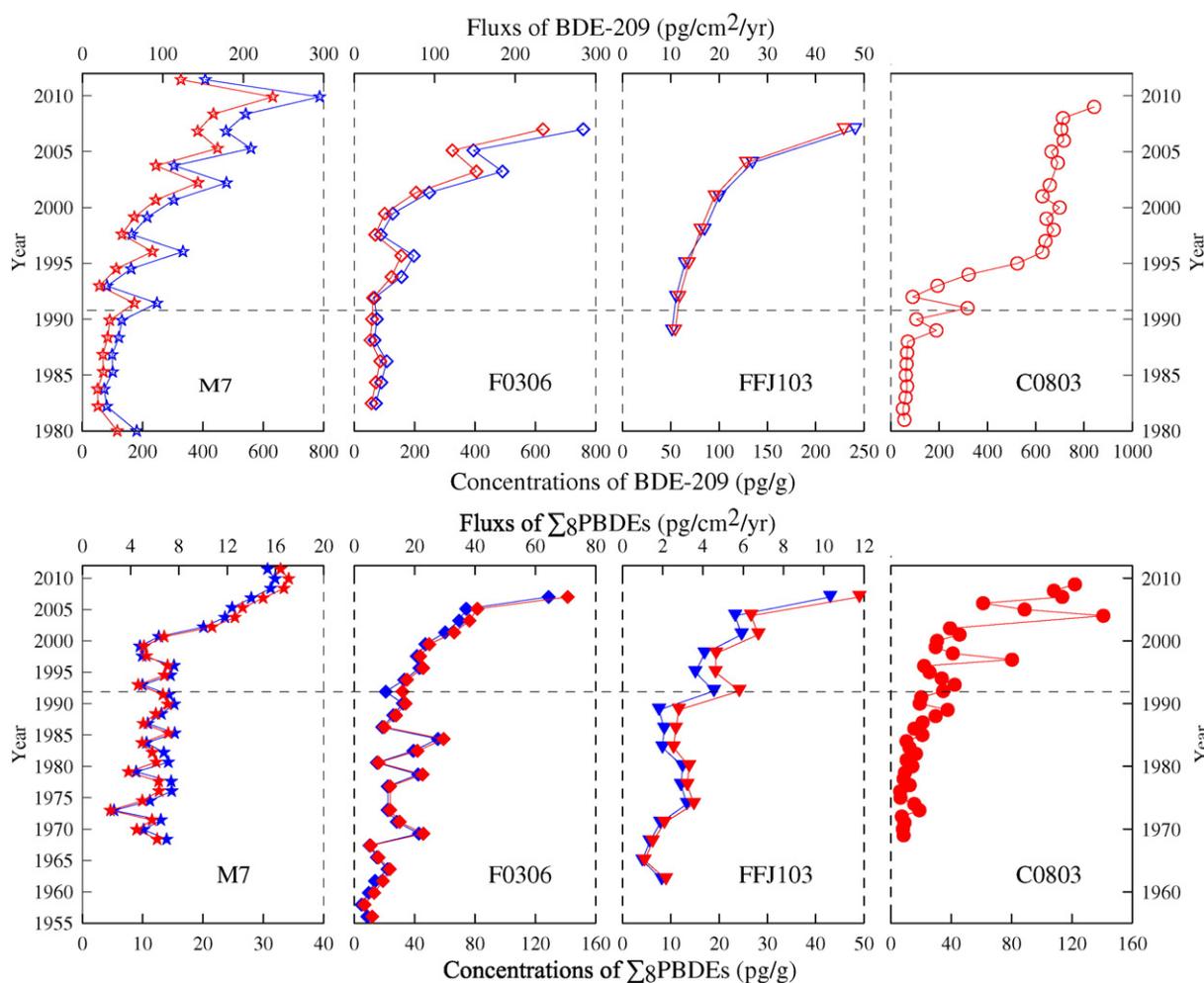


Fig. 3. Vertical profiles of concentrations and deposition fluxes of BDE-209 and Σ_8 PBDEs in core M7 in BS, core F0306 in YS and cores FFJ103 and C0803 in ECS.

4. Discussion

4.1. Implication for the transfer of PBDE pollution from developed countries to China

In U.S.A., it was reported that the Σ_{12} PBDEs and BDE-209 concentrations increased exponentially from the 1960s to 1980s, and after which they leveled off in the sediment core collected from the Lake Michigan (Zhu and Hites, 2005). Historical trends of PBDEs were investigated in three countries of Western Europe, and found that the penta-BDE-derived congeners and BDE-209 were almost detected leveling off and decrease in the early or late 1990s (Zegers et al., 2003). Besides, PBDE concentrations in archived blubber tissues of Northern fur seals from Sanriku, Japan, increased during 1972–1994 sampling (increased to about 150 times between 1972 and 1994), and then decreased by 50% during 1997–1998 (Kajiwara et al., 2004). In the industrial regions of Europe, PBDEs in human breast milk increased from the mid-1970s to late 1997, and then these levels appear to be leveling off or declining, which were probably attributed to the regulatory measures in Europe to halt or regulate the use of penta- and octa-BDE products (Li et al., 2014a). In comparison, there was a persistent increase and almost no sign in the decline of PBDEs in China. This was consistent with that significantly increasing temporal trends were observed for PBDEs in Chinese sturgeon eggs from 1984 to 2008 (Sun et al., 2015). Coincidentally, there is a faster increase from 1990s in China, when opposite trends occurred in many developed countries during the same period.

Although accurately annual production and consumption data of PBDEs were deficient, sporadic data still could reveal that the world

demands of PBDEs were increasing in the past decades. Annual worldwide consumption of technical PBDE products in 1999 was estimated to be 67,000 t (de Wit, 2002); while it reached 200,000 t in 2003 (Lee and Kim, 2015). The global consumption of deca-BDE mixture as the major technical PBDE products increased about 2 fold from 1999 to 2003. Hence, under the premise of the persistent increase for consumption of PBDEs in the world, there just has been a transfer of production and usage of PBDEs from developed countries to developing countries, leading to the different time trends of PBDEs between them. Actually, China is becoming the most famous processing plant of industrial products in the world since 1990s. The export of those products has sharply increased in the past decades (the value of total export and industrial product export of China were shown in Fig. S2), e.g. about 80% of mobile phones in the world might be produced and assembled in China. As a result of a booming manufacturing sector, raw materials and equipment added PBDEs as additive flame retardants were largely imported to China from North America and Europe, inevitably leading to a release of PBDEs to the local environment greatly through volatilization and leakage during the production. Therefore, the coincidence time (from 1990s) when PBDEs appeared sharply and persistent increase in China while the PBDE pollution was gradually leveling off or even declined in some developed countries, could imply a transfer of PBDE pollution from developed countries to China.

4.2. Additional contribution from the e-waste recycling on the coastal ECS

Besides the direct emission from PBDE-consuming manufacturing industries in China, foreign wastes, especially e-wastes, were shipped

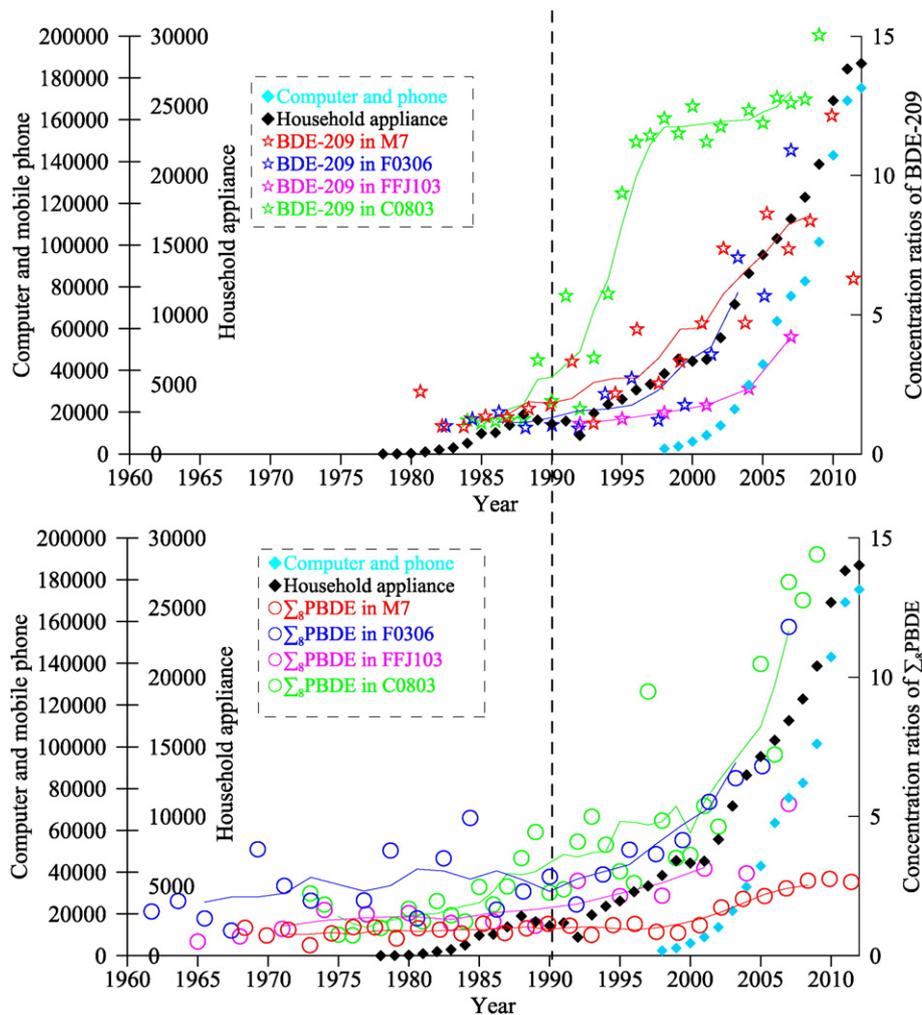


Fig. 4. Time relationships of the BDE-209 and \sum_8 PBDE concentrations in cores M7, F0306, FFJ103 and C0803 with the production of some electrical and electronic products in China (<http://www.stats.gov.cn>).

to developing countries for recycling/disposal (Martin et al., 2004). About 80% of computer e-waste is shipped to Asia, in which 90% of these exports have been sent to China due to illegal imports (Chen et al., 2009a; Schwarzer et al., 2005). To our knowledge, PBDEs dissolve in the polymers and can therefore easily escape from these products during their disposal, especially when the material dismantling is becoming a key disposal method of e-waste and plastic waste in China due to relatively low level of investments and simple technology requirements. This makes the recycling centers to be as a primary source of PBDEs in the local environment. High PBDE concentrations have been found in soils, sediments, atmosphere and organisms (including humans) in e-waste recycling areas, plastic waste recycling centers in China (Guo et al., 2015; Leung et al., 2007; Tang et al., 2014; Wang et al., 2011; Zhang et al., 2011).

The concentration of PBDEs in core C0803 could provide reasonable evidence for the contribution of e-waste recycle to the PBDE pollution in China. As seen in Fig. 2, C0803, because of its location (Fig. 1), exhibits a significantly higher concentration and growth property than those in other three cores. The inner shelf of ECS (C0803) is a sink of land and river sediment discharges from the Yangtze River and neighboring Zhejiang Provinces. The latter is one of the largest e-waste processing centers (Taizhou) in China (Fig. 1). The concentration of BDE-209 in core C0803 rapidly increased from 90.5 pg/g to 674.6 pg/g in 1989–1998 with an average growth rate of 52.1%, which increased faster than \sum_8 PBDEs in the same core. Actually, BDE-209 (deca-BDE technical mixture) is widely added in electrical/electronic products which were

dominantly detected in various environmental media in e-waste recycling areas of Taizhou (Han et al., 2009; Wang et al., 2011; Zhang et al., 2011). The marked increasing stage of BDE-209 during 1989–1998 corresponds to the rapid development of the e-waste recycling industry in Taizhou during this period. Therefore, e-wastes treatment might be another important source of PBDEs, which could intensify the increasing trend of PBDEs in China and was significantly different from that in some developed countries.

4.3. Implication for the treatment of disposal PBDE-containing products

According to the sediment records of PBDEs, the continuous increase of PBDE pollution in China deserves attention greatly. In developing countries, e-wastes are usually not well sorted before disposal in solid-waste landfills, most of which are open dumps without adequate measures to prevent environmental pollution (Kajiwara et al., 2014). On the contrary, the advanced and normative treatment of e-waste in some developed countries was adopted to control the emissions of PBDEs effectively. Sakai (1996) found that the total PBDE observed in the sediments in Japan was not proportional to its electrical and electronic equipment due to employing a system of stringent waste segregation, recycling and reuse of waste including plastic materials and household appliances, and minimal landfilling of incineration residuals, which may be effective in preventing the distribution of PBDE-containing waste into the environment. Osako et al. (2004) compared the concentrations of PBDEs in leachate from landfills in Japan, and

found that high removal efficiency for BFRs in the leachate treatment process was confirmed. In comparison, higher PBDE concentrations were found in leachate from younger landfill facilities in the urban area of China (Li et al., 2014b). Huang et al. (2013) also revealed the elevated PBDE concentrations in topsoil and proved PBDE leakage from one Shanghai municipal landfill. Guo et al. (2015) detected high concentrations of PBDEs (6780–2,280,000 pg/m³) in indoor air of a recycling process for waste TV sets. The PBDE-containing solid-waste disposal from a simple combustion and discard became significant PBDE emission sources nearby and involved a significant risk to workers and communities. This implies that a more stringent regulatory policy and better management of PBDE products, such as improving the collection and treatment technology of PBDE waste, are urgently needed in China.

5. Conclusions

This work examined the time trend of PBDEs in China based on the dated sediment cores collected from East China Seas. The concentrations of PBDEs sharply increased in 1990s and almost no sign of declining trend; while a gradually leveling off or even declining trends appeared in the some major developed countries during the same period. This could provide a significant evidence for the booming of the manufacturing activities in China and further indicates an inevitable transfer of PBDE pollution from developed countries to China. In addition, the highest concentrations and fluxes of PBDEs were detected in the coastal ECS core located near a well-known e-waste recycling area in China, suggesting a high emission from e-waste recycling and disposal operation in the coastal area. Different trend and increasing PBDE levels have been found in China possibly due to the lag behind in terms of nationwide regulation of PBDE usage (in production) and treatment of PBDE-containing products (in disposal). Thus, more stringent policies and management of these PBDE-containing products are urgently needed in China.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2016.04.033>.

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