



# Seasonal variation of polybrominated diphenyl ethers in PM<sub>2.5</sub> aerosols over the East China Sea



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## HIGHLIGHTS

- The seasonal variation of the PM<sub>2.5</sub>-bound PBDEs over ECS was firstly reported.
- PBDEs increase in winter and spring could be attributed to the continental outflow.
- The strong dust storm could increase the PBDE loads to the atmosphere over ECS.
- OC could be a key factor on the PBDE level in PM<sub>2.5</sub> over ECS in warm season.

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## ABSTRACT

PM<sub>2.5</sub> aerosol samples were collected from a receptor site in the East China Sea (ECS) to explore the seasonal variation and sources of polybrominated diphenyl ethers (PBDEs). The concentrations of BDE-209 and total 11 PBDEs without BDE-209 ( $\sum_{11}$ PBDEs) were  $7.1 \pm 6.8$  and  $0.97 \pm 0.52$   $\mu\text{g m}^{-3}$ , respectively. A distinct seasonal variation was observed for both BDE-209 and  $\sum_{11}$ PBDEs, that higher concentrations in winter and spring dominated by the northwesterly winds while lower concentrations in autumn and summer when the southeasterly winds prevailed, suggesting a significant role of continental outflow on the elevated concentrations of PM<sub>2.5</sub>-bound PBDEs in winter and spring. Besides, the strong dust storm could increase the load of PBDEs in continental outflow to the atmosphere over ECS. Differently, due to the absence of continental outflow in autumn and summer, the good correlations between BDE-209 and  $\sum_{11}$ PBDEs implied a potential contribution of the low brominated PBDEs from photoproducts of BDE-209 in high temperature circumstance, while the good correlations of OC with BDE-209 and BDE-99 suggested a significant role of OC in the occurrence of PM<sub>2.5</sub>-bound PBDEs over ECS.

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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardants that are applied to reduce the flammability of many industrial and commercial products such as electrical and electronic products, textiles, plastics, building materials and furnishings. The worldwide production in 1990 was estimated to be 4000, 6000 and 30000 metric tons for Penta-, Octa- and Deca-BDE technical products, respectively (De Wit, 2002). PBDEs can be dissolved in the polymer without chemical bond, thus they can easily escape into the environment during material crushing (Rahman et al., 2001; De Wit, 2002). Since PBDEs were first detected in soil and sludge of the United States in 1979 and in fish

of Sweden in 1981, their environmental occurrence has been of increasing concern due to their persistence, bioaccumulation and toxicity for animals and humans (Szymanska, 1996; Siddiqi et al., 2003; Mai et al., 2005).

With the fast development of China, in particular as a global manufacturing center, the market demand for PBDEs in China has increased markedly over the past twenty years (Mai et al., 2005; Wang et al., 2007). Meanwhile, China has been considered to be the main country for receiving and disposing electronic waste (E-waste) from developed countries (Martin et al., 2004). Consequently, PBDEs have been widely detected in the environment of China. It was reported that the concentrations of PBDEs in air particles in Shanghai were  $108\text{--}744$   $\mu\text{g m}^{-3}$  (Yu et al., 2011), and in Guangzhou  $204\text{--}372$   $\mu\text{g m}^{-3}$  (Deng et al., 2007). Taizhou (Zhejiang province) and Guiyu (Guangdong province), as two well-known e-waste recycling areas, were both revealed to have high concentrations of PBDEs in air (Deng et al., 2007; Han et al., 2009). It has been

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shown that the major emission of PBDEs has shifted from developed countries to China in the last two decades (Wang et al., 2007).

The climate in Northeast Asia and the adjacent oceanic region is influenced substantially by the East Asian monsoon, one of the strongest monsoon systems in the world (Ding and Chan, 2005). The East China marginal seas including the East China Sea (ECS), Yellow Sea and Bohai Sea are heavily influenced by the East Asian monsoon, therefore, understanding the relationship between the fate of East Asian continental pollutants and the East Asian monsoon is essential to assess the impact of continental outflow from China on the occurrence of these toxic chemicals over the East China marginal seas. In order to achieve this goal, remote islands with less local emission in the monsoon transport pathway were chosen as the observation sites. For instance, Gosan, located at the western edge of Jeju Island, ECS (Lee et al., 2006; Kim et al., 2012), and Changdao Island, located at the demarcation line between the Bohai Sea and Yellow Sea (Feng et al., 2007; Liu et al., 2007), were targeted to characterize the continental outflow from North China to the Bohai Sea and Yellow Sea.

ECS is one of the main transport paths of continental outflow from East China and North China to Northwest Pacific Ocean when northwesterly winds prevail. Compared with the studies in the Bohai Sea and Yellow Sea, the influence of continental outflow on organic pollutants from China to the atmosphere of ECS was seldom explored. More importantly, as a major manufacturing center and e-waste recycling area in China, East China is one of the high PBDE emission areas in the world (Chen et al., 2006b; Han et al., 2009; Yu et al., 2011), the impact of PBDEs atmospherically transported from East China to ECS has been even untouched. In this study, Huaniao Island (HNI) (N30.86°, E122.67°), a remote island in ECS, is selected for this purpose (Fig. 1). Total 38 PM<sub>2.5</sub> (aerodynamic diameter of particles in atmosphere <2.5 μm) samples were collected at HNI for four seasons in order to explore the seasonal variation of the PM<sub>2.5</sub>-bound PBDEs in this receptor site, and to reveal the influence of continental outflow on the ambient atmosphere over ECS.

## 2. Materials and method

### 2.1. Sampling site and collection

The PM<sub>2.5</sub> samples were collected at HNI (N30.86°, E122.67°) in ECS approximately 66 km east to the shore off Shanghai. This

island has only a population of ~1000. There is almost no industrial activity on the island, making it an ideal receptor place to assess the continental outflow pollutants from Mainland China to ECS.

A PM<sub>2.5</sub> sampler at a flow rate of 300 L min<sup>-1</sup> (Guangzhou Mingye Technology Company) was used to collect PM<sub>2.5</sub> samples. Total 75 samples were collected in four seasons from October 25, 2011 to August 14, 2012. There was one operational blank sample (sampling passively) in each season. Each sample was usually collected about 24 h. Quartz filters (8 × 10 in PALL Tissuquartz, 2500QAT-UP, USA) were used to collect PM<sub>2.5</sub>. Prior to sampling, all quartz filters were wrapped with aluminum foil and then baked at 450 °C for 4 h to remove the residual organic contaminants. After sampling, all samples were stored in a freezer at -20 °C until organic analysis.

### 2.2. Materials

All standard mixtures were purchased from AccuStandard, Inc. (USA). 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 were used for quantification. PCB-209 was added as surrogate. BDE-77 was used as an internal standard. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were Soxhlet extracted with dichloromethane for 72 h prior to use. Sodium sulfate was baked at 450 °C and stored in sealed containers.

### 2.3. Extraction and instrumental analysis

Due to their low concentrations in the atmosphere over ECS, the two continuous 24 h PM<sub>2.5</sub> samples were merged as one sample for PBDE measurement. Each sample was spiked with PCB-209 and extracted with dichloromethane in a Soxhlet apparatus for 48 h. After extraction, the extracts were firstly concentrated and solvent-exchanged to n-hexane using a rotary evaporator, and then they were cleaned and fractionated on 8 mm i.d. alumina/silica columns. The columns were packed with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), 50% (on a weight basis) sulfuric acid silica (2 cm), and anhydrous sodium sulfate (1 cm) from the bottom to top. The PBDEs fraction was eluted with 50 mL of dichloromethane/n-hexane (1:1), 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 gas chromatography–mass spectrometer (GC–MS) analysis.

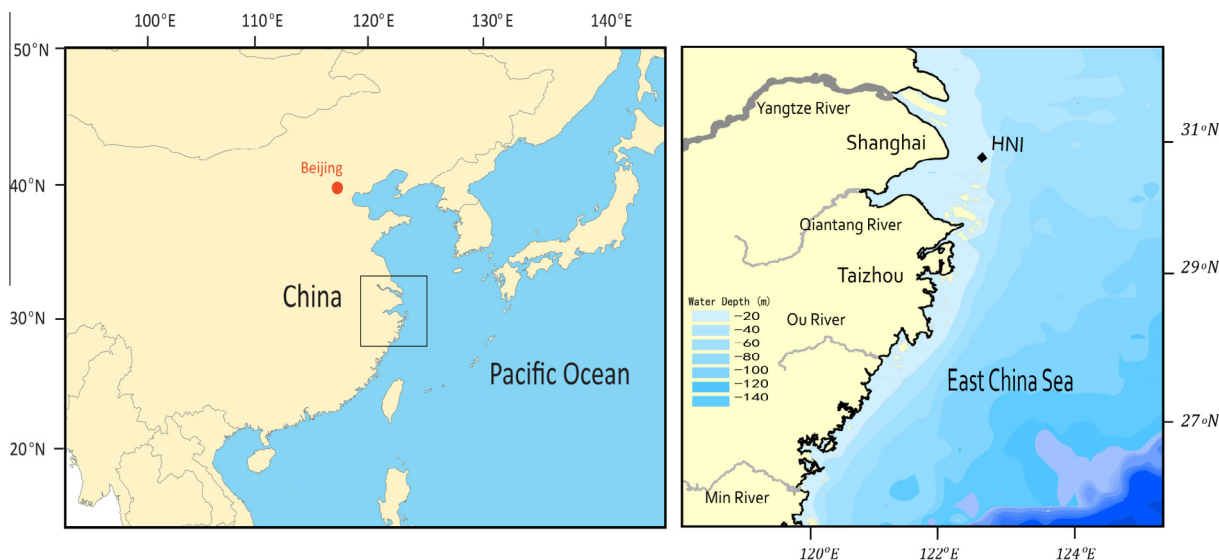


Fig. 1. Map of sampling site at HNI in ECS.

PBDEs were measured by GC–MS (Agilent GC7890 coupled with 5975C MSD) with negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-5MS capillary column (9 m × 0.25 mm × 0.1 μm) was used for BDE-209 and a longer DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) was used for other PBDE congeners. The oven temperature set at 130 °C for 1 min, ramped at 12 °C min<sup>-1</sup> to 155 °C, 4 °C min<sup>-1</sup> to 215 °C, then up to 300 °C at 3 °C min<sup>-1</sup> and hold for 10 min. Injector temperature was 290 °C. Split-less injection of a 1 μL sample was performed with a 5 min solvent delay time. Ion fragments *m/z* 79 and 81 were monitored for tri- to hepta-BDEs, and *m/z* 79, 81, 486.7 and 488.7 for BDE-209, while PCB-209 was monitored using *m/z* 496, 498 and 500.

#### 2.4. Quality assurance/quality control

For each season, one parallel operational blank sample was processed with the same extraction and instrumental analysis. No target compounds were detected in these samples. The surrogate recovery in those samples was 72.8 ± 11.0% for PCB-209. The limit of detection was 0.04 pg m<sup>-3</sup> for BDE-209 and 0.01 pg m<sup>-3</sup> for other individual PBDE congeners except BDE-209.

#### 2.5. Organic carbon (OC) analysis

Only a 0.544 cm<sup>2</sup> punch area of each sample was used to analyze the OC fractions by the IMPROVE thermal/optical reflectance (TOR) method with Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer. The targeted carbon fractions include four OC (OC1, OC2, OC3, OC4), and a pyrolyzed carbon fraction (OP). These fractions were produced under various temperature and oxidation conditions, with four OC fractions in pure He atmosphere at 140 °C (OC1), 280 °C (OC2), 480 °C (OC3) and 580 °C (OC4), respectively. OP is determined as reflecting a transmittance laser light attained its original intensity after oxygen was added to the analysis atmosphere. OC was calculated as OC1 + OC2 + OC3 + OC4 + OP.

### 3. Results and discussion

#### 3.1. Concentrations of PM<sub>2.5</sub>-bound PBDEs

Twelve PBDE congeners were detected including BDE-17, -28, -47, -66, -71, -85, -99, -100, -153, -154, -183 and BDE-209. The detection frequencies ranged from 63% to 100%. BDE-47, -99, -100 and BDE-209 were detected in all samples, followed by BDE-153 and BDE-154 with the detection frequencies of 92% and 87%, respectively. These PBDE congeners were also widely detected in other environmental media in China, such as sediment and soil (Mai et al., 2005; Chen et al., 2006b; Wang et al., 2009), implying that the pattern of PBDE pollution in the atmosphere over ECS was similar with that of Mainland China. In most studies, ∑PBDEs was defined as the sum of all targeted PBDE congeners without BDE-209 (Su et al., 2007; Han et al., 2009). Similarly, BDE-17, -28, -47, -66, -71, -85, -99, -100, -153, -154 and BDE-183 were expressed as ∑<sub>11</sub>PBDEs in this study. The concentrations of measured 12 PBDEs were listed in four seasons in Table 1. The yearly average concentrations of ∑<sub>11</sub>PBDEs and BDE-209 were 0.97 ± 0.52 pg m<sup>-3</sup> (0.23–2.1 pg m<sup>-3</sup>) and 7.1 ± 6.8 pg m<sup>-3</sup> (0.75–31.8 pg m<sup>-3</sup>), respectively. Overall, BDE-209 was the dominant congener which was fivefold higher than ∑<sub>11</sub>PBDEs in PM<sub>2.5</sub>. The concentrations of BDE-209 in different seasons displayed in descending order as followed: winter 11.8 ± 7.2 pg m<sup>-3</sup>, spring 8.9 ± 8.1 pg m<sup>-3</sup>, autumn 3.8 ± 1.8 pg m<sup>-3</sup> and summer 2.7 ± 2.5 pg m<sup>-3</sup>, respectively. A similar trend for ∑<sub>11</sub>PBDEs was found that higher levels in winter (1.3 ± 0.64 pg m<sup>-3</sup>)

and spring (1.2 ± 0.42 pg m<sup>-3</sup>) while lower ones in autumn (0.58 ± 0.23 pg m<sup>-3</sup>) and summer (0.63 ± 0.14 pg m<sup>-3</sup>). The PBDEs in atmospheric particles were widely detected in various places of the world (Han et al., 2009; Wang et al., 2012; Li et al., 2012a). The comparisons of atmospheric PBDE concentrations at HNI in ECS with those from other regions were summarized in Table 2. It should be noted that different numbers of target compounds (PBDE compounds) were employed in different studies. In addition, some reports focused on the distribution of PBDEs on aerosol particles of different sizes. Mandalakis et al. (2009) reported that more than 46% of PBDEs were associated with the particles of <0.57 μm in diameter. In the atmosphere of Taizhou (a major E-waste dismantling area in China), the average PM<sub>2.5</sub>/TSP ratio of PBDE concentrations was up to 84% in winter while 55% in summer (Han et al., 2009). Nevertheless, these data collected from various published reports at different monitoring stations worldwide could still be useful to assess the current pollution level over ECS. Compared with Guiyu and Taizhou, two major e-waste dismantling areas with serious PBDE pollution (Deng et al., 2007; Han et al., 2009; Chen et al., 2011), the PM<sub>2.5</sub>-bound concentrations of both ∑<sub>11</sub>PBDEs and BDE-209 over ECS were exceedingly low. Especially in Guiyu, the concentrations of ∑PBDEs and BDE-209 presented up to thousands times higher than those in this study (Chen et al., 2011). The concentrations of both ∑<sub>11</sub>PBDEs and BDE-209 over ECS were lower than those detected in some urban and rural sites in China (Deng et al., 2007; Yu et al., 2011; Wang et al., 2012), while they were comparable with those in the King George island of Antarctica (Li et al., 2012a), the Atlantic and the Southern Ocean (Xie et al., 2011), but slightly higher than that in the East Greenland Sea (Möller et al., 2011).

#### 3.2. Congener profiles and sources

In general, the distribution pattern of atmospheric PBDEs around source region and adjacent areas is highly related to the usage of these chemicals, land emission resulting from source areas and its physicochemical properties. In this study, the PM<sub>2.5</sub>-bound BDE-209 over ECS was predominant and contributed to 59–98% of the total PBDE concentrations. This was in good agreement with the observations in the surrounding areas of ECS and the fact that BDE-209 was widely detected with high concentrations in China (Rahman et al., 2001). The predominance of BDE-209 (23.4–1306 pg m<sup>-3</sup>) was widely detected in the atmosphere of Taizhou (Zhejiang province), a large receiving and disposing city of obsolete computers and electronic components (Han et al., 2009). The PBDEs in the surface sediments collected from the coastal ECS showed that the congener pattern was mostly constituted by BDE-209 with a mean percentage of 75.8% of total eight PBDE concentrations (Li et al., 2012b). Generally, the sources of PBDEs in the atmosphere can be mainly attributed to the usage of commercial products of PBDEs which are called Penta-, Octa- and Deca-BDE technical mixtures (Siddiqi et al., 2003). Penta-BDE mixture was mainly composed of penta-BDE (50–62%), tetra-BDE (24–38%) and hexa-BDE (4–8%), Octa-BDE mixture contained hepta-BDE (43–44%), octa-BDE (31–35%), hexa-BDE (10–12%) and nona-BDE (9–11%), Deca-BDE mixture almost contained BDE-209 with more than 97% (Darnerud et al., 2001). Due to the relative lower toxicity compared with Penta- and Octa-BDE, Deca-BDE has become a more prevalent product widely used in high impact polystyrene, flexible polyurethane foam, textiles coating (not clothing), wire and cable insulation, electrical and electronic connectors and other interior parts (Rahman et al., 2001; La Guardia et al., 2006). In 2001, the Deca-BDE product accounted for 83.3% of the PBDE global market demand, while the Penta- and Octa-BDE products were only 11.1% and 5.6%, respectively (La Guardia et al., 2006). Besides, Chen et al., 2006a reported that BDE-209 was mainly

**Table 1**  
Seasonal concentration of measured individual PM<sub>2.5</sub>-bound PBDEs over ECS (pg m<sup>-3</sup>).

PBDEs	Autumn	Winter	Spring	Summer
BDE-17	nd <sup>a</sup> -0.15(0.06 ± 0.05)	nd-0.07(0.03 ± 0.02)	nd-0.05(0.01 ± 0.02)	nd-0.03(0.01 ± 0.01)
BDE-28	nd-0.15(0.03 ± 0.05)	0.03–0.15(0.10 ± 0.04)	0.03–0.29(0.12 ± 0.08)	nd-0.09(0.03 ± 0.03)
BDE-47	0.02–0.35(0.16 ± 0.12)	0.05–0.60(0.28 ± 0.21)	0.06–0.35(0.19 ± 0.10)	0.07–0.21(0.13 ± 0.06)
BDE-66	nd-0.08(0.03 ± 0.03)	nd-0.16(0.05 ± 0.05)	nd-0.07(0.04 ± 0.03)	0.03–0.07(0.06 ± 0.02)
BDE-71	nd-0.12(0.04 ± 0.04)	nd-0.08(0.02 ± 0.03)	nd-0.19(0.09 ± 0.05)	0.02–0.09(0.05 ± 0.02)
BDE-85	nd-0.10(0.02 ± 0.04)	nd-0.11(0.03 ± 0.04)	nd-0.07(0.04 ± 0.02)	nd-0.08(0.05 ± 0.02)
BDE-99	0.01–0.31(0.11 ± 0.09)	0.03–0.97(0.34 ± 0.31)	0.10–0.80(0.33 ± 0.24)	0.05–0.17(0.11 ± 0.05)
BDE-100	0.01–0.08(0.04 ± 0.02)	0.02–0.33(0.16 ± 0.11)	0.06–0.31(0.15 ± 0.08)	0.02–0.10(0.05 ± 0.03)
BDE-153	nd-0.04(0.02 ± 0.02)	0.01–0.28(0.11 ± 0.10)	0.04–0.17(0.09 ± 0.04)	0.02–0.07(0.05 ± 0.02)
BDE-154	nd-0.10(0.04 ± 0.04)	0.01–0.26(0.09 ± 0.10)	0.04–0.12(0.09 ± 0.03)	0.04–0.09(0.06 ± 0.02)
BDE-183	nd-0.07(0.04 ± 0.03)	nd-0.18(0.07 ± 0.05)	0.04–0.24(0.09 ± 0.05)	nd-0.07(0.03 ± 0.03)
BDE-209	1.3–6.7(3.8 ± 1.8)	3.4–23.2 (11.8 ± 7.2)	1.8–31.8(8.9 ± 8.1)	0.75–8.7(2.7 ± 2.5)
∑ <sub>11</sub> PBDEs	0.23–0.96(0.58 ± 0.23)	0.34–2.1(1.3 ± 0.64)	0.77–2.0 (1.2 ± 0.42)	0.47–0.92(0.63 ± 0.14)
Total	1.7–7.6 (4.4 ± 2.0)	5.0–23.7(13.1 ± 7.2)	2.7–33.8(10.2 ± 8.3)	1.3–9.6(3.3 ± 2.6)
Tri-BDE	0.02–0.30(0.09 ± 0.09)	0.05–0.19(0.13 ± 0.05)	0.03–0.29(0.13 ± 0.08)	nd-0.10(0.04 ± 0.04)
Tetra-BDE	0.07–0.46(0.23 ± 0.12)	0.11–0.77(0.36 ± 0.22)	0.10–0.51(0.32 ± 0.13)	0.13–0.34(0.24 ± 0.08)
Penta-BDE	0.02–0.34(0.16 ± 0.11)	0.05–1.30(0.52 ± 0.41)	0.24–1.16(0.52 ± 0.28)	0.15–1.27(0.21 ± 0.05)
Hexa-BDE	nd-0.10(0.06 ± 0.04)	0.03–0.47(0.21 ± 0.16)	0.09–0.23(0.18 ± 0.04)	0.07–0.15(0.11 ± 0.04)
Hepta-BDE	nd-0.07(0.04 ± 0.03)	nd-0.18(0.07 ± 0.05)	0.04–0.24(0.09 ± 0.05)	nd-0.07(0.03 ± 0.03)

<sup>a</sup> nd = not detected.

**Table 2**  
Comparison of atmospheric PBDE concentrations (pg m<sup>-3</sup>) in PM<sub>2.5</sub> over ECS with those in other regions.

Sampling sites	∑PBDEs	BDE-209	N <sup>a</sup>	Description	References
East China Sea	0.97	7.1	12	PM <sub>2.5</sub>	This study
<i>e-Waste sites</i>					
Guiyu, China	16575		22	PM <sub>2.5</sub>	Deng et al. (2007)
Taizhou, China	58 (summer) 336 (winter)	186 (summer) 602 (winter)	13	PM <sub>2.5</sub>	Han et al. (2009)
Guiyu China	3354 (summer) 26600 (winter)	1949 (summer) 12374 (winter)	20	TSP	Chen et al. (2011)
<i>Urban and rural sites</i>					
Guangzhou	118–200		22	PM <sub>2.5</sub>	Deng et al. (2007)
Hong Kong	24–196		22	PM <sub>2.5</sub>	Deng et al. (2007)
Shanghai	34–104	59–640	20	TSP	Yu et al. (2011)
Northern China	9.1	37	14	TSP	Wang et al. (2012)
<i>Remote regions</i>					
King George island Antarctica	0.67–2.98		14	TSP	Li et al. (2012a)
East Greenland Sea	0.03–0.46 <sup>b</sup>		10	TSP	Möller et al. (2011)
The Atlantic and the Southern Ocean	0.33		9	TSP	Xie et al. (2011)

<sup>a</sup> Numbers of PBDE congeners.

<sup>b</sup> Including BDE-209.

found in particulate phase, while others were detected in both particulate and gaseous phases. The increase in the bromine content of PBDE congeners could result in a significant decrease of vapor pressure and increase of lipophilicity, which could enhance the absorption of PBDEs to particles (Tittlemier et al., 2002). Therefore, BDE-209 is mainly existed in particulate phase that could induce the higher proportions of BDE-209 to total PBDEs in the fine particles over ECS.

The concentrations of tri- to hepta-BDE, calculated as percent of ∑<sub>11</sub>PBDEs, displayed descending as followed: penta-BDE (sum of BDE-85, 99 and 100), 34.5 ± 13.0% (10.6–63.4%); tetra-BDE (sum of 47, 66 and 71), 32.1 ± 11.2% (11.3–68.9%); hexa-BDE (sum of 153 and 154), 16.4 ± 9.4% (nd-43.9%); tri-BDE (sum of 17 and 28), 10.7 ± 6.6% (nd-31.7%) and hepta-BDE (BDE-183), 6.3 ± 4.1% (nd-14.7%). Large abundance of penta-BDE (dominated by BDE-99 with the percentage of 20.9 ± 11.7% for ∑<sub>11</sub>PBDEs) and tetra-BDE (dominated by BDE-47 with the percentage of 20.4 ± 11.1% for ∑<sub>11</sub>PBDEs) detected in the atmosphere over ECS was consistent with the composition of Penta-BDE technical mixture used in China. Duan et al. (2010) reported that the Penta-BDE technical mixture was another major formula except Deca-BDE technical mixture in the surface soils from the Yangtze River Delta. Taizhou, a major e-waste

dismantling area in China, was also suffered from the pollution of Penta-BDE technical mixture in the atmosphere (Han et al., 2009). Moreover, the high proportion of tetra-BDE and low proportion of hepta-BDE suggested that the influence of physico-chemical properties of PBDE congeners on the PBDEs profile in PM<sub>2.5</sub> was not evident. Therefore, Penta-BDE technical mixture could be considered as another potential source for PBDEs in PM<sub>2.5</sub> over ECS besides Deca-BDE technical mixture (Alaee et al., 2003).

### 3.3. Seasonal variations and the influence of continental outflow from China

As shown in Fig. 2, there were significantly seasonal variations both for the concentrations of ∑<sub>11</sub>PBDEs and BDE-209. Overall, the relatively higher levels of ∑<sub>11</sub>PBDEs and BDE-209 were observed in winter and spring; while the lower concentrations (by a factor of approximately 2–5) were detected in autumn and summer. The continental outflow from Mainland China could be a significant contribution to the increase of PM<sub>2.5</sub>-bound PBDEs in winter and spring, based on the fact that the composition of PBDEs was consistent with the original sources in the surrounding areas of ECS. To further establish the relationship of the PBDE



concentrations with the air mass origins, 3 d air parcel back trajectories from the altitudes of 700 m during the sampling periods were drawn by the Hybrid-Single Particle Intervals Trajectories (HYSPLIT) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (<http://www.arl.noaa.gov/HYSPLIT.php>). Most air masses were originated from the Mainland China in winter and spring; while they were mainly from the remote open sea in autumn and summer (Fig. S1). The air masses during the winter and spring passed over North China or East China, where PBDE congeners were widely detected with higher concentrations in atmosphere of urban and rural areas due to the extensive anthropogenic activities and PBDE emissions (Yu et al., 2011; Wang et al., 2012). Compared with the concentrations of PBDEs in those urban and rural areas, the atmospheric PBDE concentrations in the remote open sea were extremely lower. Thus, high concentrations both for BDE-209 and  $\sum_{11}$ PBDEs observed over ECS were closely associated with continental outflow from China in winter and spring dominated by the northwesterly winds. Differently, the air from the remote open sea should be relatively clean with low concentrations of PBDEs in summer and

autumn when the southeasterly winds prevail. The continental outflow played a key role in the elevated concentrations of PM<sub>2.5</sub>-bound PBDEs in winter and spring.

During the sampling period, one dust episode with high concentrations of PBDEs was observed in March 31 to April 1, 2012. The concentrations of BDE-209 and  $\sum_{11}$ PBDEs were 31.8 and 2.0  $\text{pg m}^{-3}$  in these days, respectively, while the average concentrations in other days in this season were only 6.6 and 1.2  $\text{pg m}^{-3}$ , respectively. According to the back trajectories of March 31 and April 1, 2012 and indicated by notably increased of TSP, Ca and Al concentrations (Wang et al., 2014), ECS was influenced by a strong Asian dust storm originated from North China and Mongolia, and passed over East China in this episode. Wang et al. (2014) also observed the high level of PAHs in this episode and suggested contribution from the long-range transport of East Asian dusts mixed with anthropogenic pollutants in the transport path. It indicated that the strong dust storm could increase the transport load of PBDEs into ECS when passing through the high polluted areas.

It was reported that BDE-209 could be degraded to lower brominated PBDE congeners in the atmosphere under the strong

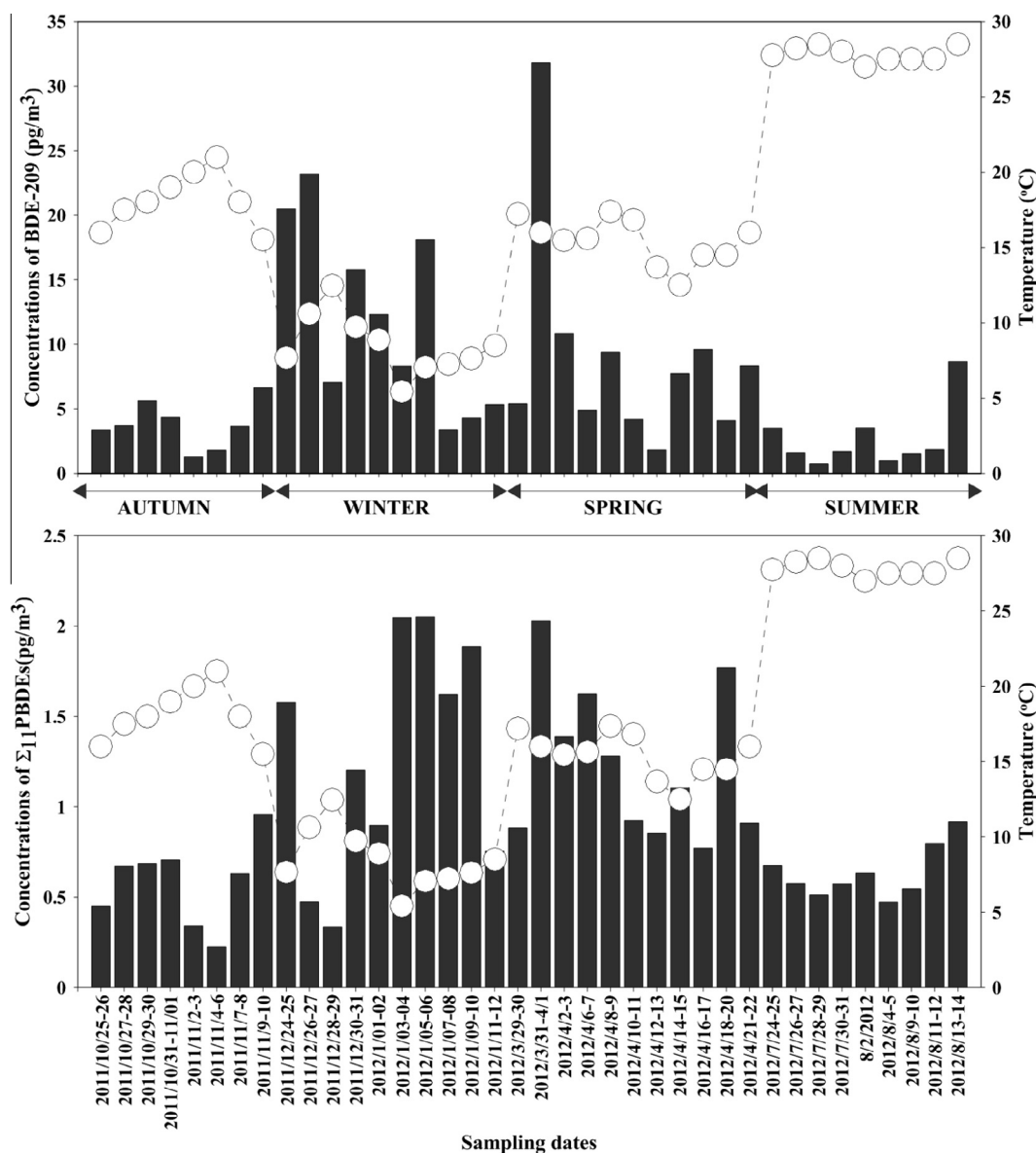


Fig. 2. Daily concentrations of  $\sum_{11}$ PBDEs and BDE-209 in PM<sub>2.5</sub> samples at HNI in ECS.

sunlight (Strandberg et al., 2001; Söderström et al., 2003). Bezares-Cruz et al., 2004 observed that BDE-209 could degrade to 43 PBDEs ranging from nona- to tri-PBDEs, including BDE-17, -28, -47, -85, etc. during 34 h of solar irradiation. In this study, BDE-209 had higher proportions of the total PBDEs in winter and spring (86–98%) compared with those in autumn and summer (59–84%). Besides, there were good correlations between BDE-209 and  $\sum_{11}$ PBDEs in autumn and summer while they did not in winter and spring (Fig. 3). This suggested that photoproducts of BDE-209 could be a potential source to the low brominated PBDEs in autumn and summer. However, due to the continuous and intensive input under the influence of continental outflow in winter and spring, the temporal variation of PBDE emissions in the upwind areas largely determined the relationship between BDE-209 and  $\sum_{11}$ PBDEs in the atmosphere of ECS.

PBDEs were expected to be associated with organic carbon-rich particles during the long-range transport because of their strong lipophilicity (Mai et al., 2005; Li et al., 2009). The relationships of OC with BDE-209, BDE-99 and BDE-47 were shown in Fig. 4. Poor correlations of OC with these three PBDE congeners ( $R^2 < 0.28$ ) were found in winter and spring although the most air masses originated from China. This could be mainly attributed to their different sources and emission areas between OC and PBDEs during the transport pathway, e.g., biomass burning at rural sites could be the important source of OC emission in North China and East China in winter and spring, while PBDE emissions concentrated in urban areas. The two could be unable to reach equilibrium in particles in a short time from Mainland China to ECS. In contrast, there were good correlations of OC with BDE-209 and BDE-99 in summer and autumn. Actually, the good correlations between OC and these chemicals might be attributed to the absence of the continuous and intensive input from continental outflow, and then the absorption of PBDE congeners on OC particles could become a dominant factor in controlling the concentrations of particle-bound PBDEs. Higher brominated congeners appeared to absorb more favorable to OC particles than lower brominated ones as shown by higher correlation coefficients for BDE-209 and BDE-99 than that of BDE-47 (Fig. 4). This finding further provided evidence that the OC could play an important role for the occurrence of PM<sub>2.5</sub>-bound PBDEs over ECS in warm seasons (Fig. 4). The lower brominated PBDEs were easily redistributed or unstable between

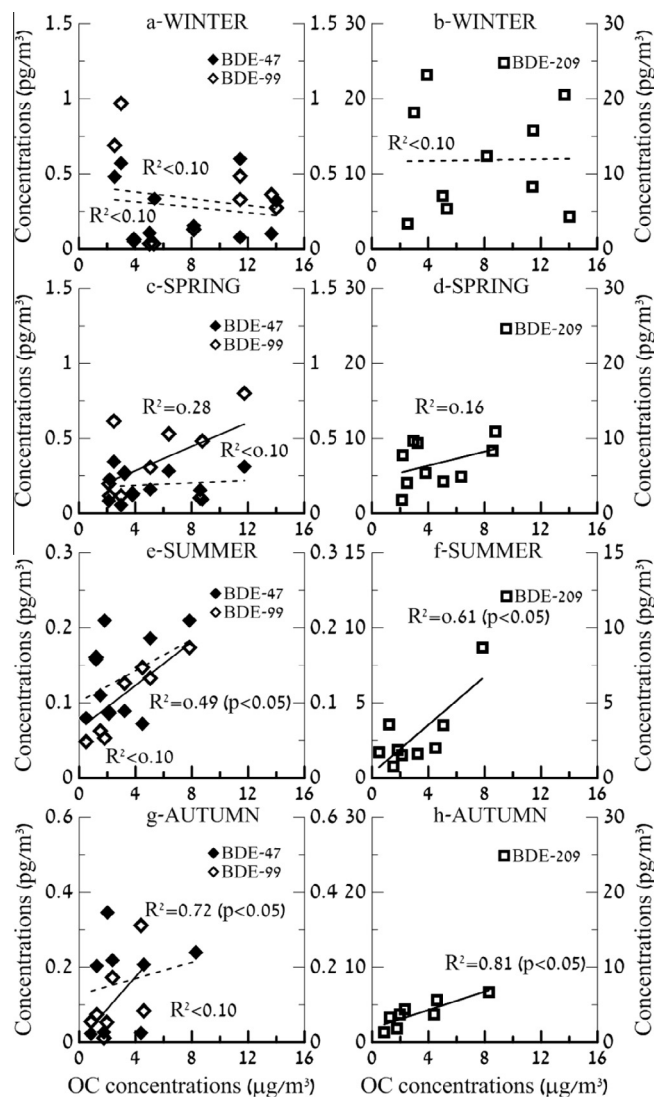


Fig. 4. Pearson correlation coefficients of OC with BDE-209, -99 and -47.

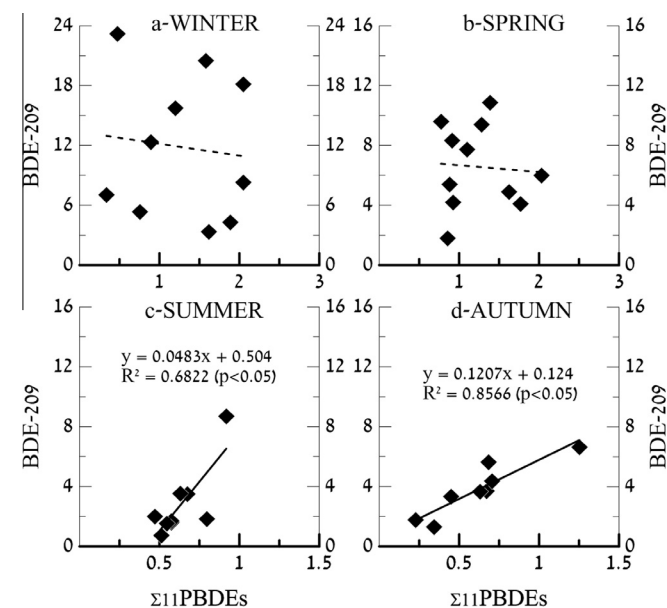


Fig. 3. Pearson correlation coefficients between BDE-209 and  $\sum_{11}$ PBDEs.

particulate phase and gaseous phase in high temperature circumstance (Yang et al., 2013), which likely affected the significance of OC for the adsorption of the lower brominated PBDEs in particles. This could explain the poor correlation between OC and BDE-47 in warm seasons (Fig. 4). The result indicated that the gas-particle partitioning could be another cause for the seasonal variations in the PM<sub>2.5</sub>-bound PBDE concentrations, especially for the low brominated species in warm seasons.

#### 4. Conclusions

The yearly average concentration of total PBDEs in PM<sub>2.5</sub> over ECS was  $8.1 \pm 7.1 \text{ pg m}^{-3}$ . BDE-209 was the dominant congener detected in sampling period, suggesting that the Deca-BDE technical mixture was the major source of PBDEs in PM<sub>2.5</sub> over ECS. BDE-47, BDE-99 and BDE-100 were the most detected congeners among  $\sum_{11}$ PBDEs. This was consistent with the widely usage of Penta-BDE technical mixture in China besides the Deca-BDE technical mixture. BDE-209 and  $\sum_{11}$ PBDEs exhibited a strong seasonal variation with the high concentrations in winter and spring while low in autumn and summer. Based on the back trajectory analysis, it was demonstrated that the continental outflow from China was the main contributor for the increased PM<sub>2.5</sub>-bound PBDEs in

winter and spring. However, due to the absence of continental outflow in autumn and summer, the photoproducts of BDE-209 in autumn and summer could be a potential source for the low brominated PBDEs in PM<sub>2.5</sub>, and the adsorption of PBDEs on the organic particles could play an important role on the PBDE concentrations in PM<sub>2.5</sub> over the region.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.07.083>.

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