



## Polybrominated diphenyl ethers in atmosphere and soil of a production area in China: Levels and partitioning

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### Abstract

Polybrominated diphenyl ethers (PBDEs) were measured in atmosphere and soil samples taken in winter and summer at a PBDE production area of Laizhou Bay in China. The concentrations of  $\sum_{11}$ PBDE were 0.017–1.17 ng/m<sup>3</sup> in gaseous phase, 0.5–161.1 ng/m<sup>3</sup> in particulate phase, and 73–2629 ng/g dry weight in soil samples. The PBDE congener pattern in the gaseous phase differed from that in the particulate phase, and the PBDE congener pattern in the particulate phase was similar with that in soil. This demonstrated that there was little difference with atmospheric particle-soil transfer efficiency among PBDE congeners. In addition, there were seasonal variations in percentages on particle for lower brominated congeners. The BDE-28 was mostly in the gaseous phase in summer (88.3%), whereas the average proportion of BDE-28 in gaseous phase in winter was 38.9%. Higher brominated congeners (i.e., BDE-206, BDE-207, BDE-208, and BDE-209) were bound to the atmospheric particulate phase, and their potentials for long-range migration were mainly affected by the environmental behavior of atmospheric particles. Results indicated that PBDE congeners in summer were closer to gas-particle partition equilibrium than in winter. Temperature should be considered the main factor causing nonequilibrium in winter.

**Key words:** polybrominated diphenyl ethers; atmosphere; soil; partitioning; production area

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### Introduction

Polybrominated diphenyl ethers (PBDEs) as flame retardants are persistent organic pollutants found globally in the environment. They enter the environment during production and migrate from the treated products over their entire lifetimes (Strandberg et al., 2001). Worldwide PBDE production was dominated previously by deca-BDE technical mixture, with an estimated global demand of 56,100 tons in 2001 (BSEF, 2004). The domestic demand for brominated flame retardants (including PBDEs) in China increased at an annual rate of 8% (Mai et al., 2005), with deca-BDE technical mixture amounting to 30,000 tons in 2005 (Zou et al., 2007). Increasing production inevitably resulted in continuously increasing PBDE levels in the environment. To date, however, almost no studies on environmental levels of PBDEs in production areas have been reported. Since PBDEs can enter the environment through atmospheric emission during manufacture, it is more helpful to understand PBDE distribution and environmental processes through investigating the environmental levels surrounding manufacture.

The fate, transport, and removal of persistent organ-

ic pollutants (POPs) from the atmosphere are strongly influenced by their gas-particle partitioning (Cetin and Odabasi, 2007). Like other semi-volatile organic compounds, PBDEs are partitioned between the gaseous and particulate phases in air, and are likely to undergo air-surface exchange and long-range atmospheric transport (LRAT) (Wania and Dugani, 2003; Gouin and Harner, 2003).

The objectives of this research were: (1) to determine PBDE concentrations in atmosphere and soil at a PBDE production area and assess their impact on the local environment; (2) to investigate the spatial variations and factors that control PBDE concentration and distribution in different media; and (3) to further understand the PBDE environmental processes and distribution using data from the production source area.

### 1 Materials and methods

#### 1.1 Air sampling

The south coast area of Laizhou Bay is a major PBDE production area in China. Air samples were taken at six sites: (1) TY site (37°07'31.3"N, 119°00'51.3"E); (2) HZ site (36°58'45.5"N, 118°57'32.8"E); (3)

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TL site (36°59'40.4"N, 118°47'08.5"E); (4) YK site (37°15'56.5"N, 118°51'33.2"E); (5) YZ site (37°02'51.7"N, 119°09'14.8"E); and (6) GH site (37°07'30.8"N, 118°58'52.7"E). The PBDE production factory is situated at the TY site, with the other sampling sites located 20–30 km from the TY site.

Two separate sampling campaigns were undertaken in winter (Jan 22–31, 2007) and summer (Jul 18–29, 2007). During the sampling periods, 46 samples were taken (Table 1). Field blank samples were also collected during the sampling period.

Air samples were collected by a modified high-volume sampler (TE-1000, Tisch Environmental Inc., USA). The compounds in atmospheric particulate phase were collected by 10.2-cm-diameter quartz filters and the gaseous phase compounds were collected in a cartridge containing polyurethane foam (PUF) (6.2 cm diameter, 7.8 cm length). Prior to sampling, quartz filters were baked at 500°C for 6 hr and then cooled to room temperature in a desiccator. The PUF was cleaned by Soxhlet-extraction using 200 mL 1:1 acetone/hexane for 24 hr. After sampling, quartz filters and PUF cartridges were stored at –18°C until analysis. The possibility of chemical breakthrough from PUF was also checked by connecting a second trap in series. No breakthrough was observed and it was assumed that PUF effectively captured the gaseous phase fraction.

## 1.2 Soil sampling

Soil samples were collected at HZ, TL, YK, YZ, and TY at the end of January 2007. Surface soil samples were collected at 0–5 cm depth. Samples were transported back to the laboratory, and stored in clean, solvent-rinsed

stainless steel boxes at –18°C until analysis. Ten gram homogenized soil samples were prepared for extraction.

## 1.3 Materials

The BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-206, BDE-207, BDE-208, BDE-209, <sup>13</sup>C<sub>12</sub>-BDE-209, <sup>13</sup>C<sub>12</sub>-BDE-139, and <sup>13</sup>C<sub>12</sub>-PCB-138 were obtained from Cambridge Isotope Laboratories (Andover, USA). All organic solvents and water were of LC-grade or pesticide-grade, and obtained from Tedia (Osaka, USA). Other chemicals were of analytical grade. Helium gas (99.999%) and methane gas (99.999%) were obtained from HaiPu (Beijing, China).

## 1.4 Analytical method

After extraction, the solvent was reduced to 1 mL by rotary evaporation, and then cleaned with multilayer silica columns (15 mm i.d.) filled from the bottom with 1 g activated silica, 4 g silica/NaOH (1 mol/L), 1 g activated silica, 8 g H<sub>2</sub>SO<sub>4</sub>/silica 44% (W/W), and 2 g silica topped with 4 g Na<sub>2</sub>SO<sub>4</sub>. The sample was eluted with 20 mL hexane and 100 mL hexane/DCM (V/V = 1:1), the first fraction was discarded. The following fraction was collected in an amber vial and reduced to 50 µL by N<sub>2</sub> blow down. The final extract was spiked with quantization standard <sup>13</sup>C<sub>12</sub>-PCB-138 prior to analysis.

The samples were analyzed for PBDEs by a gas chromatograph-mass spectrometer (GC-MS) (Agilent 5975N MS equipped with a 6890 GC, USA). The analytical column was a 30 m × 0.25 mm i.d. DB-5 MS capillary column with a 0.10 µm film thickness (J & W Scientific, Folsom, USA). Initial column temperature was 100°C (held for 2 min) before being increased to 300°C at 4°C/min (held for 25 min). Injector and interface temperatures were 280 and 320°C, respectively. The carrier gas was helium at a flow rate of 1.0 mL/min. A 1-µL pulse splitless injection was analyzed by GC-MS operated with negative chemical ionization source in selected ion monitoring mode. Methane was used as the chemical ionization gas.

The identification of specific PBDEs was performed by comparing peak retention time with a standard solution containing BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-206, BDE-207, BDE-208, and BDE-209. All PBDEs were determined by internal standard, except BDE-209 which was determined by isotope dilution. Two masses *m/z*: 79.0, 81.0 from the molecular ion cluster were used to monitor target compounds, while for BDE-209 *m/z*: 407.6, 486.6 were used. *m/z*: 415.6, 494.6 were monitored for <sup>13</sup>C<sub>12</sub>-BDE-209 and *m/z*: 574.6, 576.6 were for <sup>13</sup>C<sub>12</sub>-BDE-139 as surrogate standard. In addition, *m/z* = 372.0 and *m/z* = 374.0 were used to monitor <sup>13</sup>C<sub>12</sub>-PCB-138 as injection standard.

One procedural blank and one spiked recovery sample containing PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-206, BDE-207, BDE-208, and BDE-209) were run with each batch samples. Field blank samples were collected at each season. The PBDE levels in the blank samples were low enough

**Table 1** Sampling information at all sites

Sample no.	Sampling site	Date(dd/mm/yyyy)	TSP (µg/m <sup>3</sup> )	<i>f</i> <sub>oc</sub> (%)	Mean air temp. (°C)
Summer					
1	HZ	20–21/07/2007	277	2.7	29.3
2	HZ	22–23/07/2007	240	3.2	28.2
3	HZ	24–25/07/2007	286	3.0	29.5
4	HZ	26–27/07/2007	304	4.7	32.9
5	HZ	28–29/07/2007	289	3.3	31.2
6	TY	24–25/07/2007	243	2.0	29.5
7	TY	26–27/07/2007	226	2.7	32.9
8	TY	28–29/07/2007	211	2.4	31.2
Winter					
9	GH	22–23/01/2007	77	5.3	–1.3
10	GH	23–24/01/2007	204	6.0	–1.1
11	YZ	26–27/01/2007	273	6.9	–1.9
12	YK	27–28/01/2007	178	6.4	–1.1
13	YK	28–29/01/2007	227	6.1	0.8
14	TL	29–30/01/2007	294	4.2	1.1
15	TL	30/01–01/02/2007	352	4.2	–0.4
16	HZ	31/01–01/02/2007	294	3.9	–0.7
17	TY	22–23/01/2007	143	6.0	–1.3
18	TY	23–24/01/2007	289	6.9	–1.1
19	TY	24–25/01/2007	390	5.2	–1.2
20	TY	25–26/01/2007	283	4.5	0.5
21	TY	26–27/01/2007	274	7.1	–1.5
22	TY	27–28/01/2007	181	5.4	–1.1
23	TY	28–29/01/2007	268	5.2	0.8

TSP: total suspended particulate; *f*<sub>oc</sub>: fraction of organic carbon.

that we did not correct the concentration in the samples. The recoveries for PUF were (72 ± 9)% (BDE-28), (80 ± 28)% (BDE-47), (66 ± 13)% (BDE-100), (79 ± 25)% (BDE-99), (60 ± 18)% (BDE-154) and (78 ± 25)% (BDE-153). The recoveries for quartz filter were (85 ± 7)% (BDE-28), (72 ± 2)% (BDE-47), (77 ± 18)% (BDE-100), (87 ± 7)% (BDE-99), (91 ± 15)% (BDE-154), and (68 ± 19)% (BDE-153). The detection limit of the method was defined as the mean blank mass plus three standard deviations. Method detection limits for individual PBDEs varied depending on sample size and instrument sensitivity, and ranged from 1–5 pg/g (tri- to nona-BDEs) to 100 pg/g (BDE-209) for soil, 0.02–0.06 pg/m<sup>3</sup> (tri- to nona-BDEs) for gas samples, and 0.07–0.2 pg/m<sup>3</sup> (tri- to nona-BDEs) for particulate samples.

### 1.5 Determination of organic carbon content in sediment

Organic carbon content in the soil and atmospheric particulate phase samples were analyzed using a CHN Elemental Analyzer (Model MT-5, Yanaco, Japan).

## 2 Results

Concentrations of target PBDEs in air and soil are summarized in Table 2. The concentrations range for  $\sum_{11}$ PBDE was 0.017–1.17 ng/m<sup>3</sup> in the gaseous phase and 0.5–161.1 ng/m<sup>3</sup> in the particulate phase. The  $\sum_{11}$ PBDE concentrations in the gaseous and particulate phase were (0.38 ± 0.35) ng/m<sup>3</sup> and (39.0 ± 56.7) ng/m<sup>3</sup> in summer and (0.19 ± 0.23) ng/m<sup>3</sup> and (40.6 ± 47.2) ng/m<sup>3</sup> in winter, respectively. The concentrations in the particulate phase were higher than those in the gaseous phase among all samples, and higher brominated congener class was mainly found in the particulate phase. Air concentrations for BDE-209 were dominated by the particulate fraction and ranged from 0.3 to 126.1 ng/m<sup>3</sup>. The BDE-28 was the most abundant congener in the gaseous phase. For all samples, the observed concentrations at the TY source emission site were significantly higher than other sampling sites. The  $\sum_{11}$ PBDE concentrations in this study were higher than other outdoor air studies. For instance, Ter Schure et al. (2004) reported that BDE-209 levels in air samples from

the Baltic Sea ranged from 1.1 to 74.5 pg/m<sup>3</sup>. In Japan, Hayakawa et al. (2004) observed concentrations of PBDEs of less than 48 pg/m<sup>3</sup> in air. Agrell et al. (2004) reported a median air concentration near a solid waste incineration plant of 10.4 pg/m<sup>3</sup>. Wang et al. (2005a) reported the mean level of 58.3 pg/m<sup>3</sup> for  $\sum_{11}$ PBDE (BDE-28, BDE-47, BDE-66, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-138, BDE-183, and BDE-209) in particulates collected from the Bohai and Japan Seas. Watanabe et al. (1992) reported that the total air level (tri- to hexa-BDEs) in Taiwan ranged from 100 to 190 pg/m<sup>3</sup> in 1991. Total levels of tri- to deca-BDEs in the air of Kyoto and Osaka were also determined in 2001, ranging from 6.5 to 80 pg/m<sup>3</sup> and from 104 to 347 pg/m<sup>3</sup>, respectively (Hayakawa et al., 2004; Ohta et al., 2002). Cahill et al. (2007) showed that indoor concentrations at an electronics recycling facility were as high as 650,000 pg/m<sup>3</sup> for BDE-209. It is worth noting that the concentrations of PBDEs in outdoor air in this study were similar with that of indoor air mentioned above. Therefore, the atmosphere of production source area in the present study demonstrated significant pollution.

In soil, the lowest  $\sum_{11}$ PBDE concentration was 73 ng/g dry weight found in the HZ site. The highest  $\sum_{11}$ PBDE concentration was 2629 ng/g dry weight found in the TY source emission site with a maximum of 2125 ng/g dry weight for BDE-209. The concentrations of PBDEs in soil decreased with increasing distance from the TY source site. This was consistent with recent research (Cetin and Odabasi, 2007). In all soil samples, BDE-209 was the most abundant congener and accounted for 81%–94% of the total. Compared with other studies, the  $\sum_{11}$ PBDE concentrations in this study were higher than levels reported for soils in Europe (Cetin and Odabasi, 2007; Hassanin et al., 2004; Sellström et al., 2005), and were the same as point source polluted soils (close to e-waste dismantling sites) in the Pearl River Delta, China (Zou et al., 2007). Extremely high concentrations of PBDEs (up to 4250 ng/g) were found in soils at an e-waste dismantling site of Guiyu, a small town in Guangdong Province of South China (Wang et al., 2005b; Cai and Jiang, 2006; Leung et al., 2007). However, it was less than our previous study. The  $\sum_8$ PBDE concentrations in soil sampled from the south coast area of

**Table 2** Concentrations of PBDEs in air and soil

Congener	Air concentrations (ng/m <sup>3</sup> )				Soil concentrations (ng/g dry weight)
	Gaseous phase		Particulate phase		Winter (n = 5)
	Summer (n = 8)	Winter (n = 15)	Summer (n = 8)	Winter (n = 15)	
BDE-28	0.100 ± 0.101	0.019 ± 0.029	0.006 ± 0.001	0.029 ± 0.044	0.4 ± 0.4
BDE-47	0.045 ± 0.058	0.001 ± 0.001	0.006 ± 0.002	0.027 ± 0.039	0.4 ± 0.4
BDE-100	0.007 ± 0.010	0.003 ± 0.001	0.003 ± 0.001	0.004 ± 0.001	0.1 ± 0.04
BDE-99	0.032 ± 0.061	0.004 ± 0.003	0.006 ± 0.002	0.011 ± 0.012	0.4 ± 0.5
BDE-154	0.008 ± 0.004	0.004 ± 0.002	0.004 ± 0.001	0.008 ± 0.007	0.7 ± 1.3
BDE-153	0.008 ± 0.003	0.007 ± 0.003	0.013 ± 0.013	0.053 ± 0.093	8.3 ± 16.9
BDE-183	0.005 ± 0.002	0.005 ± 0.003	0.021 ± 0.016	0.041 ± 0.046	10.1 ± 20.2
BDE-208	0.006 ± 0.001	0.003 ± 0.005	0.12 ± 0.15	0.75 ± 1.6	9.4 ± 16.9
BDE-207	0.010 ± 0.002	0.008 ± 0.017	0.21 ± 0.25	1.4 ± 2.9	20.7 ± 38.8
BDE-206	0.009 ± 0.003	0.003 ± 0.008	0.9 ± 1.2	2.2 ± 5.2	60.9 ± 124.3
BDE-209	0.16 ± 0.21	0.14 ± 0.20	37.7 ± 55.1	36.1 ± 39.5	575.8 ± 872.3
$\sum_{11}$ PBDEs	0.38 ± 0.35	0.19 ± 0.23	39.0 ± 56.7	40.6 ± 47.2	687.2 ± 1091.1

Data are expressed as average ± SD.

Laizhou Bay were in the range of 58.2–7190.7 ng/g dry weight (Jin et al., 2008).

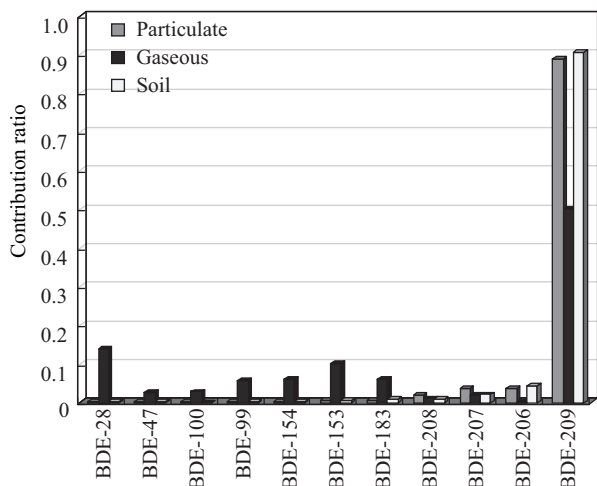
### 3 Discussion

#### 3.1 PBDEs pattern profile in gaseous, particulate phase and soil

Atmospheric deposition is a major source for PBDEs in soil. Moreover, soil is a major reservoir and sink of PBDEs due to their large sorption capacity. Investigating PBDE patterns in air and soil can provide useful information for further understanding their environmental processes and fate. Hence, the PBDE congener pattern profiles of these media were compared in the present study. Figure 1 shows the average percentage contributions of individual congeners to  $\sum_{11}$  PBDE concentrations in gaseous and particulate phases and soil collected in winter from HZ, TL, YK, YZ, and TY. We analyzed whether PBDE congener distributions exhibited statistically significant differences among the gaseous phase, particulate phase and soil. Using 11 variables (the ratio of each PBDE congener concentration to total PBDE congeners), the result of multivariate analysis of variance (MANOVA) indicated that there was a statistically significant PBDE congeners pattern difference between the gaseous phase and particulate phase samples (Hotelling's Trace = 3.19,  $F = 9.86$ ,  $P = 1.07 \times 10^{-7}$ ). However, there was no statistically significant PBDE congener pattern difference between the particulate phase and soil samples in winter (Hotelling's Trace = 1.17,  $F = 1.70$ ,  $P = 0.162$ ). This result indicated there was little difference in atmospheric-particle-soil transfer efficiency among the PBDE congeners. In addition, the congeners profile of soil broadly reflected that of atmospheric particles as noted before (Watanabe et al., 1992; Lee et al., 2004).

#### 3.2 Partitioning of PBDEs between gaseous and particulate phase

Once released in environment, PBDEs exist in the atmosphere in both the gaseous and particulate phase. The fate, transport, and removal of PBDEs from the atmosphere by



**Fig. 1** Contribution ratio of individual congeners to  $\sum_{11}$  PBDEs concentrations in gaseous and particulate phase and soil from HZ, TL, YK, YZ and TY (sampling in the winter).

dry and wet deposition processes are strongly influenced by their gas-particle partitioning. Lower brominated congeners have greater proportions in the gaseous phase at a given temperature than the higher brominated counterparts (Ter Schure and Larsson, 2002). Differences in gas-particle partitioning can lead to differences in atmospheric reactivity and LRAT potential (Wania and Dugani, 2003; Gouin and Harner, 2003). The partitioning of semi-volatile organic compounds between the gaseous and particulate phase are described by a partition coefficient ( $K_p$ ):

$$K_p = \frac{F}{TSP \times A} \quad (1)$$

where,  $F$  ( $\text{ng}/\text{m}^3$ ) and  $A$  ( $\text{ng}/\text{m}^3$ ) are the particulate and gaseous phase concentrations, respectively, and TSP ( $\mu\text{g}/\text{m}^3$ ) is the total suspended particulate matter level in air (Pankow, 1994). The fraction on particles,  $\phi$ , was calculated as:

$$\Phi = \frac{K_p \times TSP}{K_p \times TSP + 1} \quad (2)$$

On the basis of Eqs. (1) and (2), the percentages on particles were calculated for the winter and summer samples, with our results in agreement with measurements of gaseous and particulate PBDEs in the Great Lakes atmosphere by Strandberg et al. (2001) at 20°C. Figure 2 shows the seasonal variation of percentages on particles for PBDE congeners. The average proportion of BDE-28 was 88.3% in the gaseous phase in summer, whereas BDE-28 was only 38.9% in winter. More than 90% of the higher brominated congeners (i.e., BDE-206, BDE-207, BDE-208, BDE-209) were bound to the particulate phase in summer and winter. A significant positive relationship was obtained for  $\log K_{OA}$  and percentage on particles for PBDEs ( $r = 0.774$ ,  $P < 0.01$ ). The  $K_{OA}$  values of the PBDE congeners at 30.6°C and -0.6°C were calculated as  $\log K_{OA} = (A+B)/T$  using the regression parameters ( $A$  and  $B$ ) given by Harner and Shoeib (2002). The higher brominated congeners with a higher value of  $\log K_{OA}$  were bound to particles, and the PBDE congeners in the particles decreased with increasing environmental temperature (Fig. 3). Thus, seasonal variations of percentages on particles for PBDE congeners were observed. The concentrations of lower brominated congeners (i.e., BDE-28, BDE-47) in the gaseous phase significantly increased with increasing temperature, which may lead to long-distance migration of lower brominated congeners via a series of deposition/volatilization processes. As most of the higher brominated congeners (i.e., BDE-206, BDE-207, BDE-208, and BDE-209) were bound to the particulate phase of the atmosphere, their potentials for long-range migration were mainly affected by the environmental behavior of atmospheric particles.

#### 3.3 Evaluation of the gas/particle partitioning

For the low concentrations typically encountered under ambient conditions, the partitioning of organic compounds between air and condensed phases often follows a linear

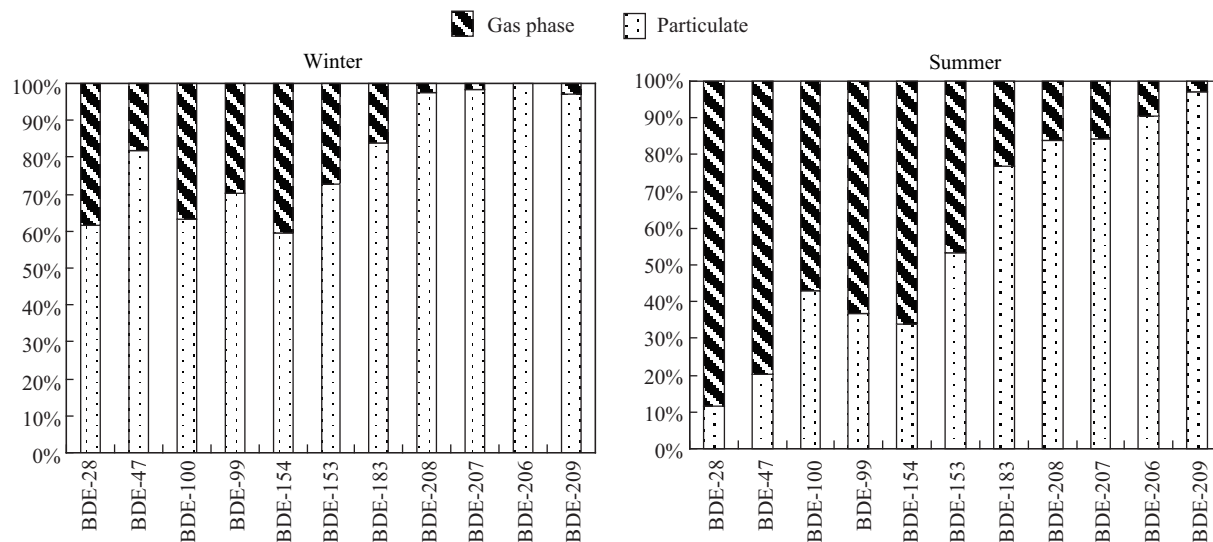


Fig. 2 Seasonal gas-particle partitioning variation of PBDEs.

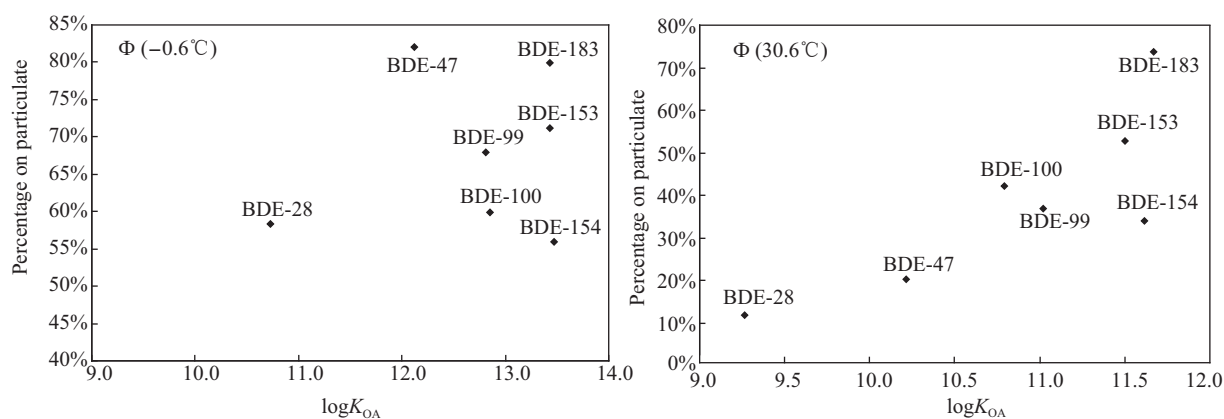


Fig. 3 Average percentage of PBDEs on particles at  $-0.6^{\circ}\text{C}$  and  $30.6^{\circ}\text{C}$ .

isotherm and can be characterized by a partition constant (Goss and Schwarzenbach, 1998). There is still a considerable lack of knowledge regarding partitioning of PBDEs between the atmosphere and other non-aqueous phases. In most cases, it is not clear whether adsorption (partitioning to a surface/interface) or absorption (partitioning into a bulk phase) is the dominating process (Goss and Schwarzenbach, 1998). The Junge-Pankow adsorption ( $P_L^0$ -based) model and the  $K_{OA}$  based absorption model have been conventionally used to predict the fraction of SOCs associated with particle.

A linear fit between  $K_p$  and sub-cooled liquid vapor pressure  $P_L^0$  (Torr) of a specific compound class has often been observed (Harner and Shoeib, 2002) according to the general expression.

$$\log K_p = m \times \log P_L^0 + b_r \quad (3)$$

Plots of  $\ln K_p$  vs.  $\ln P_L^0$  have mostly been used to evaluate experimental gas/particle partitioning data. As discussed by Pankow and Bidleman (1992), experimental field data on gas/particle partitioning may often not represent a true partitioning equilibrium. Therefore, experimental data are assigned symbols  $(F/TSP)/A$  and  $m_r$  that are different from the symbols used for true thermodynamic partitioning ( $K_p$  and  $m$ ). The values of  $\log P_L^0$

Table 3 Values of  $\log P_L^0$  for PBDE congeners at  $30.6$  and  $-0.6^{\circ}\text{C}$

	$\Delta H_{\text{vap}}$	$B$	$A$	$\log P_L^0$ ( $30.6^{\circ}\text{C}$ )	$\log P_L^0$ ( $-0.6^{\circ}\text{C}$ )
BDE-28	79.7	-4162	11.30	-2.40	-3.90
BDE-47	94.6	-4940	12.85	-3.41	-5.20
BDE-99	108	-5640	14.13	-4.44	-6.47
BDE-100	102	-5327	13.37	-4.17	-6.09
BDE-153	110	-5745	13.66	-5.25	-7.32
BDE-154	113	-5901	14.38	-5.05	-7.18
BDE-183	118	-6162	14.43	-5.86	-8.08

for PBDE congeners with  $30.6$  and  $-0.6^{\circ}\text{C}$  in this study were calculated from the Clausius-Clapeyron equation ( $\log P_L^0 = A + B/T$ ) (Table 3). Coefficients  $A$  and  $B$  of the integrated Clausius-Clapeyron equation for PBDEs were obtained from literature (Tittlemier et al., 2002). Table 4 summarizes the observed regression coefficients for  $\log K_p$  ( $\text{m}^3/\mu\text{g}$ ) vs.  $\log P_L^0$  for different seasons for air samples. Significant linear correlation coefficients ( $-0.630 \sim -0.972$ ;  $P < 0.05$ ) were obtained for all sites in summer. However, no significant linear correlation coefficients ( $-0.007 \sim -0.117$ ;  $p > 0.05$ ) were obtained for sampling sites in winter, which was attributed to lower temperature ( $-0.6^{\circ}\text{C}$ ) and higher organic carbon concentration in particles (Table 1) from coal fired heating by local residents in winter.

If it is assumed that measured  $K_p$  values represent a true

**Table 4** Observed regression coefficients for  $\log K_p$  vs.  $\log P_L^0$  for different sampling seasons in air samples

	Sampling site	Slope ( $m$ )	$b$	$r^2$
Summer	HZ	-0.191	-3.533	0.682
	HZ	-0.342	-4.736	0.396
	HZ	-0.287	-3.927	0.914
	HZ	-0.213	-3.642	0.629
	HZ	-0.183	-3.440	0.620
	TY	-0.686	-5.524	0.895
	TY	-0.585	-5.222	0.944
	TY	-0.566	-4.839	0.802
Winter	GH	-0.063	-1.850	0.114
	GH	-0.075	-2.711	0.401
	YZ	0.158	-1.241	0.455
	YK	0.044	-1.852	0.540
	YK	-0.026	-2.344	0.014
	TL	-0.117	-2.863	0.534
	TL	0.031	-2.207	0.023
	HZ	-0.028	-2.365	0.049
	TY	-0.165	-1.984	0.112
	TY	0.002	-1.386	0.000
	TY	-0.066	-2.727	0.177
	TY	-0.248	-3.478	0.745
	TY	0.002	-2.379	0.001
	TY	-0.077	-2.126	0.113
	TY	-0.039	-2.322	0.014

thermodynamic equilibrium, then a slope of  $m$  contains information about the factors that determine the sorption process, e.g., type of adsorbates, adsorbent, temperature, and relative humidity (RH) (Fernández et al., 2002). Extreme values of  $m$  hint at the type of the sorption process: (1)  $m < -1$ , surface adsorption, (2)  $m > -0.6$ , absorption by the organic matter, and (3)  $-1 < m < -0.6$  for coexistence of both mechanisms (Goss and Schwarzenbach, 1998). The  $m$  values (slope) and intercepts in this study varied from -0.183 to -0.686 for summer and 0.158 to -0.248 in winter. Thus, the absorption mechanism should be the dominant sorption process in this study if this kind of direct hint is reasonable. In general, octanol-air partitioning coefficient ( $K_{OA}$ ) is a better descriptor of the gas-particle partitioning than  $P_L^0$  when the absorption mechanism is the predominant gas-particle partitioning process (Finizio et al., 1997).

The logarithmic form of the relationship between  $K_p$  and  $K_{OA}$  can be written as:

$$\log K_p = m_r \times \log K_{OA} + \log f_{om} + \log(10^{-12}(\gamma_{oct}/\gamma_{om})(M_{oct}/M_{om})/\rho_{oct}) \quad (4)$$

where,  $f_{om}$  is the fraction of organic matter in the collected particles;  $\gamma_{oct}$  and  $\gamma_{om}$  are the activity coefficients of the absorbing compound in octanol and particulate organic matter, respectively;  $M_{oct}$  and  $M_{om}$  are the molecular weights of octanol and the organic matter, respectively; and  $\rho_{oct}$  is the density of octanol (0.820 kg/L). Assuming that  $\gamma_{oct}/\gamma_{om}$  and  $M_{oct}/M_{om} = 1$ , Eq. (4) can be written as:

$$\log K_p = m_r \times \log K_{OA} + \log f_{om} - 11.91 \quad (5)$$

The OC content of particles in our samples ranged from 2.4%–7.1%, with an average of 4.7% (Table 1). We assumed organic carbon was equivalent to approximately

50% of organic matter. We used Eq. (5) to predict values of  $K_p$  and the particulate fractions. The gas-particle partitioning ratio of BDE-28 and BDE-47 in summer samples and of BDE-28 in winter samples showed good agreement between measured particulate fractions and those calculated by the equilibrium partitioning model. Similarly, Cetin and Odabasi (2008) observed that BDE-28 showed good agreement between the experimental particulate fractions and those predicted by the equilibrium partitioning model. However, the other PBDE congeners were overestimated by absorption model. Thus, the absorption model is suitable for predicting lower brominated congeners, which are more volatile than higher brominated congeners. In addition, the  $m_r$  values were also calculated using Eq. (5). The median  $m_r$  values for BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, and BDE-183 in summer were 1.06, 0.99, 0.98, 0.94, 0.90, 0.93 and 0.94, respectively; while in winter they were 0.98, 0.91, 0.83, 0.85, 0.79, 0.80 and 0.83, respectively. This result indicated that PBDE congeners in summer were closer to gas-particle partition equilibrium than in winter. Temperature should therefore be considered a main factor causing nonequilibrium in winter at PBDE production areas.

## 4 Conclusions

The PBDE concentrations in the atmosphere at the studied PBDEs production area were high, indicating that PBDEs have seriously polluted the environment of Laizhou South Bay. At the PBDEs production area, the PBDE congener profiles of soil were similar with that of atmospheric particles, suggesting there was little difference in atmospheric particle-soil transfer efficiency among the PBDE congeners. Seasonal variations were also observed in percentages on particles for PBDE congeners. The potentials for long-range migration of the higher brominated congeners were mainly affected by the environmental behavior of atmospheric particles. In addition, PBDE congeners in summer were closer to gas-particle partition equilibrium than in winter, and temperature should be considered the main factor related to nonequilibrium in winter.

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