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# Concentration Levels, Compositional Profiles, and Gas-Particle Partitioning of Polybrominated Diphenyl Ethers in the Atmosphere of an Urban City in South China

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Air samples were collected in June of 2004 from four sites in the city of Guangzhou, a typical urban center in South China, to determine the levels, compositional profiles, and gas-particle distribution of 11 polybrominated diphenyl ether (PBDE) congeners (BDE-28, -47, -66, -100, -99, -85, -154, -153, -138, -183, and -209). The arithmetic mean atmospheric concentrations of  $\Sigma$ PBDEs (sum of all target PBDE congeners except for BDE-209) in samples from the urban and city background sites were comparable to or slightly higher than those from other places around the world. The arithmetic mean atmospheric concentrations of BDE-209, however, were higher than those in North America and Europe, and similar to the values from Japan. Congener compositions were dominated by BDE-209 in all (>70%) but an industrial site, with an average abundance of 48% for BDE-209. The PBDE patterns were generally similar to that in the technical penta-BDE mixture, Bromkal 70-5DE. Partitioning of PBDEs between the gas and particle phases ( $K_p$ ) was well correlated with the subcooled liquid vapor pressure ( $P_L^\circ$ ) for all of the samples, but the relationship differed between samples from different sites. The measured fractions of PBDEs in the particulate phase were compared to the predictions from the Junge–Pankow adsorption and  $K_{OA}$ -based absorption models. The results indicated that the  $K_{OA}$ -based model worked better than the Junge–Pankow model that tended to overestimate the particulate fractions for most PBDE congeners.

## Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of additive flame-retardants that are recognized as ubiquitous

environmental pollutants (1) and are similar in physico-chemical properties to a number of other persistent organic pollutants (POPs). Three major commercial PBDE products (penta-BDE, octa-BDE, and deca-BDE) have been or are used in a wide range of commercial and household products including polyurethane foam, plastics, textiles, and electronics. Degassing from bulk materials allows PBDEs to enter the environment and leads to human exposure. Therefore, the atmosphere has been recognized as an important route for PBDEs and other flame retardants to redistribute.

Air concentrations of PBDEs have been measured at background locations in the Great Lakes region (2), the Canadian Arctic (3), and Europe (4–6), as well as in occupational settings such as electronic recycling and dismantling plants (7–9) and domestic and workplace environments (10, 11). By contrast, only a few studies on the atmospheric distribution of PBDEs in urban locations were conducted in the U.S. and Japan (2, 12–15). These investigations concluded that urban centers were a significant source of PBDEs.

Atmospheric PBDEs, like other POPs, partition between the vapor and particulate phases, which is an important process that affects the deposition, degradation, transportation, and subsequent fate of these environmentally significant constituents. Distribution between the vapor and particulate phases can also be important to human exposure to these potentially harmful chemicals. The gas-particle partitioning of other groups of POPs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) in the atmosphere has been well documented, and a vast number of publications are available in the literature. On the other hand, relatively fewer field data have been acquired for PBDEs (2, 12, 16). Recent measurements of the octanol-air partition coefficient ( $K_{OA}$ ) (17) and vapor pressure ( $P_L$ ) (18, 19) have allowed estimates of the gas-particle partitioning coefficients for PBDEs that are consistent with measured data (2, 16). Hoh and Hites (12) demonstrated that this partitioning was highly dependent on the atmospheric temperature. Clearly, additional efforts are needed to study the partitioning of PBDEs in the atmospheric environment so as to understand their environmental behavior and fate.

This study aimed to address the above-mentioned data inadequacy through intensive sampling of airborne PBDEs in an economically fast growing city, Guangzhou, in South China (Figure 1). Guangzhou, the capital of Guangdong Province, is the largest urban center in southern China with dense population and heavy traffics. About 40% of the annual gross industrial output, estimated at \$70 billion in 2004, was contributed from manufacturing of electronics, automobiles, and petrochemicals. The Pearl River Delta, where Guangzhou situates, is subject to the typical sub-tropical monsoon climate characterized by year-round mild to high temperatures (from 19 to 28 °C), rich rainfalls (annual volume from 1300 to 2280 mm), and strong NW-N breezes in summer and SW-S winds in winter. Because of these attributes, Guangzhou would be an ideal place for sampling of air samples with distinct characteristics.

## Experimental Section

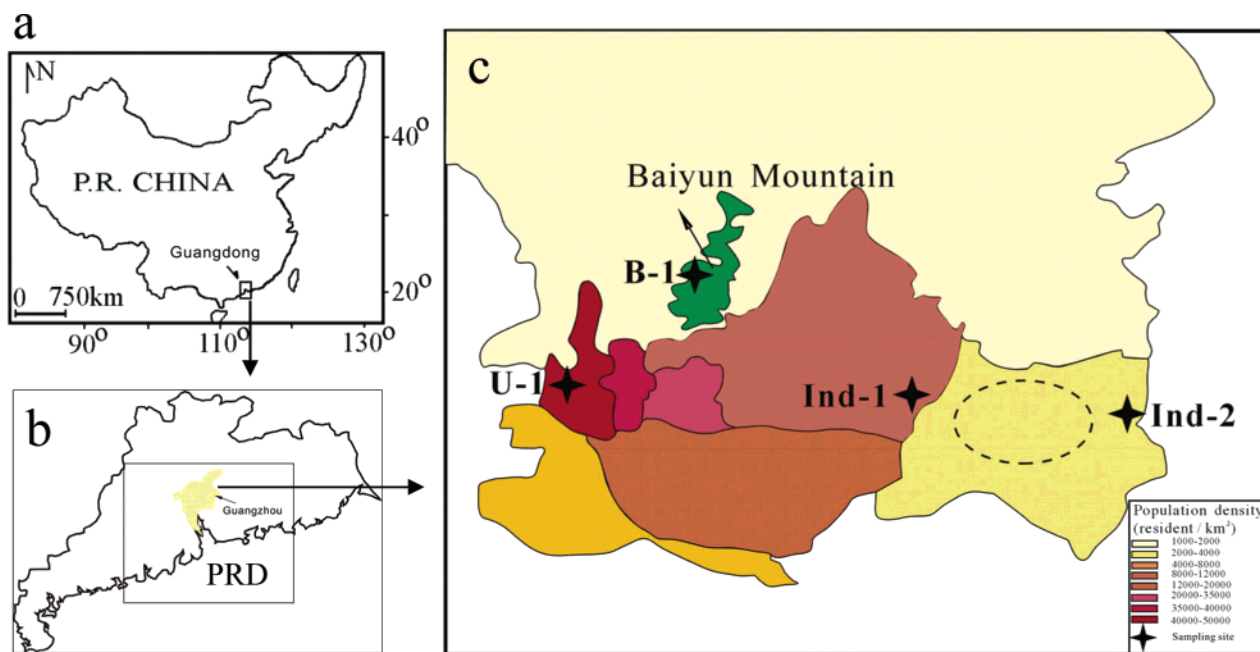
**Sampling Region.** Four sampling sites were so chosen to encompass a range of aerosol types and potential PBDE sources (Figure 1). Two sites are located on the western (Ind-1) and the eastern sides (Ind-2), respectively, of the largest industrial zone of Guangzhou. The industries in this zone include electronic/electrical equipment, plastics, textile,

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**FIGURE 1.** Schematic showing the geographical locality of (a) the Guangdong Province in China; (b) the city of Guangzhou in the Guangdong Province and Pearl River Delta (PRD) region; and (c) the sampling sites within Guangzhou with colors indicating the population densities. The dotted circle indicates the largest industrial zone in Guangzhou.

polyurethane foam, and automobile manufacturing, all of which are heavy users of BRFs. An urban sampling site (U-1) is situated in a typical urban area of Guangzhou, with a population density of 43 000 residents/km<sup>2</sup> and high traffic flows. A city background site (B-1) is on the top of a 350-m hill in the Baiyun Mountain within an evergreen broad-leaf forested area of ~21 km<sup>2</sup> with limited anthropogenic activities. Samplers were deployed on top of high buildings with heights of 15, 10, and 25 m at Ind-1, Ind-2, and U-1, respectively. A sampler was installed outside a radar station at B-1.

**Sample Collection and Preparation.** Thirty-two pairs of samples were collected simultaneously from the four sites during June 15–30, 2004. Air volumes of 417–952 m<sup>3</sup> were drawn at 0.3–0.5 m<sup>3</sup>/min for 24 h through 20.3 cm × 25.4 cm GFF glass fiber filters (Whatman, Maidstone, England), and subsequently through 6.5 cm in diameter × 7.5 cm in thickness (a density of 0.030 g/cm<sup>3</sup>) polyurethane foam (PUF) plugs using a high-volume air sampler. Prior to sampling, GFFs were baked at 450 °C for 12 h to remove any organic contaminant, and PUF plugs were Soxhlet extracted for 48 h with methanol and for another 48 h with an acetone and hexane mixture (1:1). After sampling, loaded GFFs were wrapped with prebaked aluminum foils and sealed with double layers of polyethylene bags, and PUFs were placed in solvent rinsed glass jars with aluminum foil-lined lids, and then transported to the laboratory and stored at –20 °C until extraction. Meteorological data, such as temperature and wind direction, were obtained from the China Meteorological Administration located in Guangzhou. Sampling details are summarized in Table 1.

Prior to extraction, portions of GFF filters were cut out for determination of organic carbon (OC) contents. The extraction protocol was a modified version of a previously described method for processing sediment samples (20). Briefly, the PUF plugs and GFF filters were spiked with PCB 209 and <sup>13</sup>C-PCB 141 and were Soxhlet extracted with a mixture of acetone:hexane (1:1) for 72 h. Activated copper granules were added during extraction to remove elemental sulfur. Concentrated extracts were cleaned and fractionated on acid/basic multilayer silica gel columns with 70 mL of methylene chloride:hexane (1:1). The final extracts containing PBDEs

were concentrated to 200 µL, and a known amount of internal standard (<sup>13</sup>C-PCB 208) was added.

**Chemical Analysis.** Sample analysis was performed with a Shimadzu model 2010 gas chromatograph (GC) coupled with a model QP2010 mass spectrometer (MS) (Shimadzu, Japan) using negative chemical ionization (NCI) in the selective ion monitoring mode with methane as reagent gas. Quantification of tri- to hepta-BDEs (BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183) was carried out with the internal calibration procedure, whereas BDE-209 was quantified with the external standard method. The limit of detection (LOD) ranged from 0.14 to 0.58 pg/m<sup>3</sup> for all congeners except for BDE-209 when an average air volume of 700 m<sup>3</sup> was collected. The LOD for BDE-209 was 14.3 pg/m<sup>3</sup>. Other details were described previously (21).

**QA/QC.** Breakthrough of gas-phase chemicals was tested once at each sampling site by using a second PUF plug (6.5 cm in diameter × 2.5 cm in thickness) in series with the first PUF plug. The PBDE contents in the second plug were less than 5% of those in the first plug for all but BDE-85, which yielded an average of 8%.

Field blanks were prepared by loading a PUF plug and GFF filter to the sampler for 24 h at each site during the sampling period with no air drawing through. Only low concentrations of BDE-47 (average 0.48 and 0.43 ng for PUF and GFF, respectively) and -99 (average 0.94 and 0.68 ng for PUF and GFF, respectively) were detected in the field blanks. The blank levels were less than 5% of the mass in the samples, and they were appropriately subtracted from the sample concentrations. PBDE levels in three solvent blanks were lower than those in the field blanks. The recoveries from six spiking experiments (11 PBDE standards spiked into three clean GFF filters and three PUF plugs) ranged from 73.5% to 86.7%. Two individual samples were subsampled each from the GFF filters for four samples and analyzed. Differences between the duplicate samples were typically less than 20%. The surrogate recoveries in 81 field and laboratory prepared samples ranged from 69% to 118% for <sup>13</sup>C-PCB 141 and from 78% to 104% for PCB 209. Reported concentrations were not surrogate recovery corrected.

**TABLE 1. Collection Data, TSP, and Total PBDE Concentrations (Gaseous + Particle) in Air Samples from Guangzhou**

sample no.	1	2	3	4	5	6	7	8	arith mean	arith SD	geom mean
sampling date	06-15-04	06-18-04	06-19-04	06-20-04	06-22-04	06-28-04	06-29-04	06-30-04			
predominant wind direction <sup>a</sup>	SE	SE	S-SW	SW-W	SE	NW-SE	W	NW			
wind speed (km/h)	10	8	13	8	3	3	5	3			
ambient <i>T</i> (°C)	25–30(27)	26–31(28)	26–32(30)	23–33(28)	22–31(27)	25–35(30)	28–36(32)	28–36(32)			
relative humidity (%)	74	80	72	81	88	69	65	62			
Ind-1 air volume (m <sup>3</sup> )	936.0	897.0	897.0	897.0	897.0	952.2	945.3	952.2	921.7	26.9	921.4
TSP (μg/m <sup>3</sup> )	56.3	88.2	83.9	82.6	228.2	156.7	162.6	154.0	126.6	57.9	115.1
OC (μg/mg)	183.5	121.5	146.5	143.2	198.1	136.0	132.5	133.7	149.4	26.9	147.4
ΣPBDEs (pg/m <sup>3</sup> )	<b>6594</b>	<b>5903</b>	<b>5298</b>	<b>3516</b>	<b>6271</b>	<b>1450</b>	<b>170.4</b>	<b>179.2</b>	<b>3673</b>	<b>2734</b>	<b>1941</b>
BDE209 (pg/m <sup>3</sup> )	<b>230.2</b>	<b>246.2</b>	<b>2382</b>	<b>1692</b>	<b>2981</b>	<b>6975</b>	<b>11 464</b>	<b>7628</b>	<b>4200</b>	<b>4048</b>	<b>2125</b>
Ind-2 air volume (m <sup>3</sup> )	907.2	756.0	756.0	756.0	756.0	756.0	756.0	83.16	690.8	251.2	586.9
TSP (μg/m <sup>3</sup> )	108.9	97.1	131.3	141.4	248.1	241.8	223.8	226.1	177.3	63.5	166.7
OC (μg/mg)	156.2	167.8	165.9	145.7	141.1	150.3	138.6	167.8	154.2	12.0	153.8
ΣPBDEs (pg/m <sup>3</sup> )	<b>172.7</b>	<b>213.0</b>	<b>216.9</b>	<b>263.9</b>	<b>354.3</b>	<b>197.4</b>	<b>168.0</b>	<b>250.7</b>	<b>229.6</b>	<b>60.6</b>	<b>223.4</b>
BDE209 (pg/m <sup>3</sup> )	<b>308.8</b>	<b>233.2</b>	<b>459.0</b>	<b>1420</b>	<b>1231</b>	<b>1160</b>	<b>1017</b>	<b>169.4</b>	<b>749.8</b>	<b>507.5</b>	<b>572.5</b>
U-1 air volume (m <sup>3</sup> )	547.2	501.6	501.6	501.6	501.6	501.6	501.6	501.6	507.3	16.1	507.1
TSP (μg/m <sup>3</sup> )	117.9	134.4	131.8	123.0	192.2	207.7	258.6	215.9	172.7	52.7	165.8
OC (μg/mg)	149.9	169.8	166.7	146.1	157.7	126.4	124.9	131.4	146.6	17.7	145.7
ΣPBDEs (pg/m <sup>3</sup> )	<b>90.7</b>	<b>85.4</b>	<b>76.5</b>	<b>64.0</b>	<b>105.2</b>	<b>81.2</b>	<b>97.5</b>	<b>110.0</b>	<b>88.8</b>	<b>15.3</b>	<b>87.6</b>
BDE209 (pg/m <sup>3</sup> )	<b>99.9</b>	<b>310.8</b>	<b>253.2</b>	<b>116.3</b>	<b>443.7</b>	<b>219.6</b>	<b>399.2</b>	<b>267.8</b>	<b>263.8</b>	<b>121.7</b>	<b>235.7</b>
B-1 air volume (m <sup>3</sup> )	432.0	417.0	432.0	432.0	432.0	432.0	432.0	418.5	428.4	6.6	428.4
TSP (μg/m <sup>3</sup> )	78.5	134.3	141.4	111.3	180.8	217.6	208.3	183.3	156.9	48.7	149.5
OC (μg/mg)	155.3	145.6	118.4	112.8	121.3	111.0	144.8	144.1	131.6	17.5	130.6
ΣPBDEs (pg/m <sup>3</sup> )	<b>90.8</b>	<b>84.6</b>	<b>256.8</b>	<b>41.5</b>	<b>91.4</b>	<b>139.6</b>	<b>76.7</b>	<b>60.4</b>	<b>105.2</b>	<b>67.5</b>	<b>91.3</b>
BDE209 (pg/m <sup>3</sup> )	<b>145.1</b>	<b>268.1</b>	<b>421.4</b>	<b>457.0</b>	<b>888.7</b>	<b>749.8</b>	<b>728.5</b>	<b>165.6</b>	<b>478.0</b>	<b>283.2</b>	<b>395.8</b>

<sup>a</sup> Direction from which the wind blew.

**Organic Carbon Determination.** A Thermal/Optical Carbon Aerosol Analyzer (Sunset Laboratory, Forest Grove, OR) was used to determine OC contents based on thermal-optical transmittance (TOT) using the National Institute for Occupational Safety and Health (NIOSH) Method 5040 protocol.

## Results and Discussion

**Ambient Air PBDE Concentrations and Distribution.** The total PBDE concentration data are summarized in Table 1, whereas the mean PBDE concentrations in the particulate and gaseous phases are reported in Table S1 of the Supporting Information. In the rest of the paper, ΣPBDEs refers to the sum of all target PBDE congeners except for BDE-209. The PBDE concentrations were substantially higher in the air samples collected at Ind-1 for both ΣPBDEs and BDE209 than in other samples. This was consistent with the closeness and relative position of Ind-1 to a large industrial zone as described previously (Figure 1). The PBDE concentrations were significantly affected by the wind directions at this sampling site (Table 1 and Figure S1 in the Supporting Information). A positive correlation ( $r^2 = 0.92$ ) was obtained between ΣPBDEs and the time duration that winds blew from southeast, suggesting that the industrial zone was a major contributor of tri- to hepta-BDEs. On the other hand, a positive correlation ( $r^2 = 0.83$ ) was obtained between BDE-209 and the time duration that winds blew from west. About 3-km southwest of Ind-1 are located several big electronic markets where electronic products (such as computers) are often assembled and dismantled, probably allowing deca-BDE to be released from circuit boards and computer casings to the atmosphere (7, 8). The much lower PBDE concentrations at Ind-2 relative to Ind-1 indicated that the emission from the industrial zone may have been depressed by the prevailing westward and northward winds during the sampling period.

It is interesting to note that both the 8-day arithmetic and geometric mean concentrations of ΣPBDE and BDE-209 were higher at B-1 than at U-1 (Table 1), although U-1 locates in

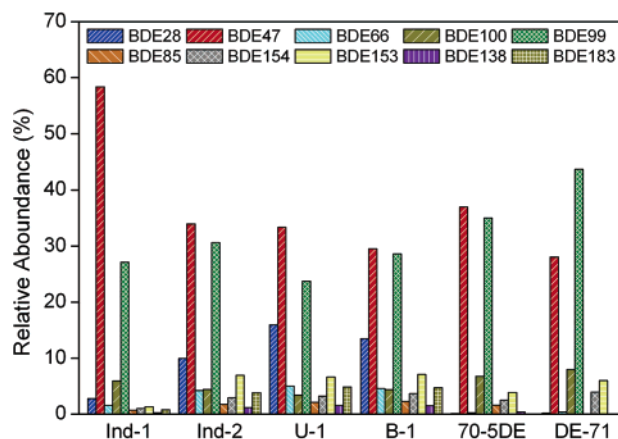
a densely populated area with heavy traffic flows. This is probably because the air quality of B-1 was directly impacted by the industrial zone mentioned above (Figure 1) due to the prevailing northward and northwestward winds typically encountered in summer.

The ΣPBDEs concentrations in the urban and city background sites of Guangzhou were similar to or slightly higher than the comparable data from Chicago (2, 12) and Japan (13–15). In addition, the BDE-209 concentrations in the present study were higher than those in samples collected from North America and Europe and were comparable to those from Japan (Table S2 of the Supporting Information). A plausible explanation for these results may be the higher air temperatures (~30 °C) during our sampling period than those in other studies (e.g., 20 ± 3 °C in Chicago) and the proximity of B-1 and U-1 to populated and industrial areas.

**Congener Profiles and Potential Source.** BDE-209 was the dominant congener among the total PBDEs, with average contributions of 72%, 79%, 48%, and 70% in samples from U-1, B-1, Ind-1, and Ind-2, respectively. Except for five samples with relatively low abundances (3.4–33%) of BDE-209, all other samples contained BDE-209 in the range of 40–99%. The samples with relatively low abundances of BDE-209 were collected from the industrial site Ind-1 where the wind blew from the industrial zone and were dominated by BDE-47 and -99.

The congener profiles in most of our samples were similar to those from Japan (7, 13–15), but were different from those in the ambient air of North America and Europe (2, 12, 22) where the relative abundance of BDE-209 was much lower. The difference in atmospheric PBDE profiles between Asia and North America may reflect the different PBDE formulas predominantly used in the two regions. For example, penta-BDE products are more in demand in North America than in Asia (1). On the other hand, the “absence” of BDE-209 in the atmosphere of Europe (22) was resulted from an analytical bias; that is, BDE-209 was not included in the list of target analytes. In another study on the atmospheric transport of PBDEs to the Baltic Sea (23), air samples collected from the





**FIGURE 2.** Average compositional profiles of PBDEs and commercial penta-BDE technical mixtures, Bromkal 70-5DE and DE-71 (24, 28). The order of the vertical bars follows the eluting sequence on the GC column.

island Gotska Sandön were dominated by BDE-209 and to a less extent by BDE-47 and BDE-99, similar to the results from the present study. Apparently, deca-BDE mixtures are extensively used in both Asia and Europe.

Pearson correlation analyses were performed on the concentration distribution of the 11 PBDE congeners. Significant linear correlations were present among BDE-28, -47, -66, -100, -99, -83, -154, and -153 and between BDE-138 and -183 ( $p < 0.001$ ), whereas poor correlation was found between BDE-209 and all other congeners ( $p < 0.05$ ) (Table S3 of the Supporting Information). This suggests that the commercial penta-, octa-, and deca-BDE formulas are all possible original sources of PBDEs to the atmospheric environment of Guangzhou.

The PBDE patterns in the samples collected from Ind-2, U-1, and B-1 were similar to that in the technical penta-BDE mixture (Bromkal 70-5DE) reported by Sjödin et al. (24) (Figure 2). Two main components, BDE-47 and -99, had a combined relative abundance of greater than 50% of  $\Sigma$ PBDEs, similar to the composition of the penta-BDE commercial formula (24). These two congeners with BDE-100, -153, and -154, usually found in the technical penta-BDE mixture, comprised 61–97% of  $\Sigma$ PBDEs with a mean value of 79% in our samples (Figure 2). Clearly, the penta-BDE commercial mixture is another major BFR product used in Guangzhou, in addition to the deca-BDE mixture. It is interesting to note that the proportion of low molecular weight congeners (e.g., BDE-28 > 10%) in our samples was greater than that (0.11%) in Bromkal 70-5DE (24). This may be explained by the stronger tendency of lower brominated congeners to vaporize relative to higher brominated congeners and the potential decomposition of higher brominated congeners under sunlight (25, 26). In addition, the samples collected from Ind-1 displayed a slightly different compositional pattern (Figure 2) with a much higher relative abundance of BDE-47 than those in the samples from other sites and in Bromkal 70-5DE and DE-71 (24, 27, 28). Although no plausible explanation can be given at this time, it may reflect the complexity of emission rates, transport pathways, and transformation rates for PBDEs in the environment.

**Gas-Particle Partitioning.** The average relative abundances of PBDEs in all sampling sites are shown in Figure S2 of the Supporting Information. The tri-BDE (BDE-28) was present almost exclusively in the gas phase (96–98%), whereas the deca-BDE (BDE-209) was found only in the particulate phase. The tetra- to hepta-BDEs were present in both the particulate and the gas phases. These results were similar to those from a previous study on the atmospheric

PBDEs in the Great Lakes (2). The partitioning of semi-volatile organic compounds (SOCs) between the gas and particle phases is usually defined by the particle-gas partition coefficient,  $K_p$  (29).

$$K_p = (F/TSP)/A \quad (1)$$

where  $F$  and  $A$  are the particulate and gas-phase concentrations, respectively, and TSP is the total suspended particulate. Two different mechanisms have been used to describe the gas-particle partitioning of SOCs, that is, adsorption onto the aerosol surface and absorption into the aerosol organic matter. Both mechanisms lead to a linear relationship between  $\log K_p$  and  $\log P_L^\circ$

$$\log K_p = m_r \log P_L^\circ + b_r \quad (2)$$

where  $P_L^\circ$  is the analyte's subcooled liquid vapor pressure. Under certain conditions, the value of  $m_r$  could be an indication of whether adsorption or absorption is the dominant mechanism that determines the gas/particle partitioning of SOCs (30). The intercept  $b_r$  depends mainly on the properties associated with the aerosols (29, 31). At equilibrium, the slope of eq 2 for either adsorption or absorption should be close to  $-1$ , if the difference between the enthalpies of desorption and volatilization and the number of available adsorption sites remain constant over a compound class for adsorption, or if the activity coefficients remain constant over a compound class for absorption (29, 31). In reality, a variety of  $m_r$  values have been reported for various SOCs (32–35). This variability has been attributed to sampling artifacts, nonexchangeability (36, 37), and a lack of constancy in activities (30). Moreover, even at equilibrium some factors may still cause the slopes  $m_r$  to deviate from  $-1$  (30, 35).

Figure 3 shows the log–log plots of  $K_p$  versus  $P_L^\circ$  for PBDEs measured in the present study. Only the PBDE congeners with detectable concentrations in a given sample were included. The temperature-dependent vapor pressure was calculated for all PBDE congeners based on the method of Tittlemier et al. (19) using the average ambient temperature (27–32 °C) during each sampling time. Significant linear correlations between  $\log K_p$  and  $\log P_L^\circ$  were obtained with  $r^2$  values in the range 0.632–0.905 ( $p < 0.0001$ ), but all of the  $m_r$  values were significantly greater than  $-1$  (from  $-0.762$  to  $-0.607$ ). However, such a deviation does not necessarily indicate disequilibrium. The U-1 samples with the highest correlation coefficient ( $r^2 = 0.905$ ,  $p < 0.0001$ ) between  $K_p$  and  $P_L^\circ$  (Figure 3) agreed with the linear isotherm model for partitioning of airborne pollutants between the gas and particle phases (38, 39), suggesting that PBDEs appeared to be closer to equilibrium between the particle and gas phases at U-1 than at other sites. As Ind-1 and Ind-2 are close to the industrial zone (Figure 1), fresh PBDEs may continue to emit into the atmosphere from local sources so that an equilibrium state could not be established. On the other hand, the lower correlation coefficient ( $r^2 = 0.632$ ,  $p < 0.0001$ ) and higher  $m_r$  value ( $-0.607$ ) in the city background site (B-1) than in the other sites (particularly the urban site U-1; Figure 3) were not entirely anticipated. Two reasons could be provided to explain the difference between B-1 and U-1. First, B-1 is slightly closer to the industrial zone than U-1 (Figure 1), and consequently fresh PBDEs emitted from the industrial zone would travel a shorter distance to B-1 than to U-1. Second, site U-1 is situated in a highly populated area with heavy traffic flows. As a result, TSP in this site should be enriched with soot-type particulates that have a strong tendency to adsorb and/or absorb SOCs including PBDEs.

**Comparison of Adsorption and Absorption Models.** The Junge–Pankow adsorption ( $P_L^\circ$ -based) model and the  $K_{OA}$ -

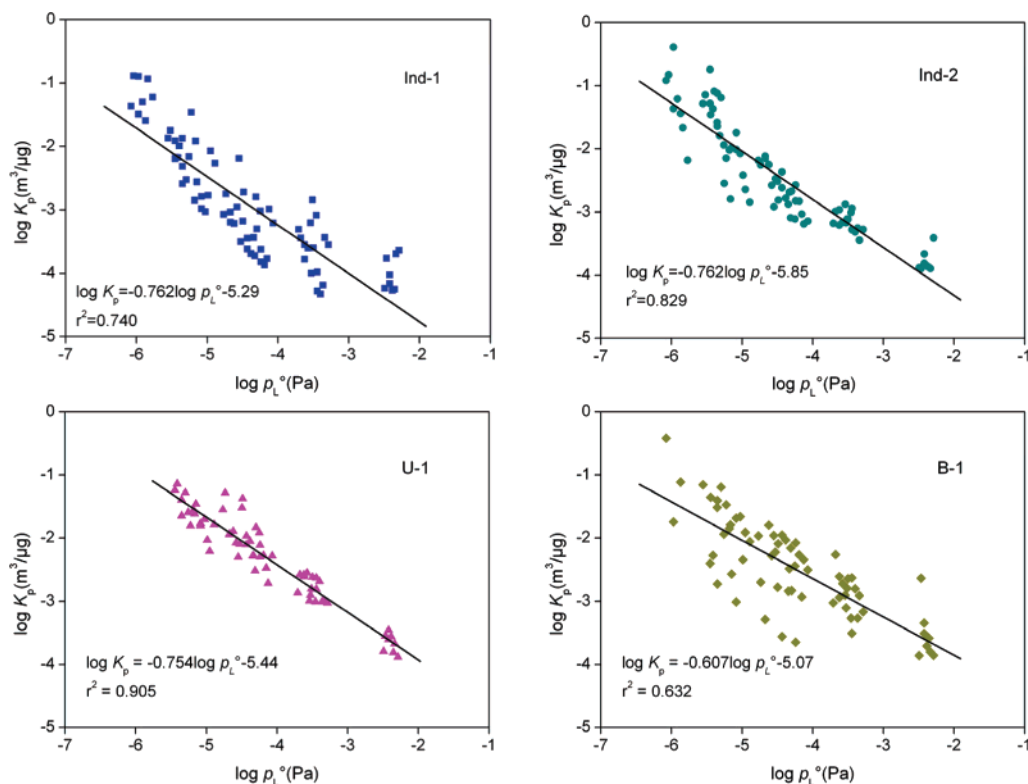


FIGURE 3. Plots of  $\log K_p$  ( $\text{m}^3/\mu\text{g}$ ) versus  $\log P_L^\circ$  (Pa) for PBDEs in all samples.

based absorption model have been conventionally used to predict the fraction of SOCs associate with particles. The classical  $P_L^\circ$ -based model predicts that the fraction ( $\varphi$ ) of SOCs adsorbed onto particles is related to the subcooled liquid vapor pressure ( $P_L^\circ$ ) of the compound and the particle surface area per unit volume of air ( $\theta$ ) by

$$\varphi = c\theta/(P_L^\circ + c\theta) \quad (3)$$

where  $c$  is a constant, relating to the heat of condensation of the chemical and the surface properties. A value of  $c = 17.2 \text{ Pa cm}$  is often used, although Pankow (38) suggested that it might vary with the class of compound. Values for surface area parameter,  $\theta$ , are often assumed to be  $1.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$  for urban air and  $4.2\text{--}35 \times 10^{-7} \text{ cm}^2/\text{cm}^3$  for rural air (40).

Figure 4a compares the percent ( $\varphi \times 100\%$ ) of PBDEs in the particle phase predicted by the Junge–Pankow adsorption model (using  $c = 17.2 \text{ Pa cm}$  and  $\theta = 1.1 \times 10^{-5} \text{ cm}^2/\text{cm}^3$ ) with the average measured values. Each measured  $\varphi$  value was calculated as the amount of the chemical in the particle phase ( $F$ ) divided by the total amount of the chemical ( $F + A$ ):

$$\varphi = F/(F + A) \quad (4)$$

A good agreement was obtained between the predicted and measured  $\varphi$  values for BDE-28 in all sites and BDE-138 and -183 at U-1. However, the Junge–Pankow adsorption model tends to overestimate the sorption of other PBDE congeners (Figure 4a). Overestimating  $\varphi$  values by the Junge–Pankow model was also reported for other classes of SOCs, particularly for PCBs, PCDD/Fs, and PCNs (37, 41–43). In some instances, the model slightly underestimated the sorption of primarily combustion-derived compounds (e.g., PAH) in the particulate phase (37, 40). The disagreement between the modeling and field measurement results can be attributed to the variability of  $c$  and  $\theta$  with respect to the aerosol type (43) and compound class (38, 44).

The  $K_{OA}$ -based absorption model relates  $K_p$  to  $K_{OA}$  and the organic fraction ( $f_{om}$ ) in aerosols (37) via

$$\log K_p = \log K_{OA} + \log f_{om} - 11.9 \quad (5)$$

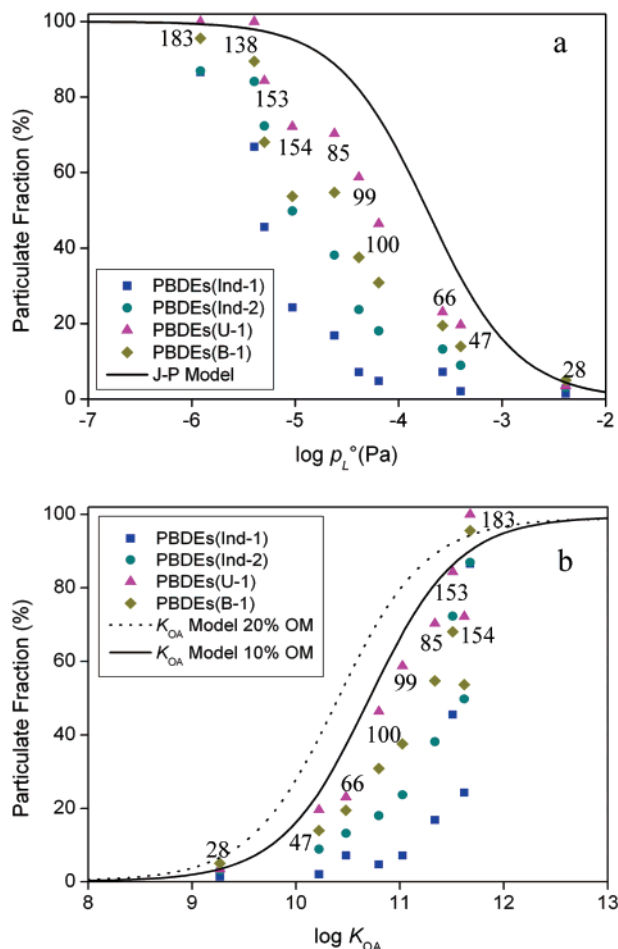
This model can be used to predict the values of  $K_p$  from the knowledge of  $K_{OA}$  and  $f_{om}$  only, if all of the aerosol organic matter is assumed to be available for absorption of gaseous compounds.  $\varphi$  is then calculated from  $K_p$  and TSP through

$$\varphi = K_p \text{TSP}/(1 + K_p \text{TSP}) \quad (6)$$

Values of  $K_{OA}$  have been reported as a function of temperature for several PBDE congeners (17). This method was also used to estimate  $K_{OA}$  values in the present study at the average ambient temperature ( $30.5^\circ\text{C}$ ) of the sampling period. The OC contents of airborne particles in our samples were in the range of 11–20% with an average of 15% (Table 1). If we assume that organic matter present in urban aerosols has, on average, the molecular formula of octanol (74% carbon), 15% of organic carbon would be equivalent to approximately 20% of organic matter. The average TSP was  $158.4 \mu\text{g}/\text{m}^3$ .

Figure 4b shows the particulate fractions predicted by the  $K_{OA}$ -based model with the organic matter contents set at 10% and 20%, which are in the range expected for urban aerosols (37). The  $K_{OA}$ -based model seemed to fit the PBDE data better than the Junge–Pankow model, and in particular well explained the partitioning data from U-1. The gas-particle distribution of PBDEs at U-1 was generally better predicted with 10% of organic matter than with 20%. The absorption model also overestimated the sorption of PBDEs in other sampling sites (Figure 4b), similar to the results from the adsorption modeling (Figure 4a). As discussed earlier, this may be explained by the fact that PBDEs in the atmosphere of site U-1 were closer to the equilibrium state than those of other sampling sites.

The  $m_i$  values from the log–log plots of  $K_p$  versus  $P_L^\circ$  can provide insights into the mechanisms governing the gas-particle partitioning (30). Slopes steeper than  $-1$  are char-



**FIGURE 4.** Comparison of the measured particulate fractions ( $\varphi \times 100\%$ ) of PBDEs with theoretical predictions of (a) the Junge–Pankow adsorption model and (b) the  $K_{OA}$ -based absorption model with 10% (—) and 20% (---) of organic matter.

acteristic of adsorption on particle surface, whereas slopes shallower than  $-0.6$  are suggestive of absorption into aerosol organic matter. The  $m_i$  values ( $0.607$ – $0.762$ ; Figure 3) in the present study are slightly lower than  $-0.6$ , which indeed points to absorption as the dominant mechanism. The  $K_{OA}$  absorption model requires only the knowledge of  $K_{OA}$  and organic matter fraction in aerosols that are both more easily measurable than the parameters required by the Junge–Pankow model. Therefore, there is an incentive to use the absorption model for PBDEs and to measure  $K_{OA}$  as a function of temperature for other brominated compounds of interest.

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### Supporting Information Available

Detailed concentrations of individual PBDE congeners, comparison of the present and other previous studies, Pearson coefficients for PBDEs in all of the samples, relationship between the PBDE concentrations in the Ind-1 samples and the wind directions, and the distribution of PBDEs between the gas and particulate phases. This material

is available free of charge via the Internet at <http://pubs.acs.org>.

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