

# Size-Dependent Dry Deposition of Airborne Polybrominated Diphenyl Ethers in Urban Guangzhou, China

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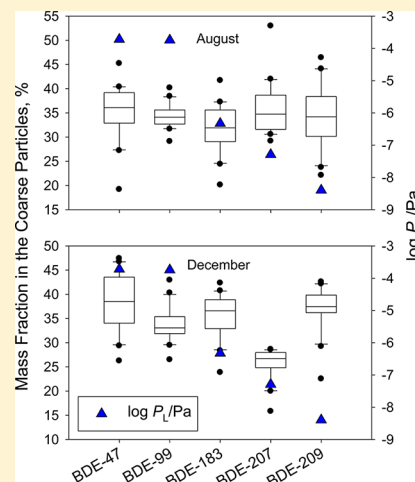
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## Supporting Information

**ABSTRACT:** Gaseous and size-segregated particulate PBDEs (specifically BDE-47, -99, -183, -207, and -209) in the air were measured in urban Guangzhou at 100 and 150 m above the ground in daytime and at night in August and December 2010, to assess dry deposition of these contaminants accurately with regards to influences of meteorological factors but without confounding surface effects. Particulate PBDEs were more abundant at night than in daytime, and slightly higher in winter than in summer, likely from varying meteorological conditions and atmospheric boundary layers. More than 60% of particulate-phase PBDEs was contained in particles with an aerodynamic diameter ( $D_p$ ) below  $1.8 \mu\text{m}$ , indicating long-range transport potential. The average daily particle dry deposition fluxes of PBDEs in August ranged from 2.6 (BDE-47) to 88.6 (BDE-209)  $\text{ng m}^{-2} \text{d}^{-1}$ , while those in winter ranged from 2.0 (BDE-47) to 122 (BDE-209)  $\text{ng m}^{-2} \text{d}^{-1}$ . Deposition fluxes of all PBDE congeners were significantly higher in daytime than at night for both months, due to the effect of diurnal variability of meteorological factors. In addition, mean overall particle deposition velocities of individual BDE congeners ranged from 0.11 to 0.28  $\text{cm s}^{-1}$ . These values were within a factor of 2 of assumed values previously used in southern China and the Laurentian Great Lakes, suggesting that such assumptions were reasonable for sites with similar particulate size distributions and PBDE sources. Dry deposition velocities of PBDEs were lower at night than those in the daytime, probably reflecting higher mechanical and thermal turbulence during daytime. Dry deposition of particulate-bound PBDEs is influenced by short-term temporal variability from meteorological factors, and also by particulate size fractions.



## INTRODUCTION

Polybrominated diphenyl ethers (PBDEs), a major group of brominated fire retardants (BFRs) applied to textiles, furniture, electronics, automotive interiors, and electronic and electric devices,<sup>1</sup> are common contaminants due to ample industrial production and widespread use of products bearing these chemicals. Because of their ubiquitous application, persistence, and probable toxic and carcinogenic/mutagenic human health effects, PBDEs have become a significant contaminant in terms of human health.<sup>2</sup> This is particularly true in urban areas, where the most severe PBDE contamination has been reported.<sup>3–5</sup> Like other semivolatile organic compounds (SVOCs), PBDEs have relatively low water solubilities and vapor pressures, and relatively large octanol–water and octanol–air partition coefficients.<sup>1</sup> Thus, they can partition to solid phases (e.g., sediment, soil, and atmospheric particles), bioaccumulate, and undergo long-range transport when released into the environment.

The fate of atmospheric PBDEs is influenced by dry deposition. This process substantially impacts their long-range transport efficiency and scope, by possibly controlling their removal rate from the atmosphere.<sup>6</sup> Dry deposition is also a major process delivering PBDEs to the earth's surface.<sup>7,8</sup> Dry deposition of PBDEs has been widely studied by collecting depositing particles via different surrogate surfaces<sup>4,8</sup> and by multiplying ambient concentrations with an empirical deposition velocity of PBDEs in other areas or even deposition velocities of other chemicals, for example, polychlorinated biphenyls.<sup>7,9,10</sup> However, surrogate surfaces seldom reasonably represent natural surfaces, and PBDEs can also revolatilize from the collection surface. In addition, deposition velocity is

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affected by meteorological parameters, physical properties of the particles (i.e., size, shape, and density), particle size distributions of different chemicals in the atmosphere which are not necessarily the same, and the type and roughness characteristics of the receptor surface.<sup>11,12</sup> Thus, an empirical deposition velocity may have large associated uncertainties, for example, dry deposition velocities of PCBs can vary widely, such as from 0.4 to 49 cm s<sup>-1</sup>.<sup>13</sup>

Another approach, via coupled size-segregated sampling and laboratory analysis and calculation of deposition velocity for each size fraction,<sup>14,15</sup> has been successfully applied to determine dry deposition fluxes of particulate trace chemicals under various meteorological conditions.<sup>12,16</sup> However, to our knowledge, only one peer-reviewed study on size-segregated distribution of atmospheric PBDEs has been published.<sup>17</sup> Nothing to date exists on size-segregated dry deposition dynamics of PBDEs. A key reason for this knowledge gap may result from detection limits becoming an issue, when particulate-bound analytes are split into multiple fractions. Furthermore, diurnal variability of meteorological factors was not considered in the majority of previous field measurements as previously noted,<sup>12</sup> and sampling was performed close to the ground surface, typically at only one height. Splitting particulate-bound analytes into diurnal fractions may also lead to detection limit problems. Thus, previously measured values may not capture diurnal variability from meteorological factors, such as turbulent mixing and changes in the depth of the atmospheric boundary layer. Near-surface measurements may also be substantially disturbed by resuspended particles, due to atmospheric mechanical turbulence caused by rough terrain. Sampling at only one height may fail to address these issues. In summary, size-segregation and diurnal variability measurements of SVOCs in air are necessary to assess dry deposition dynamics rigorously, and to ascertain if these issues are significant. However, doing so feasibly requires sufficient concentrations of particulate-bound analytes (i.e., PBDEs), as well as a suitable sampling site.

Guangzhou is one of the most severely contaminated cities in China. Atmospheric PBDE levels in urban Guangzhou were at the high range globally, for example, particulate BDE-209 levels (758–21 900 pg m<sup>-3</sup>) were more than ten times higher than those in Hong Kong (8.5–895 pg m<sup>-3</sup>), Osaka (100–340 pg m<sup>-3</sup>), U.S. cities (0–105 pg m<sup>-3</sup>), and Sweden (1.1–74.5 pg m<sup>-3</sup>).<sup>5</sup> We therefore postulated that PBDE concentrations are high enough that PBDEs in individual particle size fractions would be above analytical detection limits for 12 h sampling intervals. In addition, we took advantage of a tall urban tower for air sampling, as did a couple of previous studies.<sup>18,19</sup> Sampling devices were placed on the signal tower of the ca. 200 m tall Guangzhou Broadcast Center (23°08'37" N, 113°15'51" E) (Supporting Information (SI) Figure S1). The tower has no building taller than 50 m nearby, minimizing ground effects. To test dry deposition dynamics, sampling was simultaneously conducted on two decks of the tower, at heights of 100 and 150 m, to avoid ground-level disturbances (SI Figure S1), during both in daytime and at night, and during both the wet weather season (August) and dry weather season (December) of 2010. Thus, diurnal and seasonal variability in atmospheric deposition fluxes of particulate PBDEs could be examined for the first time, to determine if these are issues in understanding PBDE dry deposition.

## MATERIALS AND METHODS

**Sample Collection and Extraction.** Detailed sampling information was presented previously.<sup>12</sup> Briefly, size-segregated particle samples were collected using an 11-stage MOUDI impactor (MSP Corp., Minneapolis, MN) loaded with glass fiber filters in the fractions of <0.056, 0.056–0.1, 0.1–0.18, 0.18–0.32, 0.32–0.56, 1–1.8, 1.8–3.2, 3.2–5.6, 5.6–10, 10–18, and >18  $\mu\text{m}$  at a flow rate of 30 L min<sup>-1</sup>. Each sample was collected over 12 h, in daytime (7:00 a.m. to 7:00 p.m.) and at night (7:00 p.m. to 7:00 a.m.) from August 5 to 12, December 8 to 13, and December 26 to 27 in 2010. Bulk suspended particulate and gaseous samples were collected using a high-volume air sampler housing a glass fiber filter (GFF; 20.3  $\times$  25.4 cm<sup>2</sup>; Whatman International, Maidstone, England) and a polyurethane foam plug (PUF; 6.5 cm diameter and 8.0 cm thick with a density of 0.030 g cm<sup>-3</sup>). In total, 704 size-segregated particle samples were collected by the MOUDI impactor and 64 pairs (particle + gas) were collected with the high volume air sampler. In addition, meteorological data for the sampling periods were described in our recent study<sup>12</sup> and are presented in SI Table S1.

**Extraction and Instrumental Analysis.** Each sample was spiked with surrogate standards (<sup>13</sup>C<sub>12</sub>-BDE-51, <sup>13</sup>C<sub>12</sub>-BDE-115, <sup>13</sup>C<sub>12</sub>-PCB-141, PCB-204, and PCB-209) and Soxhlet-extracted for 24 h with 200 mL of a 2:2:1 by volume mixture of hexane, dichloromethane, and acetone. Further extract purification was performed on a multilayered alumina/silica column, with detailed procedures described in SI.

A DB-5 MS capillary column (30 m  $\times$  0.25 mm i.d. with 0.25  $\mu\text{m}$  film thickness) was used to separate 39 BDE (BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -181, -183, and -190), as described previously.<sup>20</sup> A DB-5HT (15 m  $\times$  0.25 mm i.d. with 0.10  $\mu\text{m}$  film thickness) capillary column was used for the more brominated BDE-196, -197, -206, -207, -208, and -209. The concentrations of PBDE congeners were determined using a Shimadzu model 2010 gas chromatograph coupled to a mass spectrometer with a negative chemical ion source in selected ion monitoring mode. The interface and ion source temperatures were set at 280 and 200 °C, respectively. All samples were automatically injected (2  $\mu\text{L}$ ) at 290 °C in the splitless mode with the split mode turned on 1 min after injection. Detailed instrumental analysis procedures are described in SI.

**Quality Assurance and Quality Control.** Among all measured BDE congeners, only BDE-47, -99, -183, -207, and -209 were detectable in more than 90% of the samples. In addition, the next most commonly detected congeners (BDE-100, -153, and -154) had detection frequencies of only 39%, 48%, and 36% respectively and collectively contributed less than 5% of the total PBDEs in the present study. For these reasons, only the five aforementioned congeners are further discussed. One procedural blank (glass fiber filter for particle samples and PUF for gaseous samples) was analyzed for every 10 samples. The levels of individual PBDEs in those final concentrated procedural blank samples were ND (not detected) for BDE-47, -99, and -183, ND–0.43 ng/mL for BDE-207, and ND–1.6 ng mL<sup>-1</sup> for BDE-209. Less than 20% of blanks had concentrations higher than the lowest calibration concentration (0.1 ng mL<sup>-1</sup> for BDE-47 and -99, 0.2 ng mL<sup>-1</sup> for -183, 0.4 ng mL<sup>-1</sup> for BDE-207, and 1 ng mL<sup>-1</sup> for BDE-209). The lowest calibration concentrations were regarded as

the minimum detection sensitivity of instrumental analysis for all these PBDEs except for BDE-209. As a result, the reporting limit for a sampling volume of 21.6 m<sup>3</sup> and a final extract volume of 0.05 mL was 0.23 pg m<sup>-3</sup> for BDE-47 and -99, 0.46 pg/m<sup>3</sup> for BDE-183, and 0.93 pg m<sup>-3</sup> for BDE-207. For BDE-209, a value of the 3-fold maximum level (11.0 pg m<sup>-3</sup>) in the procedural blanks was employed as the reporting limit. There were only four samples containing levels of BDE-209 (9.2, 8.3, 8.5, and 9.8 pg m<sup>-3</sup>) below the reporting limit. The recoveries of the surrogate standards in all samples were 84 ± 14% for <sup>13</sup>C<sub>12</sub>-BDE-15, and 82 ± 10% for <sup>13</sup>C<sub>12</sub>-BDE-51, 83 ± 16% for <sup>13</sup>C<sub>12</sub>-BDE-77, 97 ± 13% for <sup>13</sup>C<sub>12</sub>-BDE-115, 72 ± 16% for <sup>13</sup>C<sub>12</sub>-PCB-141, 65 ± 12% for PCB-204, and 67 ± 11% for PCB-209. Concentrations of field samples were not corrected for procedural blank levels or surrogate standard recoveries.

**Data Analysis.** The significance of seasonal variability of PBDE levels was tested by independent-samples *t*-test, while those of diurnal variability and vertical variability were tested by paired-samples *t*-test. The significance level was set throughout at  $\alpha = 0.05$ . All statistical analyses were conducted with SPSS version 13.0.

The overall dry deposition fluxes ( $F$ , pg m<sup>-2</sup>·s<sup>-1</sup>) of particulate PBDEs was calculated as the sum product of size-segregated PBDE concentrations ( $C_p$ ; pg m<sup>-3</sup>) and dry deposition velocities ( $V_d$ ; m s<sup>-1</sup>):

$$F = \sum(C_p \times V_d) \quad (1)$$

Size-resolved  $V_d$  was calculated using the particle dry deposition model described by Zhang et al.,<sup>16</sup> with results previously noted.<sup>12</sup> The same size-segregated  $V_d$  was used at both heights.<sup>12</sup>

Mean overall dry deposition velocities ( $V$ ) of particulate PBDEs were estimated:

$$V = F / \sum C_p \quad (2)$$

In calculating deposition fluxes of PBDEs, concentrations below the reporting limit were treated as half of the reporting limit, that is, 0.12 pg m<sup>-3</sup> for BDE-47 and -99, 0.23 pg m<sup>-3</sup> for BDE-183, 0.46 pg m<sup>-3</sup> for BDE-207 and 1.2 pg m<sup>-3</sup> for BDE-209. To verify the utility of this approach, deposition fluxes of PBDEs were also calculated with the nondetectable concentrations set as zero and at the reporting limit. Relative differences between the approaches were all <5% for individual BDE congeners, suggesting that nondetect values did not affect statistical analysis in the current study.

## RESULTS AND DISCUSSION

**Occurrence and Compositional Profiles of Gaseous and Particulate PBDEs.** Mean and median concentrations of individual PBDE congeners in total suspended particles from MOUDI (sum of the 11 stages) and the high-volume sampler and in the gaseous phase are listed in SI Tables S2–S4, respectively. The concentrations of total PBDEs (sum of BDE-47, -99, -183, -207, and -209 which were more frequently detected than other congeners in the present study; designed as  $\sum$ PBDE thereafter) in total suspended particles at both heights in August and December ranged from 400 to 1300 pg m<sup>-3</sup> with an average of 745 pg m<sup>-3</sup>, while those in the gaseous phase ranged from 13.1 to 35.3 pg m<sup>-3</sup> with an average of 21.6 pg m<sup>-3</sup> (Table 1). Concentrations of PBDEs in total suspended particles from MOUDI were comparable (approximately 70%) to those in particle samples from the high-volume

**Table 1. Diurnal Concentrations (pg m<sup>-3</sup>) of Total Particulate and Gaseous Polybrominated Diphenyl Ethers (Sum of BDE-47, -99, -183, -207, and -209 or  $\sum$ PBDE) at Heights of 100 and 150 m above the Ground in Urban Guangzhou in Daytime and at Night during August and December of 2010**

	100 m		150 m	
	daytime	night	daytime	night
Particulate $\sum$ PBDE Sampled by MOUDI				
August	667 ± 101	596 ± 159	583 ± 135	543 ± 166
December	949 ± 322	736 ± 214	922 ± 283	845 ± 264
Particulate $\sum$ PBDE Sampled by High-Volume Sampler				
August	872 ± 176	758 ± 128	767 ± 206	688 ± 248
December	1190 ± 350	822 ± 250	1190 ± 556	1080 ± 470
Gaseous $\sum$ PBDE				
August	32.1 ± 2.5	23.4 ± 3.8	22.6 ± 2.9	19.9 ± 3.3
December	16.5 ± 3.0	16.2 ± 2.8	18.6 ± 4.1	16.8 ± 3.3

sampler (Table 1 and SI Table S3), indicating that MOUDI is suitable for determination of particle-bound PBDEs. A possible explanation for the lower measured values from MOUDI than from the high-volume sampler is that evaporation losses from filter samples were less than those from impactor samples.<sup>21</sup> Of all the targeted PBDEs (particulate plus gaseous phases), BDE-209 was the dominant congener at 72.2 ± 8.3% and 78.5 ± 6.9% by weight in summer and winter, respectively. Heavy prevalence of BDE-209 compared to other BDE congeners has been widely reported in various environmental compartments nearby,<sup>7,20,22,23</sup> and is related to the fact that BDE-209 tends to affiliate with particle because it has the highest  $K_{ow}$  value among BDE congeners.<sup>7,8</sup>

Temporal and vertical distributions of  $\sum$ PBDE in both phases are shown in SI Figure S2. Concentrations of particulate  $\sum$ PBDE in daytime and at night in August were lower than those in December, respectively, for both heights, but not significantly so. Particulate  $\sum$ PBDE levels in the daytime were only slightly lower than those at night for both August and December. In addition, no statistical differences of  $\sum$ PBDE concentrations with height were found in both August and December. Similar seasonal and vertical variability of PAH levels were also reported; however, PAH levels were much lower in the daytime than at night for both months.<sup>12</sup>

The different diurnal distributions of PBDE and PAH levels may be attributed to their different input pathways. In urban areas, PAHs are generally from incomplete combustion of fossil fuels,<sup>24</sup> and can be discharged via both the gaseous and particulate phases. By comparison, it is highly likely that atmospheric PBDEs are mainly generated from vaporization from objects containing these flame retardants,<sup>25</sup> for which temperature dependence of atmospheric PBDE levels at different sites has been observed.<sup>26</sup> Although a previous study found that physical processes such as abrasion or weathering are major mechanisms for transfer of BDE-209 from PBDE-containing products into indoor environments,<sup>27</sup> particles generated from these processes generally have an aerodynamic diameter greater than 2 μm.<sup>25</sup> Thus, proportions of PBDEs in <2 μm particles were predominant over those in >2 μm particles, indicating that volatilization from PBDE-containing products is the major source of PBDEs in the particles from the sampling sites.

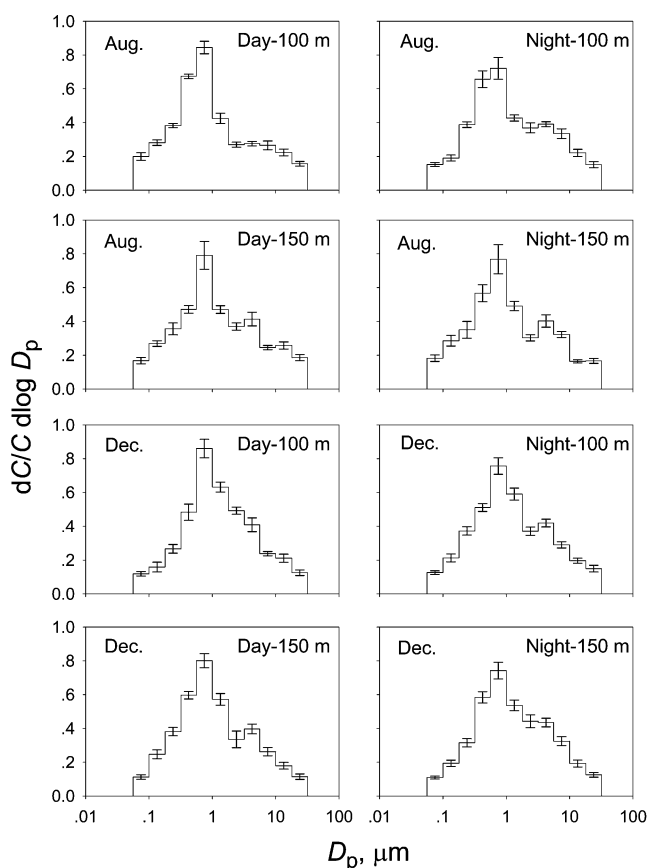


**Particle Size Distributions of PBDEs and Implications for Impact Mechanisms.** Investigations on the distribution of organic pollutants in atmospheric particles with respect to particle size have mainly focused on PAHs,<sup>12,28–32</sup> with only a very few focusing on other semivolatile contaminants, namely polychlorinated dibenzo-*p*-dioxins and dibenzofurans,<sup>33,34</sup> PCBs,<sup>35</sup> and especially PBDEs.<sup>17</sup> To describe the size distributions of PBDE-bearing particulates succinctly, geometric mean diameters (GMD) and geometric standard deviations ( $\sigma_g$ ) were calculated on a mass basis.<sup>36</sup> In August, all of the average GMDs of individual particle fractions with PBDEs were around 1  $\mu\text{m}$ , and no significant individual, diurnal, and vertical difference was noticed for both GMDs and  $\sigma_g$  (SI Table S5), indicating approximately identical mass size distribution. Similarly, no significant diurnal and vertical difference was noticed for both GMDs and  $\sigma_g$  of particulates containing the same BDE congener. However, at night in December, GMDs and  $\sigma_g$  of particulates bearing BDE-207 ( $0.93 \pm 0.53$  and  $0.91 \pm 0.55$   $\mu\text{m}$  for 100 m and 150 m, respectively) were both statistically lower than those of the other congeners (SI Table S5), indicating a relative longer atmospheric residential time and narrower mass size distribution compared with the others. Particulates with PBDEs had larger GMDs in the present study than those with  $\sum_{12}\text{PBDE}$  (sum of BDE-15, -17, -28, -47, -49, -62, -71, -99, -100, -153, -154, and -183) in Athens (0.21  $\mu\text{m}$ ), and in Heraklion and Finokalia (0.14–0.63  $\mu\text{m}$ ).<sup>17</sup>

Figure 1 and SI Figures S3–S7 show the size distributions ( $dC/Cd\log D_p$  versus  $D_p$ ) of  $\sum\text{PBDE}$  and individual PBDEs, where  $dC$  is the mass concentration on each filter,  $d\log D_p$  is the logarithmic aerodynamic diameter ( $D_p$ ) size interval for each impactor stage, and  $C$  is the sum of concentrations in the 11 size fractions. Concentrations of individual target PBDEs at particle size  $<0.056$   $\mu\text{m}$  were all below reporting limits. The size distribution profiles of individual PBDEs (Figure 1) both in the daytime and at night were almost identical at 100 and 150 m in both months. In most cases, these distributions were bimodal, with a major peak at 0.56–1.0  $\mu\text{m}$  and a minor peak at 3.2–5.6  $\mu\text{m}$  in both August and December (Figure 1 and SI Figures S3–S7). By comparison, the size distribution of individual PAHs in the same samples showed different patterns. Those in August were unimodal with a peak at 0.32–0.56  $\mu\text{m}$  in summer, but in December they were at larger sizes (0.32–1.8  $\mu\text{m}$ ) with nearly even contributions.<sup>12</sup>

Both the observation of peak migration toward larger sizes for size-segregated PAHs from August to December, and that of elevated levels of particulate PAHs in December compared with those in August, indicate stronger effects of nonlocal sources to atmospheric PAHs in Guangzhou.<sup>12</sup> However, the consistent size distribution profiles of PBDEs in different seasons suggest local effects, such as association of locally volatilized PBDEs with air particles. Therefore, differences between size distributions of particulate-bound PAHs and PBDEs may be due to different impact mechanisms.

Aside from different input sources as noted above, other processes can also alter size distributions of atmospheric SVOCs, such as selective dry deposition, particle coagulation, volatilization/reabsorption, and chemical affinity.<sup>28,36</sup> Efficient dry deposition of large particles during air mass transport will decrease the proportion of PBDEs in these particles, as will coagulation of fine particles. Therefore, these mechanisms both lead to a peak in the middle range of particle size. For example, compared with the size distribution profile of PBDEs in the present study, those near the earth surface of Heraklion were



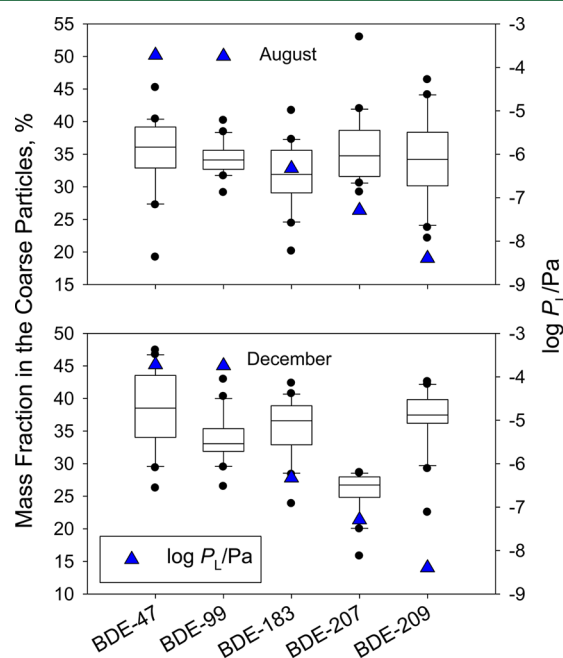
**Figure 1.** Particle size distributions of  $\sum\text{PBDE}$  (sum of BDE-47, -99, -183, -207, and -209) in the atmosphere at the heights of 100 and 150 m above the ground in urban Guangzhou in daytime and at night during August and December of 2010, where  $dC$  is the mass concentration on each filter,  $d\log D_p$  is the logarithmic size interval for each impactor stage in aerodynamic diameter ( $D_p$ ), and  $C$  is the sum of concentrations in the 11 size fractions. The error bars stand for one standard deviation from the mean concentrations.

bimodal, with a major peak in the size fraction  $<0.57$   $\mu\text{m}$  and a minor peak  $>8.1$   $\mu\text{m}$ .<sup>17</sup> In our study, however, the size distribution of  $\sum\text{PBDE}$  in a group of 48 h samples at 1.5 m height was bimodal with peaks in the 0.56–1.0 and 5.6–10  $\mu\text{m}$  size fractions (SI Figure S8). The significant difference between size distributions of  $\sum\text{PBDE}$  in particles from near-ground air and those from 100/150 m above the ground suggests that particle coagulation between those heights may be significant. Alternatively, a much higher proportion of BDE-209 is distributed in large particles in near-ground air, compared to that at 100/150 m height. Thus, a greater near-ground deposition velocity could be expected. Therefore, near-surface effects on dry deposition can be significant, as we hypothesized.

To determine whether volatilization/reabsorption and chemical affinity affect size distributions of PBDEs in urban Guangzhou, particles were classified into fine particles ( $<1.8$   $\mu\text{m}$ ) and coarse mode particles ( $>1.8$   $\mu\text{m}$ ). Fine particles were contained the most of the particulate PBDEs ( $63 \pm 6\%$  of BDE-47,  $66 \pm 3\%$  of BDE-99,  $66 \pm 5\%$  of BDE-183,  $69 \pm 7\%$  of BDE-207, and  $64 \pm 6\%$  of BDE-209), with no significant difference among these percentages. This observation was consistent with PBDEs being enriched in fine particles ( $D_p < 1.66$   $\mu\text{m}$ ) from Greece, that is, 87%,  $72 \pm 13\%$ , and  $85 \pm 19\%$  in Athens, Heraklion and Finokalia, respectively.<sup>17</sup>

Size distributions of PBDEs and the predominance of PBDEs in fine particles have significant implications for their atmospheric fate. The peak location in the size fraction of 0.56–1.0  $\mu\text{m}$  for PBDEs, in particles from both air near ground and upper air, indicates that PBDEs in fine particles will undergo less dry deposition, can be transported to high altitudes, and therefore may be subject to long-range transport.

The predominance of other SVOCs in fine particles has been widely observed, including PAHs in the same samples,<sup>12</sup> in indoor air of Guangzhou,<sup>32</sup> in urban and suburban areas of Saitama City in Japan,<sup>29</sup> and in Massachusetts.<sup>28</sup> Polychlorinated dibenzo-*p*-dioxins and dibenzofurans were also observed predominantly in fine particles.<sup>34</sup> However, all these studies found gradual decreases of mass fractions of congeners in the coarse mode particles as their vapor pressures decreased, except for the present study (Figure 2) in which mass size distributions



**Figure 2.** Subcooled liquid vapor pressures ( $P_L$ ) of PBDEs at 298 K<sup>44</sup> and mass fractions of PBDEs associated with coarse particles (larger than 1.8  $\mu\text{m}$  in aerodynamic diameter) at the heights of 100 and 150 m above the ground in urban Guangzhou; sampling was conducted in daytime and at night during August and December of 2010. The whiskers stand for 5th and 95th percentiles, and horizontal lines from the bottom to the top of each box stand for the 25th, 50th, and 75th percentiles, respectively.

of PBDEs was less dependent on volatility than those of PAHs. A nonequilibrium hypothesis was used to interpret this observation for PAHs.<sup>12,28,32</sup> In this hypothesis, chemicals with higher volatility can preferentially migrate to larger particles through volatilization and condensation, compared to those of lower volatility. This hypothesis is consistent with observed PAH size distributions,<sup>12</sup> because particle-bound PAHs freshly emitted are mainly distributed in the ultrafine particles.<sup>37,38</sup> It does not work with PBDEs in these particles (Figure 2). Differences in chemical affinities between individual PBDEs and different size particles may possibly explain why mass fractions of PBDEs in the coarse mode particles decrease as their volatilities decrease.<sup>17</sup> However, the insignificant differences among mass fractions of individual PBDEs in coarse particles in the present study (Figure 2) indicate that

neither mechanism is plausible here. Because of limited data for comparison, we can only conclude that volatility and chemical affinity have little influence on particle size distributions of PBDEs in the urban atmosphere of Guangzhou.

**Dry Deposition Fluxes of Particulate and Gaseous PBDEs.** Only overall deposition fluxes (sum of the 11 fractions) of each PBDE congeners are discussed, to compare directly with previous studies. Particle dry deposition velocities of individual size fractions have been given in our previous study,<sup>12</sup> and are also listed in SI Table S6. Based on these particle dry deposition velocities of different size fractions, overall dry deposition fluxes (Table 2 and SI Table S7) of particulate PBDEs were calculated with eq 1. The average fluxes of PBDEs in the daytime were from 1.2- (BDE-99 and BDE-207 at 150 m) to 1.9-fold (BDE-183 at 150 m) of those at night in August, respectively, and were from 1.1- to 1.7-fold of those at night in December, respectively (SI Table S7). Significant differences were observed between fluxes of  $\Sigma\text{PBDE}$  in daytime and at night for both months. Because only slight diurnal differences were observed for particulate  $\Sigma\text{PBDE}$  levels, the significant diurnal differences for particle dry deposition fluxes of PBDEs can be attributed to meteorological influences affecting  $V_d$ , a size-dependent parameter. As noted, atmospheric resistance is stronger at night versus daytime due to enforced atmospheric stability. Seasonally, average fluxes of BDE-47, -99, and -183 in December were significantly lower than those in August (0.6- to 0.7-fold). This contrasts with fluxes of BDE-207 (almost similar in both months) and BDE-209 (0.4 times higher in December than those in August) (SI Table S7). In addition, no significant differences of deposition fluxes of either  $\Sigma\text{PBDE}$  or BDE-209 at either height in daytime or at night were noticed in both sampling months. However, this might be questionable, because the same size-segregated  $V_d$  was used at both heights due to lack of data, which therefore ignores any potential impact of vertical variability in meteorological factors (e.g., wind speed).

Based on these results, the average daily particle dry deposition fluxes of PBDEs in August ranged from 2.6 (BDE-47) to 88.6 (BDE-209)  $\text{ng m}^{-2} \text{d}^{-1}$ , whereas those in winter ranged from 2.0 (BDE-47) to 122 (BDE-209)  $\text{ng m}^{-2} \text{d}^{-1}$  (Table 2). Thus, daily mean dry deposition fluxes of particulate  $\Sigma\text{PBDE}$  were  $116 \pm 26$  and  $146 \pm 54$   $\text{ng m}^{-2} \text{d}^{-1}$  in August and December, respectively. By comparison, the daily dry deposition fluxes of BDE-47, -99, -183, -207, and -209 in the present study were substantially higher than those in nearby Dongguan in both dry and wet weather seasons (Table 2). The fluxes of BDE-47, -99, -183 of the present study were higher than those in nearby Shunde in both the dry and wet weather seasons, while those of BDE-209 were much lower than those reported in Shunde (Table 2). Dongguan is a major center for manufacture of PBDE-bearing electronic products in China. However, the deposition fluxes of PBDEs calculated simply from multiplying the bulk concentration of particle-bound analytes with an empirical mean deposition velocity in Dongguan were much lower than those in Shunde, which has little electronic manufacturing activity.<sup>7</sup> This unexpected result was caused by the higher concentration of particulate PBDEs in near-ground air from Shunde than that from Dongguan, probably due to site-specific near-ground effects and meteorology conditions. Thus, particulate samples collected without regard to size, surface and meteorology conditions are not suitable enough to monitor dry deposition. Furthermore, the particle dry deposition fluxes of BDE-47 (mean: 2.5  $\text{ng m}^{-2}$

Table 2. Particle Dry Deposition Fluxes of PBDEs ( $\text{ng m}^{-2} \text{d}^{-1}$ ) in Different Places

	BDE-47	BDE-99	BDE-183	BDE-207	BDE-209
Dongguan, China, dry season <sup>7</sup>	$1.2 \pm 0.5$	$1.9 \pm 0.8$	$2.0 \pm 0.6$	$6.0 \pm 1.1$	$70.0 \pm 28.1$
Dongguan, wet season <sup>7</sup>	$0.4 \pm 0.2$	$0.9 \pm 0.3$	$2.2 \pm 0.7$	$2.7 \pm 1.3$	$41.0 \pm 22.0$
Shunde, China, dry season <sup>7</sup>	$1.3 \pm 0.4$	$1.7 \pm 0.6$	$2.1 \pm 0.7$	$16.4 \pm 7.8$	$300 \pm 114$
Shunde, wet season <sup>7</sup>	$0.6 \pm 0.2$	$0.7 \pm 0.2$	$3.7 \pm 1.6$	$6.0 \pm 3.1$	$175 \pm 94$
Urban Izmir, Turkey <sup>4</sup>	$6.0 \pm 3.5$	$6.7 \pm 5.2$			$108 \pm 115$
Suburban Izmir, Turkey <sup>4</sup>	$6.1 \pm 2.6$	$4.9 \pm 2.8$			$49.4 \pm 89.0$
Coastal Izmir, Turkey, summer <sup>9</sup>	$23 \pm 16$	$62 \pm 30$			$89 \pm 47$
Coastal Izmir, Turkey, winter <sup>9</sup>	$42 \pm 22$	$26 \pm 16$			$116 \pm 84$
The Atlantic and Southern Ocean <sup>43</sup>	$0.002^a$	$0.0012^a$			
Urban Guangzhou, present study					
100 m, August	$3.1 \pm 0.8$	$4.4 \pm 1.0$	$9.9 \pm 3.2$	$16.1 \pm 5.5$	$88.6 \pm 26.9$
150 m, August	$2.6 \pm 0.8$	$4.3 \pm 1.0$	$8.0 \pm 1.5$	$12.9 \pm 3.4$	$82.7 \pm 13.1$
100 m, December	$2.1 \pm 0.9$	$3.2 \pm 1.1$	$5.9 \pm 1.8$	$15.7 \pm 4.7$	$119 \pm 44$
150 m, December	$2.0 \pm 0.8$	$3.2 \pm 1.0$	$5.0 \pm 1.6$	$13.7 \pm 4.6$	$122 \pm 49$

<sup>a</sup>Median value.Table 3. Particle Dry Deposition Velocities of PBDEs ( $\text{cm s}^{-1}$ ) in Different Places

	BDE-47	BDE-99	BDE-183	BDE-207	BDE-209
Dongguan, Shunde, and Guangzhou, China <sup>7</sup>	$0.5^a$	$0.5^a$	$0.5^a$	$0.5^a$	$0.5^a$
Hong Kong, China <sup>8</sup>	$0.32 \pm 0.12$	$0.24 \pm 0.16$			$0.28 \pm 0.01$
Urban Izmir, Turkey <sup>4</sup>	$3.9 \pm 1.7$	$3.1 \pm 1.6$			$2.9 \pm 1.8$
Suburban Izmir, Turkey <sup>4</sup>	$9.2 \pm 4.6$	$5.7 \pm 3.1$			$3.9 \pm 3.6$
The Atlantic and Southern Ocean <sup>43</sup>	$0.1^a$	$0.1^a$			
The Great Lakes, North America <sup>10</sup>	$0.4^a$	$0.4^a$	$0.4^a$	$0.4^a$	$0.4^a$
Urban Guangzhou, August, present study					
100 m, daytime	$0.26 \pm 0.07$	$0.28 \pm 0.03$	$0.25 \pm 0.03$	$0.27 \pm 0.05$	$0.25 \pm 0.03$
100 m, night	$0.23 \pm 0.04$	$0.18 \pm 0.04$	$0.19 \pm 0.05$	$0.19 \pm 0.01$	$0.18 \pm 0.05$
150 m, daytime	$0.28 \pm 0.04$	$0.26 \pm 0.05$	$0.28 \pm 0.06$	$0.26 \pm 0.03$	$0.28 \pm 0.03$
150 m, night	$0.19 \pm 0.05$	$0.20 \pm 0.02$	$0.16 \pm 0.03$	$0.22 \pm 0.10$	$0.19 \pm 0.06$
urban Guangzhou, December, present study					
100 m, daytime	$0.28 \pm 0.06$	$0.24 \pm 0.02$	$0.24 \pm 0.06$	$0.17 \pm 0.02$	$0.22 \pm 0.02$
100 m, night	$0.21 \pm 0.03$	$0.17 \pm 0.03$	$0.18 \pm 0.03$	$0.11 \pm 0.02$	$0.19 \pm 0.02$
150 m, daytime	$0.25 \pm 0.03$	$0.27 \pm 0.03$	$0.26 \pm 0.02$	$0.17 \pm 0.02$	$0.21 \pm 0.03$
150 m, night	$0.25 \pm 0.03$	$0.18 \pm 0.01$	$0.22 \pm 0.02$	$0.12 \pm 0.02$	$0.17 \pm 0.02$

<sup>a</sup>Empirical value.

$\text{d}^{-1}$ ) and BDE-99 (mean:  $3.5 \text{ ng m}^{-2} \text{d}^{-1}$ ) in the present study are comparable to those at both suburban and urban sites of Izmir, Turkey, significantly lower than those of coastal Izmir of Turkey (mean:  $32.5 \text{ g m}^{-2} \text{d}^{-1}$  for BDE-47 and  $44 \text{ g m}^{-2} \text{d}^{-1}$  for BDE-99), but substantially higher than those over the Atlantic and Southern Ocean (median:  $0.02 \text{ g m}^{-2} \text{d}^{-1}$  for BDE-47 and  $0.0012 \text{ g m}^{-2} \text{d}^{-1}$  for BDE-99) (Table 2). For BDE-209, the fluxes in this study were much higher than those in suburban Izmir ( $49.4 \text{ g m}^{-2} \text{d}^{-1}$ ), comparable to those in urban ( $108 \text{ g m}^{-2} \text{d}^{-1}$ ) and coastal Izmir, Turkey (Table 2).

Dry deposition of PBDEs in the gaseous phase is mainly caused by molecular and eddy diffusion. Although quite a few studies have reported on dry deposition of PBDEs,<sup>4,7,10</sup> no results on gaseous PBDEs has been reported. Previous studies documented that dry deposition velocity of gaseous PAHs is usually lower than that of particle-bound PAHs, and reported values have large uncertainties.<sup>39–42</sup> A conservative value of  $0.02 \text{ cm s}^{-1}$ <sup>42</sup> has been used for the dry deposition velocity of gaseous PAHs in our previous study to calculate fluxes.<sup>12</sup> Based on this value, none of the dry deposition fluxes of gaseous  $\Sigma$ PBDE and BDE-209 were above  $0.01 \text{ pg m}^{-2} \text{s}^{-1}$ , less than  $1/60$  of the dry deposition fluxes of particulate  $\Sigma$ PBDE and BDE-209. If a much higher but still plausible dry deposition

velocity of  $0.5 \text{ cm s}^{-1}$  is used,<sup>41</sup> none of the dry deposition fluxes of gaseous BDE-209 was above  $0.03 \text{ pg m}^{-2} \text{s}^{-1}$ , while none of the dry deposition fluxes of gaseous  $\Sigma$ PBDE exceeded  $0.2 \text{ pg m}^{-2} \text{s}^{-1}$ , which is a tiny fraction of the dry deposition fluxes of particulate PBDEs (less than 5%). In summary, dry deposition of PBDEs in Guangzhou is dominated by dry particle deposition.

**Dry Deposition Velocities of PBDEs.** Mean overall particle dry deposition velocities of PBDEs (Table 3) were calculated by dividing the particulate fluxes by the sum of concentrations of particulate PBDEs in the size fractions. These results, which minimized surface effects and with respect to the particle sizes, variability of meteorology factors, and particle size fractions of PBDEs, should be more plausible in dry deposition monitoring of PBDEs compared with previous studies.

Mean overall deposition velocities of PBDEs in the present study were higher by a factor of 10–27 than the empirical value used over the Atlantic and Southern Ocean,<sup>43</sup> but lower by only 0.5–0.8-fold than empirical values employed in Dongguan, Shunde and Guangzhou,<sup>7</sup> and over the Great Lakes<sup>10</sup> (Table 3). Deposition velocities of PBDEs in the present study were comparable to those measured in Hong Kong,<sup>8</sup> but significantly lower than those in urban and suburban Izmir in Turkey<sup>4</sup>



(Table 3). These comparisons indicate that assumed values for mean overall deposition velocities of PBDEs in Dongguan, Shunde, Guangzhou and the Great Lakes area seem reasonable. In contrast, the values from Izmir were over ten times larger (Table 3), and might reflect a significant surface effect, because those deposition samples were gathered near the ground surface.<sup>4</sup>

Mean overall dry deposition velocities of PBDEs were lower at night than those in the daytime (Table 3), probably reflecting higher mechanical and thermal turbulence during daytime as with PAHs.<sup>12</sup> In addition, no statistical vertical differences of dry deposition velocities of individual PBDEs was noticed, or significant seasonal differences except for BDE-207 (Table 3). Significantly lower deposition velocities of BDE-207 in December than in August could be associated with lower mass fraction of BDE-207 in the coarse particles in December than in August (Figure 2).

Previous work on particle dry deposition of PBDEs in Izmir, Turkey found that particle dry deposition velocities of PBDEs generally decreased with decreasing volatility.<sup>4</sup> The same trend was observed for PAHs in Chicago<sup>11</sup> and PAHs in the same samples as in the present study<sup>12</sup> and was attributed to association of the greater mass fraction of the higher volatile compound in the coarse particles. However, this trend was not observed in the present study (Table 3), because the mass fraction of PBDEs did not increase with increasing volatility (Figure 2).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional tables and figures containing information concentrations, particle size distribution the target analytes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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