

# Size Distribution of Airborne Particle-Bound Polybrominated Diphenyl Ethers and Its Implications for Dry and Wet Deposition

Pei Luo,<sup>†,‡</sup> Hong-Gang Ni,<sup>\*,‡</sup> Lian-Jun Bao,<sup>†</sup> Shao-Meng Li,<sup>§</sup> and Eddy Y. Zeng<sup>†,‡</sup>

<sup>†</sup>State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, Guangdong, China

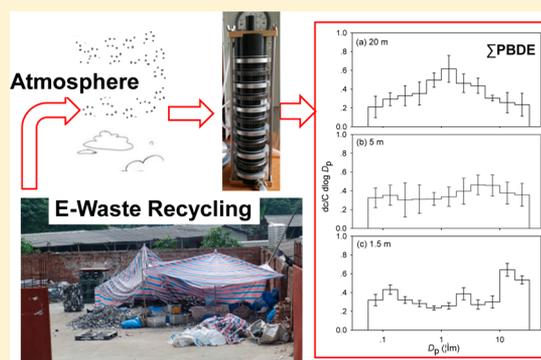
<sup>‡</sup>School of Environment, Jinan University, Guangzhou 510632, Guangdong, China

<sup>§</sup>Air Quality Research Division, Environment Canada, 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

<sup>‡</sup>University of Chinese Academy of Sciences, Beijing 100049, China

## Supporting Information

**ABSTRACT:** Size distribution of particles in part dictates the environmental behavior of particle-bound organic pollutants in the atmosphere. The present study was conducted to examine the potential mechanisms responsible for the distribution of organic pollutants in size fractionated particles and their environmental implications, using an e-waste recycling zone in South China as a case study. Size-fractionated atmospheric particles were collected at the heights of 1.5, 5, and 20 m near two residential apartments and analyzed for polybrominated diphenyl ethers (PBDEs). The concentrations of particle-bound  $\Sigma$ PBDE (sum of 18 PBDE congeners) were significantly greater at 5 and 20 m than those at 1.5 m. The size-fractionated distributions of airborne  $\Sigma$ PBDE displayed trimodal peaks in 0.10–0.18, 1.8–3.2, and 10–18  $\mu\text{m}$  at 1.5 m but only a unimodal peak in 1.0–1.8  $\mu\text{m}$  at 20 m height. Emission sources, resuspension of dust and soil, and volatility of PBDEs were important factors influencing the size distribution of particle-bound PBDEs. The dry deposition fluxes of particle-bound PBDE estimated from the measured data in the present study were approximately twice the estimated wet deposition fluxes, with a total deposition flux of 3000  $\text{ng m}^{-2} \text{d}^{-1}$ . The relative contributions of particles to dry and wet deposition fluxes were also size-dependent, e.g., coarse (aerodynamic diameters ( $D_p$ ) > 1.8  $\mu\text{m}$ ) and fine ( $D_p$  < 1.8  $\mu\text{m}$ ) particles dominated the dry and wet deposition fluxes of PBDEs, respectively.



## INTRODUCTION

Due to potential adverse health effects arising from inhalation of suspended particulate matter,<sup>1</sup> particle-bound contaminants in the ambient environment are of great concern. In general, smaller particles can penetrate into the deeper regions of lung and pose higher risk to human health compared to larger particles. For instance, ultrafine particles (aerodynamic diameters ( $D_p$ ) < 0.10  $\mu\text{m}$ ) contributed 10–30% to the deposition of polycyclic aromatic hydrocarbons (PAHs) in the alveolar region of the human respiratory tract but only 1.3–2.3% to the total particle mass.<sup>2</sup> As a result, the size distribution of particle-bound contaminants in the atmosphere is a critical parameter for assessment of health risk through inhalation.<sup>3,4</sup>

Although a large number of reports on the size distribution of particle-bound organic pollutants in the atmosphere have been published,<sup>5–10</sup> only a couple of peer-reviewed studies on the size distribution of particle-bound polybrominated diphenyl ethers (PBDEs) have been reported.<sup>11,12</sup> Moreover, there was controversy surrounding the mechanisms for particle size distribution of PBDEs. Mandalakis et al.<sup>11</sup> investigated only lightly brominated congeners (di- to hepta-BDE) in size-fractionated particles and suggested that the chemical affinities

of individual congeners determined the size distribution of PBDEs. In contrast, Zhang et al.<sup>12</sup> proposed that the particle size distributions of five PBDE congeners (i.e., BDE-47, -99, -183, -207, and 209) were not affected by volatility and chemical affinity. Therefore, further investigations into the size distributions of a wide range of PBDE congeners in the atmosphere are necessary and significant.

In addition, these particle-bound contaminants may then impact ecosystems by other mechanisms in addition to inhalation, e.g., particles function as transport vectors. Size distribution of atmospheric particles dictates the environmental behavior of particle-bound contaminants in the atmosphere, e.g., the long-range transport potential and atmospheric dry and wet deposition.<sup>12</sup> Our previous studies noticed that size-fractionated dry deposition fluxes of PAHs and PBDEs were dominated by large particles, although these fractions contained low concentrations of PAHs and PBDEs.<sup>7,12</sup> Kaupp and

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McLachlan<sup>13</sup> found that fine particles ( $D_p < 1.35 \mu\text{m}$ ) dominated wet deposition fluxes of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) and PAHs, which was also estimated from the particle size-fractionated concentrations of PCDD/F and PAHs. So far, there is limited information about the relative contributions of different sized particles to dry and wet deposition fluxes of PBDEs.

To fill the above-mentioned knowledge gap, we set out to further investigate the particle size distribution of a wide range of PBDE congeners in the atmosphere, building on our previous efforts in characterizing the human health risk from inhalation exposure to halogenated flame retardants within an e-waste recycling zone of South China.<sup>3</sup> The e-waste recycling zone (Supporting Information (SI) Figure S1) was deemed an ideal site for achieving the goal of the present study, as our previous study demonstrated that PBDEs were quite abundant in different-sized atmospheric particles.<sup>3</sup> The tasks of the present study were to (1) analyze the size distributions of atmospheric particle-bound PBDEs (from tri- to deca-BDEs); (2) examine the mechanisms controlling the size distributions of PBDEs; and (3) estimate the size-dependent dry and wet deposition fluxes of particle-bound PBDEs.

## MATERIALS AND METHODS

**Sample Collection and Analysis.** The present study reanalyzed the PBDEs data from our previous study,<sup>3</sup> which described the detailed sampling information and sample analysis procedures. Therefore, only a brief description is presented herein. Particulate samples were collected on 47 mm diameter glass microfiber filters (Whatman International, Maidstone, England) inside a Micro-Orifice Uniform Deposit Impactor (MSP Corporation, Shoreview, MN) device outside two residential apartments around the e-waste recycling zone in Qingyuan, Guangdong Province, China (SI Figure S1). The daily sampling time was 12 h from 07:30 to 19:30 (Beijing Time) during October and November 2012. Particle samples were separated into 11 fractions as >18, 10–18, 5.6–10, 3.2–5.6, 1.8–3.2, 1.0–1.8, 0.56–1.0, 0.32–0.56, 0.18–0.32, 0.10–0.18, and 0.056–0.10  $\mu\text{m}$ . Size-fractionated particles were categorized as coarse ( $D_p > 1.8 \mu\text{m}$ ), accumulation mode (0.10  $\mu\text{m} < D_p < 1.8 \mu\text{m}$ ), and ultrafine ( $D_p < 0.10 \mu\text{m}$ ), and the sum of the latter two is referred to as fine particle. Sampling took place at three heights above the ground: 1.5, 5, and 20 m, representative of the first, second, and sixth floors in a typical apartment. Overall, 24 sets of size-fractionated samples were collected, and 8 sets of samples at 20-m height were used to estimate dry and wet deposition fluxes.

All samples were spiked with the surrogate standards (BDE-51, BDE-115, <sup>13</sup>C-BDE-138, and <sup>13</sup>C-BDE-209) and Soxhlet extracted with 200 mL of hexane, dichloromethane, and acetone mixture (1:1:1 in volume) for 24 h. The extracts were purified with an acid silica/neutral silica/alumina column. The fraction containing PBDEs was collected, concentrated to 50  $\mu\text{L}$ , and spiked with the internal standards (BDE-69, <sup>13</sup>C-PCB-208, and <sup>13</sup>C-BDE-139) before instrumental analysis. A set of 18 PBDEs (sum of which is designated as  $\Sigma\text{PBDE}$ ) including tri-BDE (BDE-28), tetra-BDE (BDE-47 and -66), penta-BDE (BDE-85, -99, and -100), hexa-BDE (BDE-153 and -154), hepta-BDE (BDE-181, -183, and -190), octa-BDEs (BDE-196, -203, and -204), nona-BDEs (BDE-206, -207, and -208), and deca-BDE (BDE-209) was analyzed with an Agilent 7890A gas chromatography coupled to a 5975C mass spectrometer in the negative chemical ionization mode. A

DB-5HT capillary column (15 m  $\times$  0.25 mm i.d. with 0.1  $\mu\text{m}$  film thickness, J&W Scientific, Folsom, CA) was used for chromatographic separation. All samples were automatically injected in a programmed temperature vaporizer (PTV) with an initial temperature of 120  $^\circ\text{C}$  (held for 0.04 min) and then increased to 290  $^\circ\text{C}$  at 600  $^\circ\text{C min}^{-1}$  (held for 30 min). The column temperature was started at 110  $^\circ\text{C}$  (held for 5 min) and ramped to 200  $^\circ\text{C}$  at 40  $^\circ\text{C min}^{-1}$  (held for 4 min), 260  $^\circ\text{C}$  at 10  $^\circ\text{C min}^{-1}$  (held for 1 min), and 310  $^\circ\text{C}$  at 15  $^\circ\text{C min}^{-1}$  (held for 15 min). Quantitative analysis was performed in the selected ion monitoring mode.

**Quality Assurance and Quality Control.** The recoveries of the surrogate standards BDE-51, BDE-115, <sup>13</sup>C-BDE-138, and <sup>13</sup>C-BDE-209 were  $74 \pm 12\%$ ,  $84 \pm 11\%$ ,  $90 \pm 16\%$ , and  $70 \pm 13\%$  in all blank samples and  $72 \pm 10\%$ ,  $89 \pm 18\%$ ,  $80 \pm 18\%$ , and  $66 \pm 13\%$  in the field samples, respectively. Concentrations of PBDEs in all field samples were corrected by the corresponding procedural blanks in the same batch but not corrected by the surrogate standard recoveries. The mean recoveries of the target compounds in the spiked samples were  $64 \pm 7\%$ – $112 \pm 10\%$ . With a mean sample volume of 21.6  $\text{m}^3$  and a final extract volume of 50  $\mu\text{L}$ , the reporting limit was 0.23  $\text{pg m}^{-3}$  for PBDEs (except for BDE-209) and 2.3  $\text{pg m}^{-3}$  for BDE-209. If the concentration of a target compound was below the reporting limit, it was set as zero in the calculation of dry and wet deposition fluxes.

**Estimation of Dry and Wet Deposition Fluxes.** Dry deposition flux ( $F_{\text{dry}}$ ) of a particle-bound PBDE congener was calculated from a size-fractionated concentration ( $C_i$ ) multiplied by related dry deposition velocity ( $V_i$ )

$$F_{\text{dry}} = \sum (C_i \times V_i) \quad (1)$$

where  $V_i$  was adopted from the measured data at 100 m height in our previous study.<sup>12</sup> Similarly, wet deposition flux ( $F_{\text{wet}}$ ) was estimated by removal efficiencies ( $\eta_i$ ) of different size fractions based on the Kaupp and McLachlan method<sup>13</sup>

$$F_{\text{wet}} = W_T \times \sum (C_i \times \eta_i) \times Q \quad (2)$$

where  $W_T$  is the wet washout ratio, defined as the analyte concentration ratio in precipitation and the gaseous phase, and  $Q$  is the monthly precipitation amount. A range of  $10^3$ – $10^6$  for  $W_T$  was determined for PBDE congeners,<sup>14,15</sup> and a  $10^5$  value was chosen for all PBDE congeners in a previous study which estimated wet deposition fluxes.<sup>13</sup> In addition, values of  $\eta_i$  (i.e., the fraction of the particles removed by a precipitation event) were adopted from Radke et al.<sup>16</sup> The mean value of  $Q$  was 55 mm during dry weather seasons in Qingyuan for the past several years (<http://www.gdqy.gov.cn> and therein). The values of these parameters are summarized in SI Table S1.

The sum of dry and wet deposition fluxes is defined as total deposition fluxes herein. The overall dry deposition velocity ( $V_d$ ) and removal efficiency ( $\eta$ ) of particle-bound PBDEs were estimated by

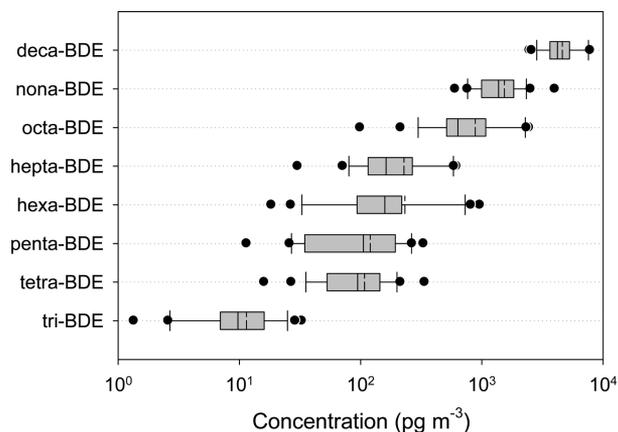
$$V_d = F_{\text{dry}} / \sum C_i \quad (3)$$

$$\eta = F_{\text{wet}} / (W_T \times Q \times \sum C_i) \quad (4)$$

## RESULTS AND DISCUSSION

**Occurrence and Vertical Distribution of PBDEs.** Overall, the concentrations of PBDEs decreased in the order

of deca-BDE > nona-BDEs > octa-BDEs > hexa-BDE, hepta-BDE, penta-BDE, and tetra-BDE > tri-BDE (Figure 1). BDE-



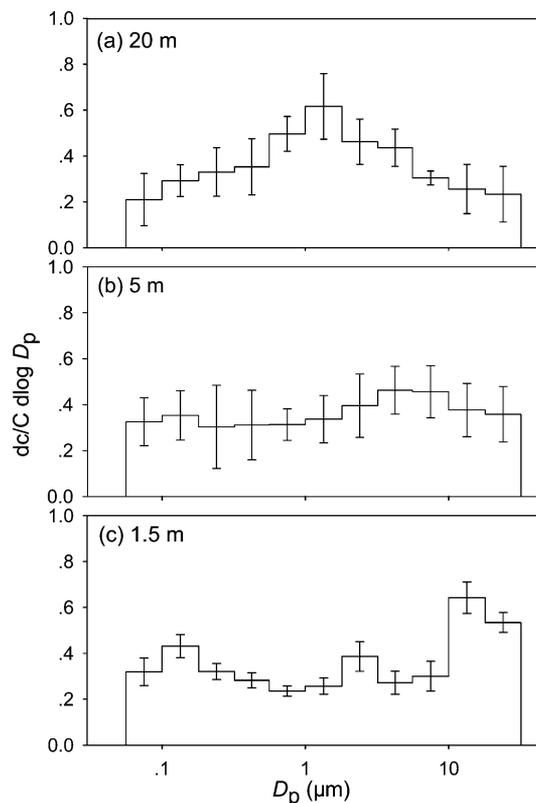
**Figure 1.** Concentration profiles of particle-bound PBDEs in the atmosphere of an e-waste recycling zone in Qingyuan (SI Figure S1). Dark solid and dashed vertical lines represent median and mean values, respectively. Box plots represent 25th–75th percentiles, whereas whiskers indicate fifth and 95th percentiles. Tri-BDE: BDE-28; tetra-BDE: BDE-47 and -66; penta-BDE: BDE-85, -99, and -100; hexa-BDE: BDE-153 and -154; hepta-BDE: BDE-181, -183, and -190; octa-BDE: BDE-196, -203, and -204; nona-BDE: BDE-206, -207, and -208; deca-BDE: BDE-209.

209 accounted for the highest proportion at 61% (range: 39–75%), followed by nona-BDEs and octa-BDEs contributing 19.5% and 10.7% of  $\Sigma$ PBDE, respectively. The relative abundance of nona-BDEs was higher than those in the deca-BDE commercial mixture (2–3%), and there was also a significant positive correlation ( $p < 0.05$ ) between the concentrations of BDE-209 and BDE-207 or BDE-208. These results indicated that debromination (photodegradation or pyrolysis) of BDE-209 had occurred during e-waste recycling.<sup>17–19</sup> Concentrations of particle-bound  $\Sigma$ PBDE ranged from 3400 to 12300  $\text{pg m}^{-3}$  with a median of 7600  $\text{pg m}^{-3}$  (SI Table S2), much greater than those (11.0–840  $\text{pg m}^{-3}$ ) of a slightly different group of PBDE congeners (SI List S1) in non-e-waste recycling zones.<sup>20</sup>

No significant difference in the concentrations of individual PBDEs (except for BDE-204, -207, and -209) was found at three heights ( $t$ -test,  $p > 0.05$ ) (SI Table S3); the concentrations of BDE-204 were higher at 20 m than at 1.5 m, and the total concentrations of BDE-209 and -207 at 20 and 5 m were significantly greater than those at 1.5 m ( $t$ -test,  $p < 0.05$ ). As such, the observed situation of significant greater concentrations of  $\Sigma$ PBDE at the 20 and 5 m heights than those at 1.5 m ( $t$ -test,  $p < 0.05$ ) (SI Table S3) was mainly caused by increased concentrations of heavily brominated congeners. A possible explanation is that atmospheric particle-bound PBDEs in the e-waste recycling zone were transported from the nearby e-waste-recycling facilities on the ground and mixed at elevated heights.<sup>3</sup> It may also suggest that emission and transportation mechanisms of lightly and heavily brominated congeners were different in the atmosphere. More discussions are detailed in the following sections.

**Emission Sources of Size-Fractionated PBDEs.** The size distribution of  $\Sigma$ PBDE was characterized by trimodal peaks in 0.10–0.18, 1.8–3.2, and 10–18  $\mu\text{m}$  at 1.5 m, bimodal peaks dominant in 3.2–10  $\mu\text{m}$  and subordinate in 0.10–0.18  $\mu\text{m}$  at 5

m, and an unimodal peak in 1.0–1.8  $\mu\text{m}$  at 20 m height on the basis of qualitative observation (Figure 2). It is notable that the



**Figure 2.** Size distributions of particle-bound  $\Sigma$ PBDE in the atmosphere at the different heights above the ground in the e-waste recycling zone: (a) 20 m, (b) 5 m, and (c) 1.5 m.  $dc$  is the concentration on each filter,  $C$  is the sum concentration on all filters, and  $d \log D_p$  is the logarithmic size interval for each impactor stage in aerodynamic diameter ( $D_p$ ). The error bars indicate standard deviation.

pattern of bimodal distribution was less significant at the 5 m height considering the large errors. A bimodal size distribution of  $\Sigma$ PBDE in Heraklion (<0.57 and >8.1  $\mu\text{m}$ ) and Guangzhou (0.56–1.0 and 5.6–10  $\mu\text{m}$ ) was also observed near the ground.<sup>11,12</sup> A shift in the abundances of PBDEs toward the midsize fractions from 1.5 to 20 m was also observed in a previous study, i.e., bimodal peaks in 0.56–1.0 and 5.6–10  $\mu\text{m}$  at 1.5 m but only an unimodal peak in 0.56–1.0  $\mu\text{m}$  at 100 or 150 m in the urban atmosphere.<sup>12</sup> The difference was attributed to coagulation of fine particles and various deposition velocities of different-size particles.<sup>12</sup>

Concentrations of  $\Sigma$ PBDE in fine particles contributed to 47%, 50%, and 59% of total concentrations at 1.5, 5, and 20 m heights, respectively. These values were slightly lower than those obtained by two previous studies conducted in urban Guangzhou (63–69%)<sup>12</sup> and Greece (72–87% for the fraction with  $D_p < 1.66 \mu\text{m}$ ).<sup>11</sup> The different distribution patterns of PBDEs in fine and coarse particles may be attributed to different emission mechanisms of PBDEs in urban areas and e-waste recycling zones. Generally, the occurrence of PBDEs in the atmosphere may be derived from various sources, including vaporization from PBDE-containing products,<sup>12,21</sup> physical mechanistic processes such as abrasion or weathering,<sup>22</sup> and combustion.<sup>23,24</sup> Particle-bound PBDEs from vaporization are

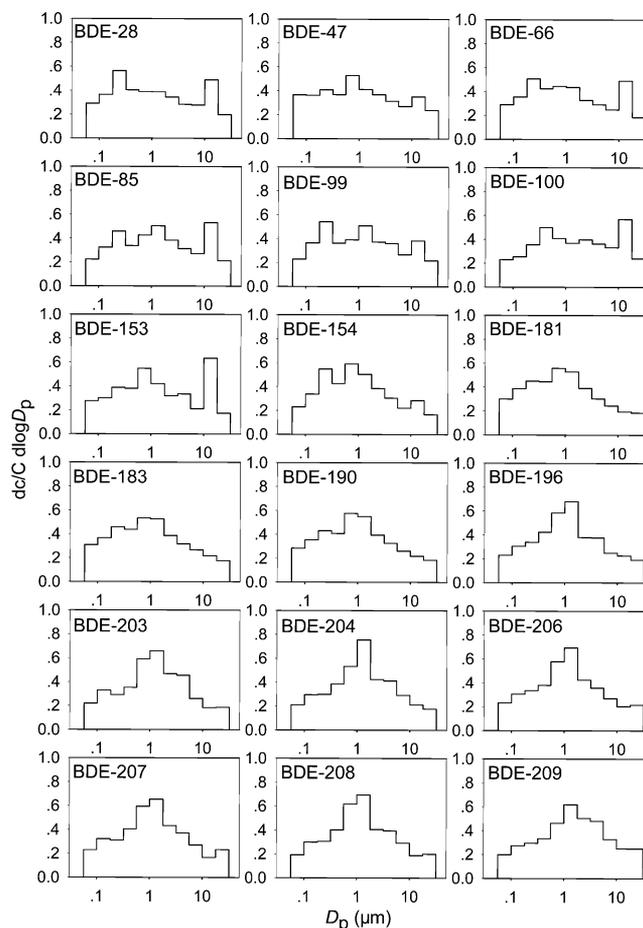
mainly affected by gas-to-particle partitioning dictated by particle surface areas and hence may prefer to affiliate with finer particles. Both adsorption and absorption models were used to explain the partitioning mechanism for PBDEs between the gaseous and particulate phases.<sup>20,21,25</sup> Mechanistic and combustion processes generally produce coarse and fine particles, respectively. Vaporization might be the main source of airborne PBDEs in urban areas such as Guangzhou<sup>12</sup> and Greece,<sup>11</sup> where PBDEs mainly distribute in fine particles. On the other hand, multiple emission mechanisms, i.e., a combination of volatilization, mechanical cracking and combustion, may have been responsible for the occurrence of PBDEs in e-waste recycling zones, because primitive procedures for e-waste recycling and disposal are still widely used in the e-waste recycling zone. In addition, the emission mechanism for PBDEs hypothesized in the present study was also different from those of PAHs<sup>2,5,26</sup> and PCDD/Fs,<sup>13</sup> which are mainly generated from incomplete combustion and therefore largely affiliated with fine particles.

Furthermore, resuspension of soil particles and dusts induced by wind or traffic has been reported as an additional source for atmospheric particle-bound pollutants.<sup>27–29</sup> Dust and soil resuspension tends to contribute large particles, and the resuspension capacity of soil and dust particles ( $D_p > 10 \mu\text{m}$ ) significantly decreases with increasing height due to large dry deposition velocities of large particles (SI Table S1).  $\Sigma\text{PBDE}$  associated with particles of  $D_p > 10 \mu\text{m}$  accounted for 30%, 18%, and 11.1% of the total concentrations at 1.5, 5, and 20 m heights, respectively. Apparently, the presence of sources at or close to the ground level should be collectively responsible for this observation. As discussed above, resuspension of soil and dust was deemed an appreciable source of PBDEs. This, in combination with the emission of particle-bound PBDEs at the ground level and gravitational settling of larger particles, results in significantly higher concentrations of PBDEs at the ground level and/or at lower heights in the e-waste recycling zone than at higher heights.

#### Proposed Mechanisms for Size Distribution of PBDEs.

Figure 3 and SI Figures S2 and S3 show the size distributions of individual PBDEs at three heights in the e-waste recycling zone. To succinctly describe the size distribution of PBDEs, geometric mean diameter (GMD) and geometric standard deviation (GSD) were calculated (SI Tables S4 and S5). The GMD values (0.98–1.98  $\mu\text{m}$ ) of PBDEs at 20 m in the present study were close to those (0.85–1.38  $\mu\text{m}$ ) in Guangzhou at 100–150 m height<sup>12</sup> but were larger than those (0.14–0.63  $\mu\text{m}$ ) in Greece.<sup>11</sup> The mean GMD values of most PBDE congeners decreased from 1.5 to 20 m (SI Table S4), and less volatile PBDEs except for BDE-206, -207, and -209 had larger GMD values. The GMD values of coarse and fine particle-bound PBDEs significantly decreased and increased, respectively, with increasing heights, suggesting that coarse particles tended to be deposited and scavenged while fine particles were aggregated, with increasing height. The GSD values were larger at 1.5 m than at 20 m, indicating a relatively broader mass size distribution at 1.5 m (SI Table S5). This broader size distribution and larger mass fraction of PBDEs in coarse particles at the ground level may have resulted from more significant resuspension of soil and dust.

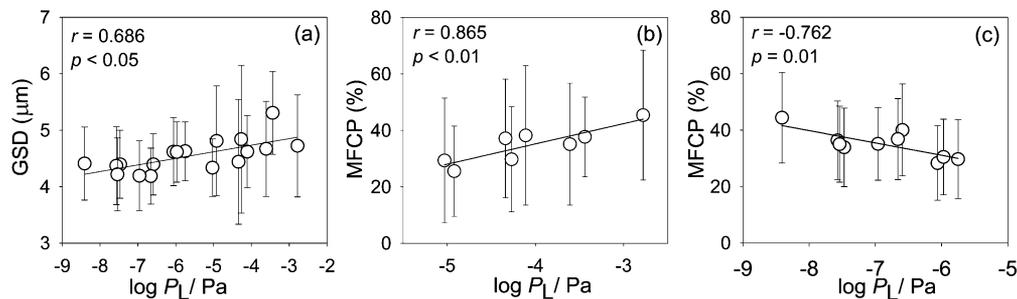
To minimize the interferences of soil and dust resuspension to the assessment results, only the data at 20 m were used to discuss the effect of vapor pressure on size distribution. No significant correlation between GMD values and vapor



**Figure 3.** Size distributions of particle-bound PBDE congeners in the atmosphere at 20 m height above the ground in the e-waste recycling zone.  $d_c$  is the concentration on each filter,  $C$  is the sum concentration on all filters, and  $d \log D_p$  is the logarithmic size interval for each impactor stage in aerodynamic diameter ( $D_p$ ).

pressures of PBDEs was observed. However, the GSD values increased weakly with decreasing level of bromination at 20 m (Figure 4a), suggesting broader size distribution for higher vapor-pressure congeners. Compounds with higher vapor pressure in particles more easily evaporate into the gaseous phase and subsequently redistribute to all size particle fractions, while less volatile congeners tend to stay in particles.

On the other hand, previous studies reported that the mass fractions of contaminants in coarse particles gradually decreased with decreasing vapor pressures.<sup>30,31</sup> In the present study, a positive correlation ( $r = 0.865$ ,  $p < 0.01$ , Figure 4b) was obtained between mass fractions of PBDE congeners in coarse particles and the logarithmic subcooled liquid vapor pressures ( $\log P_L/\text{Pa}$ ) at 298 K<sup>32</sup> for lightly brominated (tri- to hexa-BDEs) congeners, but a negative correlation ( $r = -0.762$ ,  $p = 0.01$ , Figure 4c) was observed for heavily brominated (hepta- to deca-BDEs) congeners. This discrepancy indicated that particle-bound lightly and heavily brominated congeners behave differently in the environment. Generally, heavily brominated (hepta- to deca-BDEs) congeners are predominant in particles, while lower brominated (tri- to hexa-BDEs) congeners are abundant in the gaseous phase, due to their different octanol-air partition coefficients. As a result, particle-bound heavily brominated congeners tend to stay in particles of some special sizes, while the lightly brominated congeners may



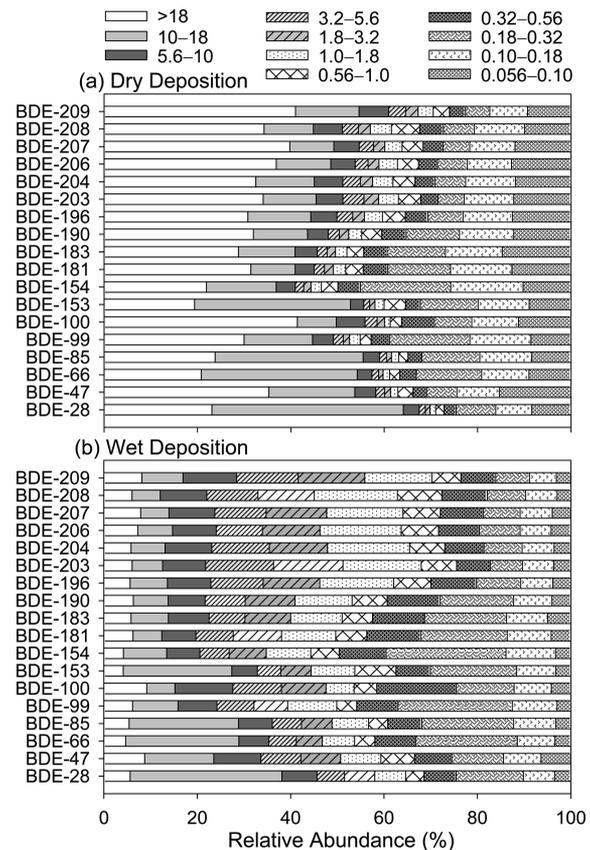
**Figure 4.** Correlation (a) between geometric standard deviations (GSD,  $\mu\text{m}$ ) of particle-bound PBDEs and logarithmic subcooled liquid vapor pressures ( $\log P_L/\text{Pa}$ ) at 298 K<sup>32</sup> and (b,c) between mass fractions in coarse particles (MFCP, coarse particles: aerodynamic diameters  $>1.8 \mu\text{m}$ ) and  $\log P_L/\text{Pa}$  in the atmosphere at 20 m height above the ground in the e-waste recycling zone. (b) For lightly (tri- to hexa-BDE) and (c) for heavily (hepta- to deca-BDE) brominated congeners.

redistribute among different-sized particles. The discrepancy may also implicate different emission sources of individual PBDE congeners, i.e., lightly brominated congeners in the atmosphere were mainly derived from evaporation and reabsorption, while heavily brominated congeners were probably emitted in affiliation with particles during the mechanical and combustion processes of e-waste. Similarly, Tian et al.<sup>21</sup> suggested that lightly brominated congeners (di- to hexa-BDEs) in the atmosphere of an e-waste recycling site were mainly derived from evaporation, while Wilford et al.<sup>33</sup> regarded mechanical formation as the main mechanism for heavily brominated congeners (hepta- to deca-BDE).

Moreover, the difference in chemical affinities between PBDE congeners and particles has also been used to explain the discrepant size distributions of particle-bound PBDEs.<sup>11</sup> Theoretically, high molecular weight PBDEs tend to affiliate with fine particles with large surface areas because of their strong hydrophobicity.<sup>31</sup> Such an explanation, however, can not adequately account for the PBDE distribution patterns observed in the present study. Perhaps heavily brominated congeners did not attain equilibrium but reached steady state between the gaseous and particulate phases due to slow mass transfer.<sup>34–36</sup>

**Implications for Dry and Wet Deposition.** So far, a large number of reports on atmospheric deposition fluxes of particle-bound PBDEs have been published,<sup>12,15,37–40</sup> but only a few accounted for the size dependency of some important parameters such as dry deposition velocity and removal efficiency of particle-bound compounds by wet deposition.<sup>7,12,16</sup> To further understand the significance of size dependency in dry and wet deposition fluxes of particle-bound PBDEs, size-fractionated data acquired in the present study were used for assessment (only the data acquired at 20 m were used, as ground mechanical disturbance was expected to be minimal at this height).

The relative abundances of dry and wet deposition fluxes for size-fractionated PBDEs are displayed in Figure 5 and SI Table S6. Dry deposition fluxes of particle-bound  $\Sigma\text{PBDE}$  were mainly contributed by coarse particles ( $D_p > 1.8 \mu\text{m}$ ), ranging from 50% to 79% with a mean of 64%. This finding was similar to the result of Holsen et al. that the particle fraction with  $D_p > 6.5 \mu\text{m}$  accounted for 62–94% of the total PCBs dry deposition fluxes in urban areas,<sup>41</sup> probably attributed to shorter residency time for coarse particles than that for fine particles. The calculated mean dry deposition velocities of individual PBDE congeners were 0.23–0.29  $\text{cm s}^{-1}$  (SI Table S7), in the approximate range of those in Hong Kong (0.24–0.28  $\text{cm}$



**Figure 5.** Calculated relative abundance of (a) dry and (b) wet deposition fluxes of particle-bound PBDE congeners by size-fractionated particles at 20 m height above the ground in the e-waste recycling zone.

$\text{s}^{-1}$ )<sup>42</sup> and Guangzhou (0.11–0.28  $\text{cm s}^{-1}$ ).<sup>12</sup> In addition, no significant difference among these dry deposition velocities was observed in the present study (*t*-test,  $p > 0.05$ ), as also obtained previously,<sup>12</sup> attributable to no link between the mass fractions of PBDE congeners in coarse particles and their volatilities. Contrary to our result, Cetin and Odabasi<sup>40</sup> observed decreased dry deposition velocities of PBDEs with increasing molecular weights and ascribed the observation to preferential affiliation of heavily brominated congeners to fine particles.

Approximately 68% (65–72%) of particle-bound PBDEs was removed by wet deposition (SI Table S7), which was more than those (50–60%) of particle-bound PAHs obtained in the previous studies.<sup>13,43</sup> Wet deposition fluxes of individual PBDE

congeners (except for BDE-28 and -209) were dominated by fine particles (Figure 5 and SI Table S6). Kaupp and McLachlan also suggested that the  $D_p < 1.35 \mu\text{m}$  fraction contributed 79–85% and 77–92% of the wet deposition fluxes of PCDD/Fs and PAHs, respectively.<sup>13</sup> Different from dry deposition, the relative contributions of fine and coarse particles were comparable for wet deposition of  $\Sigma\text{PBDE}$ . This difference resulted from larger variances among size-fractionated dry deposition velocities in the atmosphere (SI Table S1).

The total mean deposition fluxes of PBDEs ranged from 4.7  $\text{ng m}^{-2} \text{d}^{-1}$  for BDE-28 to 1960  $\text{ng m}^{-2} \text{d}^{-1}$  for BDE-209 (SI Table S6). The total mean deposition flux of particle-bound  $\Sigma\text{PBDE}$  was estimated at 3000  $\text{ng m}^{-2} \text{d}^{-1}$  in the e-waste recycling zone in the present study, similar to that (2300  $\text{ng m}^{-2} \text{d}^{-1}$ ) for the sum of several PBDE congeners (SI List S2) in urban Guangzhou,<sup>42</sup> and approximately 10 times greater than those in an e-waste recycling area of Qingyuan (SI List S3; 420  $\text{ng m}^{-2} \text{d}^{-1}$ )<sup>37</sup> and urban Hong Kong (SI List S2; 260  $\text{ng m}^{-2} \text{d}^{-1}$ ).<sup>42</sup> The difference between the results of the present study and Tian et al.,<sup>37</sup> conducted within approximately the same area, may have stemmed from different specific sampling sites (e.g., distances to various e-waste recycling facilities) and different sampling procedures in the two studies. Tian et al.<sup>37</sup> accumulated deposition samples for an entire month, so the analyte concentrations may have been underestimated due to degradation and volatilization. Furthermore, the total dry deposition fluxes of  $\Sigma\text{PBDE}$  in the present study were 1.9–2.4 times greater than the total wet deposition fluxes for the dry weather season based on these estimated results (SI Table S6). Our previous study<sup>44</sup> also found lower wet deposition fluxes of particulate matter and PAHs than dry deposition fluxes during the dry weather season in urban Guangzhou in 2010. Lower wet deposition fluxes may be ascribed to less precipitation amounts during the dry weather season. Nevertheless, deposition fluxes estimated by size-fractionated particle in the present study harbor some uncertainties because of the inherent variabilities of the parameters used, such as size-specific deposition velocities and effect of meteorological conditions. Again, only the deposition fluxes of particle-bound PBDEs during the dry weather season were estimated in the present study; therefore further studies (e.g., temporal and spatial variation and corresponding influencing mechanisms) are needed to provide insights into the atmospheric deposition of PBDEs. Although our previous studies<sup>7,12,15,44</sup> have systematically investigated dry and wet depositions of PBDEs and PAHs in urban Guangzhou, the present study has taken advantage of the size-fractionated particle-bound PBDEs data to re-examine the governing mechanisms for dry and wet depositions of PBDEs.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Additional text, tables, and figures as mentioned in the main text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: 86-755-26033017. Fax: 86-755-85293254. E-mail: nihg@pkusz.edu.cn.

### Notes

The authors declare no competing financial interest.

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