

# Health Risk Characterization for Resident Inhalation Exposure to Particle-Bound Halogenated Flame Retardants in a Typical E-Waste Recycling Zone

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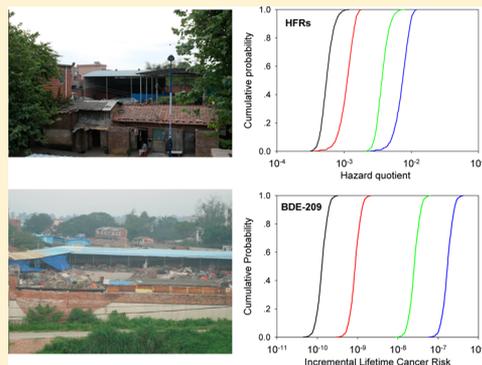
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## Supporting Information

**ABSTRACT:** Inhalation of pollutants is an important exposure route for causing human health hazards, and inhalation exposure assessment must take into account particle size distribution because particle-bound pollutants are size-dependent. Such information is scarce, particularly for residents dwelling within e-waste recycling zones where abundant atmospheric halogenated flame retardants (HFRs) commonly used in electronic/electrical devices have been widely reported. Atmospheric size-fractioned particle samples were collected using a 10-stage Micro-Orifice Uniform Deposit Impactor from an e-waste recycling zone in South China. The deposition efficiencies and fluxes of size-fractioned HFRs including polybrominated diphenyl ethers (PBDEs), alternative brominated flame retardants, and Dechlorane Plus in the human respiratory tract were estimated using the International Commission on Radiological Protection deposition model. The majority of HFRs was found to deposit in the head airways, with coarse particles (aerodynamic diameter ( $D_p$ ) > 1.8  $\mu\text{m}$ ) contributing the most (69–91%). Conversely, fine particles ( $D_p$  < 1.8  $\mu\text{m}$ ) were dominant in the alveolar region (62–80%). The inhalation intake of PBDEs within the e-waste recycling zone was 44 ng/d (95% confidence interval (CI): 30–65 ng/d), close to those through food consumption in non-e-waste recycling regions. The estimated total hazard quotient of particle-bound HFRs was  $5.6 \times 10^{-4}$  (95% CI:  $3.8 \times 10^{-4}$ – $8.8 \times 10^{-4}$ ). In addition, incremental lifetime cancer risk induced by BDE-209 was  $1.36 \times 10^{-10}$  (95% CI:  $7.3 \times 10^{-11}$ – $2.3 \times 10^{-10}$ ), much lower than the Safe Acceptable Range ( $1.0 \times 10^{-6}$ – $1.0 \times 10^{-4}$ ) established by the United States Environmental Protection Agency. These results indicate that the potential health risk from inhalation exposure to particle-bound HFRs for residents dwelling in the e-waste recycling zone was low.



## INTRODUCTION

Due to technological innovation and economic growth, upgrading cycles of electronic products have become shorter. For example, the average service lifespan of computer central processing units decreased by more than half from 1997 to 2005.<sup>1</sup> Shortened lifespans, combined with increasing demands for electronic products, have led to growing quantities of obsolete electronic devices or electronic waste (e-waste). A recent estimate has pegged the annual amount of global e-waste at nearly 50 million tons.<sup>2</sup> Because of the high cost for handling e-waste in developed countries, approximately 80% of e-waste generated in developed countries was exported to developing countries such as China, India, Nigeria, and Pakistan each year.<sup>3,4</sup> In these developing countries, primitive methods, such as manual dismantling, open burning, metals melting, and acid dipping, are

often used to recover useful materials from e-waste,<sup>4</sup> readily releasing toxic contaminants into the surrounding environment and causing adverse human health consequences.<sup>5,6</sup>

Occupational exposure in the e-waste processing facilities has long been recognized as a source of human health hazards, as indicated by high levels of toxic heavy metals and organic contaminants found in samples of air, dust, and other environmental media from these facilities.<sup>7–11</sup> This exposure can be substantially reduced, however, if proper protective measures (e.g., gloves, gowns, and respirators) are used by

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workers. At the other end of the spectrum, the general population is basically free of e-waste footprints but may still be exposed to various halogenated flame retardants (HFRs) embedded in household electronic appliances such as computers, television sets, and refrigerators.<sup>7,12</sup> The most intriguing population segment is that of residents dwelling within e-waste recycling zones, as it may present the highest level of nonoccupational exposure to HFRs<sup>13–15</sup> and thus merits further investigations.

Among the main human exposure pathways (dietary intake, dermal contact, dust ingestion, and inhalation), inhalation exposure is the hardest to control and therefore may be a good indicator of human health hazards posed by e-waste derived toxic materials. In particular, some important ingredients of HFRs such as polybrominated diphenyl ethers (PBDEs) tend to affiliate with airborne particles,<sup>7,16</sup> because they have low saturated vapor pressures and large octanol–air partition coefficients.<sup>17</sup> Furthermore, inhalation exposure to particle-bound organic contaminants is highly particle size-dependent, e.g., smaller particles can penetrate into the deeper respiratory tract so as to carry more contaminants to the lung.<sup>18–21</sup> Therefore, particle size distribution of HFRs must be taken into account when inhalation exposure is investigated. Previous studies only measured distribution of contaminants in total suspended particles and/or particles with aerodynamic diameter smaller than 2.5  $\mu\text{m}$  from e-waste recycling areas.<sup>7,22</sup> To date, no size dependency has been considered in measurements of human exposure to particle-bound HFRs, especially related to e-waste recycling.

The present study addressed this knowledge gap by quantifying the doses of resident inhalation exposure to size-fractionated particle-bound HFRs and associated health risks within an e-waste recycling zone. An e-waste recycling zone in Qingyuan, Guangdong Province of China (Supporting Information (SI) Figure S1) was chosen as a case study, because it is home to a large number of scattered dismantling and recycling workshops. Particulate samples were collected outdoor at three heights of 1.5, 5, and 20 m, representative of first, second, and sixth floors in a typical housing unit. Target chemicals included brominated and chlorinated flame retardants, such as PBDEs, alternative brominated flame retardants (ABFRs), and Dechlorane Plus (DP). Comparisons were also made with dietary intake and inhalation exposure to heavy metals and organic contaminants other than the target analytes, to strengthen the main conclusions.

## MATERIALS AND METHODS

**Materials.** Eighteen individual BDE congeners, including BDE-28, 47, 66, 85, 99, 100, 153, 154, 181, 183, 190, 196, 203, 204, 206, 207, 208, and 209, and six ABFRs, including tetrabromoethylcyclohexane (TBECH), hexachlorocyclopentadienyl dibromocyclooctane (HCDBCO), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-tetrabromophthalate (TBPH), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenyl ethane (DBDPE), were purchased from AccuStandard (New Heaven, CT). DP was purchased from Wellington Laboratories (Guelph, Canada). Surrogate standards (BDE-51, BDE-115, <sup>13</sup>C-BDE-138, and <sup>13</sup>C-BDE-209) and internal standards (BDE-69, <sup>13</sup>C-PCB-208, and <sup>13</sup>C-BDE-139) were purchased from Cambridge Isotope Laboratories (Andover, MA).

**Sample Collection.** Particulate samples were collected by a Micro-Orifice Uniform Deposit Impactor (MOUDI) (MSP Corporation, Shoreview, MN) outside selected residential

apartments around the e-waste recycling zone in Qingyuan, Guangdong Province, South China (SI Figure S1). Each sample was collected on 47 mm diameter glass microfiber filters (Whatman International, Maidstone, England) at a constant flow rate of 30 L/min and separated into 11 size fractions as follows: >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  $\mu\text{m}$ . The daily sampling time was approximately 12 h from 07:30 to 19:30 in October and November 2012. The meteorological conditions of October and November at this site were suited for field sampling, e.g., relatively stable air flow (wind speed less than 3.7 m/s), low amounts of precipitation, and mild temperature (18–26 °C). Sampling was conducted at three heights: 1.5 m above the ground and two rooftop levels of 5 and 20 m. A total of 264 particle samples (24 samples containing 11 size fractions) were collected, and one set of 88 samples was collected at each of the three heights.

**Sample Extraction and Clean-Up.** Each sample was spiked with the surrogate standards and Soxhlet extracted with 200 mL of hexane, dichloromethane, and acetone mixture (1:1:1 in volume) for 24 h. The extract was concentrated, solvent-exchanged to hexane, and further concentrated with a Zymark TurboVap 500 (Hopkinton, MA). The concentrated extract was purified with a glass column packed with 3 cm alumina, 3 cm neutral silica gel, 3 cm acid silica, and 1 cm anhydrous sodium sulfate from bottom to top. The fraction containing HFRs was successively eluted with 10 mL of hexane and 20 mL of hexane and dichloromethane mixture (1:1 in volume), then concentrated to 50  $\mu\text{L}$ , and spiked with the internal standards before instrumental analysis.

**Instrumental Analysis.** All samples were analyzed with an Agilent 7890A gas chromatograph 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) was used for chromatographic separation. The column temperature was programmed from 110 °C (held for 5 min) and elevated to 200 °C at 40 °C/min (held for 4 min), ramped to 260 °C at 10 °C/min (held for 1 min), and further increased to 310 °C at 15 °C/min (held for 15 min). All samples were automatically injected (2  $\mu\text{L}$  each) in a programmed temperature vaporizer with an initial temperature of 120 °C (held for 0.04 min) and then elevated to 290 °C at 600 °C/min (held for 30 min). Carrier gas was ultrahigh purity helium at a flow rate of 1.5 mL/min. The ion source and quadrupole temperatures were set at 200 and 150 °C, respectively. Quantitative analysis was performed in the selected ion monitoring mode. The internal standard (<sup>13</sup>C-PCB-208) and surrogate standard (<sup>13</sup>C-BDE-209) were monitored at  $m/z$  476, 474, and 478 and  $m/z$  495, 497, and 493, respectively. Other internal and surrogate standards were monitored at  $m/z$  79, 81, and 160. Characteristic ions of the target compounds for mass spectral analysis are present in the SI Table S1.

**Quality Assurance and Quality Control.** One procedural blank, one spiked blank, one matrix blank, and one matrix spiked sample were analyzed for every batch of 20 samples. The recoveries of the surrogate standards, i.e., 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. The amounts of HFRs detected in the blank samples were less than 5% of those in the field samples. Concentrations of HFRs in all field samples were corrected by those detected in the corresponding procedural blanks within the same batch but not

**Table 1. Comparison between the Median (Range) Concentrations (pg/m<sup>3</sup>) of PBDEs in Ambient Air in a Typical E-Waste Recycling Zone, South China, and Other Indoor Environments Around the World**

source of air	site	BDE-209	Σnon-209 BDEs <sup>a</sup>	sampling year	ref
gas + particles	bedroom, Massachusetts, United States	(nd <sup>b</sup> –270)	(93–1340) <sup>c</sup>	2006	35
gas + particles	main living area, Massachusetts, United States	(nd–650)	(82–3500) <sup>c</sup>	2006	35
gas + particles	office, Stockholm, Sweden	2400 (57–3600)	<i>d</i>	2006–2007	34
gas + particles	day care center, Stockholm, Sweden	820 (62–1400)	<i>d</i>	2006–2007	34
particles	house, Michigan, United States	<i>d</i>	530 (nd–3900) <sup>e</sup>	2006–2007	58
gas + particles	home, Guangzhou, China	250 (39–11500)	630 (125–2900) <sup>f</sup>	2004–2005	33
gas + particles	office, Guangzhou, China	170 (80–13700)	520 (180–8300) <sup>f</sup>	2004–2005	33
gas + particles	house, United States	<i>d</i>	440 (76–2100) <sup>g</sup>	2001	59
gas + particles	workplace, Birmingham, United Kingdom	<i>d</i>	1080 (82–15500) <sup>h</sup>	2001–2002	39
gas + particles	domestic, Birmingham, United Kingdom	<i>d</i>	125 (60–1600) <sup>h</sup>	2001–2002	39
particles	outdoor, Qingyuan, China	3600 (2500–4100)	2100 (2000–2300) <sup>i</sup>	2012	present study <sup>j</sup>

<sup>a</sup>Sum of PBDE congeners except for BDE-209. <sup>b</sup>Below the limits of detection. <sup>c</sup>Sum of BDE-17, 28/33, 47, 49, 66, 85/155, 99, 100, 153, and 154. <sup>d</sup>Not available. <sup>e</sup>Sum of BDE-17, 28, 47, 49, 66, 71, 75, 85, 99, 100, 153, and 154. <sup>f</sup>Sum of BDE-28, 47, 66, 85, 99, 100, 138, 153, 154, and 183. <sup>g</sup>Sum of BDE-17, 28/33, 47, 99, 100, 153, 154, and 183. <sup>h</sup>Sum of BDE-47, 99, 100, 153, and 154. <sup>i</sup>Sum of BDE-28, 47, 66, 85, 99, 100, 153, 154, 181, 183, 190, 196, 203, 204, 206, 207, and 208. <sup>j</sup>Data at 1.5 m height above the ground.

corrected for the surrogate standard recoveries. The mean recoveries of the target compounds in the spiked samples were 64–122% (individual standard deviations <16%). The lowest calibration concentrations divided by the actual sample volumes were defined as the reporting limits for the target compounds. In the present study with an average air sampling volume of 21.6 m<sup>3</sup> and a final extract volume of 50 μL, the reporting limit was 0.23 pg/m<sup>3</sup> for PBDEs (except for BDE-209), ABFRs (except for DBDPE), and DP and was 2.3 pg/m<sup>3</sup> for BDE-209 and DBDPE. Analyte concentrations below the reporting limits were set as zero in assessment of deposition fluxes and health risk.

**Data Analysis.** To estimate the deposition efficiency and flux of inhaled HFRs in the human respiratory tract, we adopted the simplified equations from the International Commission on Radiological Protection (ICRP) model.<sup>23,24</sup> The model calculates the deposition fractions of inhaled particles in three main regions of the respiratory tract, i.e., head airway (HA), tracheobronchial region (TB), and alveolar region (AR). More details about the model are provided in the SI. The deposition fluxes were estimated using the deposition efficiencies and concentrations of HFRs in each size fraction. The human breathing rate under normal conditions was chosen as 0.45 m<sup>3</sup>/h.<sup>20</sup>

The noncancer risk from inhalation exposure can be evaluated by hazard quotient (HQ):<sup>25</sup>

$$HQ = EI / (BW \times Rfd)$$

where EI is the estimated daily intake (pg/d), which is estimated from deposition fluxes (pg/h) and daily exposure time (h/d); BW is the body weight, which was assumed to be 60 kg for adults; and Rfd is the reference dose (pg/kg bw/d) for a specific compound, which is detailed in SI Table S1. The exposure time per day was set as 24 h because the difference between indoor and outdoor air conditions is insignificant due to generally good ventilation for residencies in rural areas of China.<sup>26</sup> Values of HQ greater than 1 suggest potential health risk.<sup>25</sup> The HQ approach has been widely applied in human health risk assessment in previous studies and by the United States Environmental Protection Agency (USEPA).<sup>12,25–28</sup> Cancer risk through inhalation was estimated with eq S7 in the SI.<sup>25</sup>

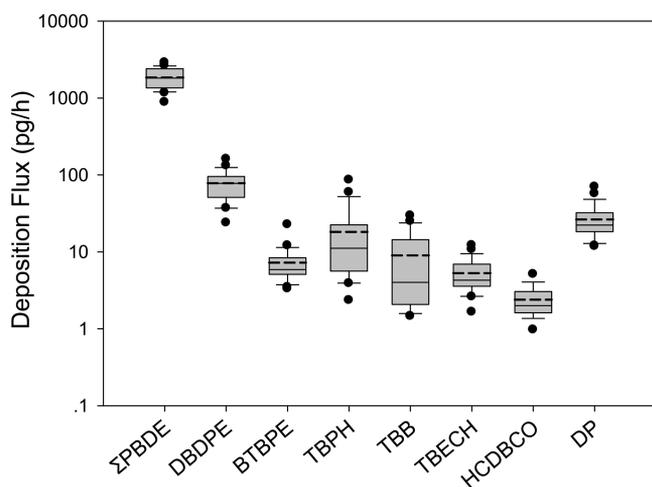
**Uncertainty Analysis.** Monte Carlo simulation was used to evaluate the uncertainty and variability of inhalation doses and predicted exposure risk. Concentrations of individual HFRs were

separately assumed to be log-normally distributed with the mean and standard deviation values set as the measured values from the present study. Particle size diameters in each size fraction were assumed to follow log-uniform distribution within the minimum and maximum size values. The Monte Carlo simulation was run 1000 times repeatedly with different input data.

## RESULTS AND DISCUSSION

**Inhalation Exposure to Polybrominated Diphenyl Ethers.** Because there are insufficient monitoring data of ABFRs and DP in air in the literature, only PBDEs are discussed here. The concentrations of PBDEs from outdoor air in the present study were greater than those in outdoor air in most urban or rural regions<sup>29–33</sup> but were comparable to those determined in many indoor samples (Table 1). For example, reported levels of PBDEs in residential areas, offices, and day care centers<sup>33–35</sup> in non-e-waste recycling zones were comparable to and/or slightly lower than those from outdoor in the e-waste recycling zone in the present study. It suggested that a large amount of electronic products containing PBDEs, such as computers, printers, and other electrical appliances, flooded the indoor environments in non-e-waste recycling zones. Moreover, Ferro et al.<sup>36</sup> noticed that personal exposure (i.e., participants carrying sampling devices) to particulate matter was 1.4–1.6 times higher than that obtained by a stationary area monitor. Allen et al.<sup>35</sup> also indicated that personal inhalation exposure to indoor air PBDEs was approximately 1–4 times higher than that by a stationary area monitor. They proposed a “personal cloud” effect to account for the difference between the actual exposure dose and stationary monitor reading. The “personal cloud” effect refers to increased personal exposure relative to stationary air because of specific activities such as walking, cooking, or dusting.<sup>37</sup> Stationary area monitors were still used in the present study, because meteorological factors such as wind can neutralize the effect in an outdoor environment. If the “personal cloud” effect was assumed to occur in indoor environments, i.e., the measured indoor pollutant concentrations were increased by 1–4 times, doses of inhalation exposure to indoor air PBDEs in these non-e-waste recycling regions would be similar to those around the e-waste recycling zone in the present study. This means that residing in indoor environments in non-e-waste recycling regions is almost equivalent to traveling in e-waste recycling sites in terms of inhalation exposure to PBDEs.

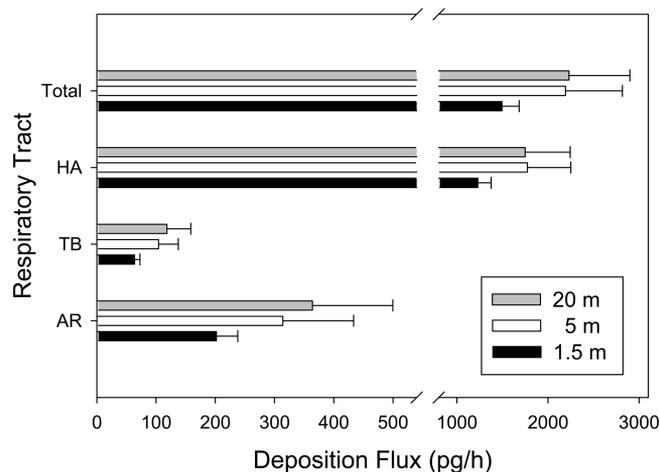
**Particle Size Distribution of Deposition Fluxes in the Human Respiratory Tract.** To evaluate the contributions of different size-fractionated particle-bound HFRs to human health risk, deposition fluxes of inhaled HFRs in the human respiratory tract were estimated with the ICRP model (Figure 1 and SI Table



**Figure 1.** Total deposition fluxes of particle-bound halogenated flame retardants in the head airways, tracheobronchial region, and alveolar region of the human respiratory tract. Dark solid and dashed horizontal lines represent median and mean values, respectively. Box plots represent 25th–75th percentiles, whereas whiskers indicate 5th and 95th percentiles. All acronyms are defined in the main text and  $\Sigma$ PBDE is the sum of BDE-28, 47, 66, 85, 99, 100, 153, 154, 181, 183, 190, 196, 203, 204, 206, 207, 208, and 209.

S2). The deposition fluxes of  $\Sigma$ PBDE (sum of 18 BDE congeners),  $\Sigma$ ABFR (sum of six ABFRs), and DP were 880–2900, 64–178, and 12–70 pg/h, respectively. Of these HFRs, BDE-209 was the dominant component contributing an average of 58% (range: 38–71%) to the total deposition fluxes, suggesting that BDE-209 was still dominating HFRs in electronic products. Other PBDEs (except for BDE-209) were responsible for only 35% (range: 19–57%) of the total deposition fluxes. In addition, PBDEs were the main constituents (accounting for 83–97%) of HFRs contributing to human inhalation exposure in the e-waste recycling zone.

The fluxes of  $\Sigma$ HFR (sum of all target compounds in the present study, i.e.,  $\Sigma$ PBDE,  $\Sigma$ ABFR, and DP) deposited in the HA, TB, and AR regions of the human respiratory tract were 860–2700, 53–155, and 152–510 pg/h, respectively, with the mean values following the sequence of HA (1600 pg/h) > AR (300 pg/h) > TB (97 pg/h). Likewise, the relative amount of polycyclic aromatic hydrocarbons (PAHs) deposited in the AR (21%) was smaller than that deposited in the HA (73%) in an urban indoor environment.<sup>20</sup> Moreover, the total mean deposition flux of PBDEs at the 20 m height (2100 pg/h) was approximately 1.5 times that at 1.5 m (1360 pg/h), while the mean AR deposition flux at 20 m (350 pg/h) was 1.9 times that at 1.5 m (180 pg/h) (Figure 2). Although the total deposition fluxes of HFRs at 5 and 20 m were not significantly different (*t*-test,  $p > 0.05$ ), they were both significantly greater than that at 1.5 m (*t*-test,  $p < 0.05$ ). This may reflect that HFRs from the nearby e-waste recycling facilities were transported at elevated height and did not mix down to the ground level. Therefore, residents living on the higher floors of a building are subject to greater inhalation



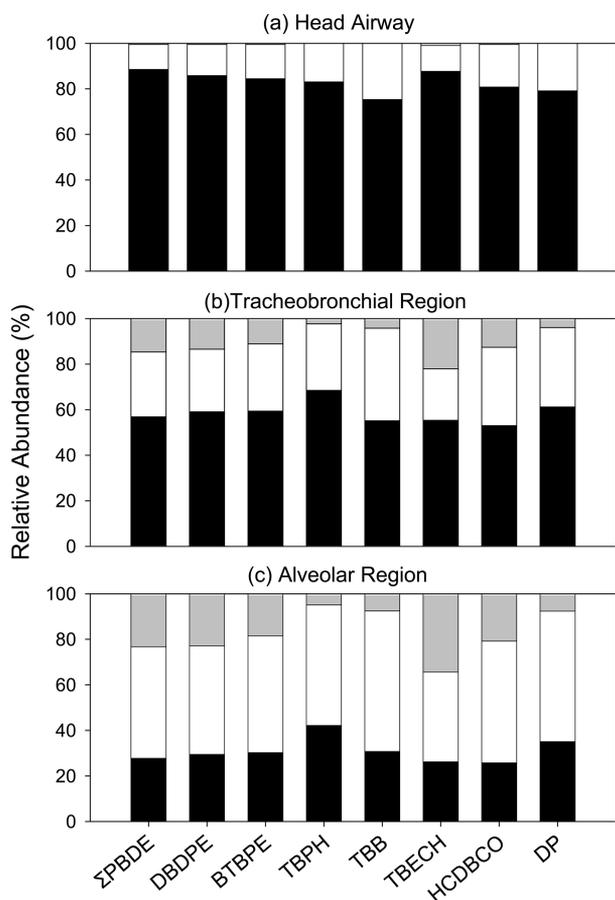
**Figure 2.** Deposition fluxes of particle-bound halogenated flame retardants in the e-waste recycling zone (SI Figure S1) in the head airways (HA), tracheobronchial region (TB), and alveolar region (AR) of the human respiratory tract at three heights: 1.5 m above the ground and two rooftop levels of 5 and 20 m. The total is sum of HA, TB, and AR.

exposure to HFRs than those living on the lower floors within the e-waste recycling zone.

The total mean deposition efficiencies of individual HFRs for the three regions in the human respiratory tract were estimated at 46–67%, higher than those (37–42%) for PAHs.<sup>18</sup> The deposition efficiencies of HFRs in the AR were 5–10%, close to or slightly lower than those of PAHs, i.e., 16–19%,<sup>18</sup> 8.6–10.2%,<sup>20</sup> and 23–28%.<sup>38</sup> The difference between the deposition efficiencies of HFRs and PAHs in the AR may be attributed to different particle size distributions of these contaminant classes. Previous studies observed greater concentrations of PAHs in particles of smaller size fractions, i.e., the majority of PAHs was distributed in fine particles.<sup>18,38</sup>

The relative amounts of size-fractionated HFRs deposited in the three regions of the human respiratory tract are shown in Figure 3 (details are displayed in SI Figure S2). Apparently, coarse particles (aerodynamic diameter ( $D_p$ ) > 1.8  $\mu$ m) contributed the most in the HA (69–91%), while fine particles ( $D_p < 1.8 \mu$ m), including accumulation mode particles (1.8  $\mu$ m >  $D_p > 0.1 \mu$ m) and ultrafine particles ( $D_p < 0.1 \mu$ m), were dominant in the AR (62–80%). In the TB, coarse and fine particles were almost equally important, i.e., 44–68% for coarse particles and 32–56% for fine particles. In particular, ultrafine particles contributed 6.1–34% to the AR deposition, approximately twice as much as their contributions to the particle phase concentrations of HFRs (2.2–14.6%), i.e., ultrafine particles can carry relatively more HFRs into the deep region of the lung. Similar findings have also been reported in previous studies.<sup>18,20,21</sup> For example, Kawanaka et al. found that ultrafine particles contributed 10–30% to the amounts of PAHs deposited in the AR but only 1.3–2.3% to the total amounts in the particle mass.<sup>18</sup> Apparently, particle size distribution is a critical factor in dictating human inhalation exposure to particle-bound HFRs and related health risk.

Inhalation exposure has been widely assessed with concentrations of total particle-bound contaminants, perhaps corrected by certain intake factors, e.g., 0.75 used to represent the fraction that can penetrate into the lung.<sup>39–41</sup> However, the present study suggested that not all inhaled HFRs can deposit in the human respiratory tract, and the estimated mean portion deposited in the human respiratory tract was only 49–74% of the inhalable



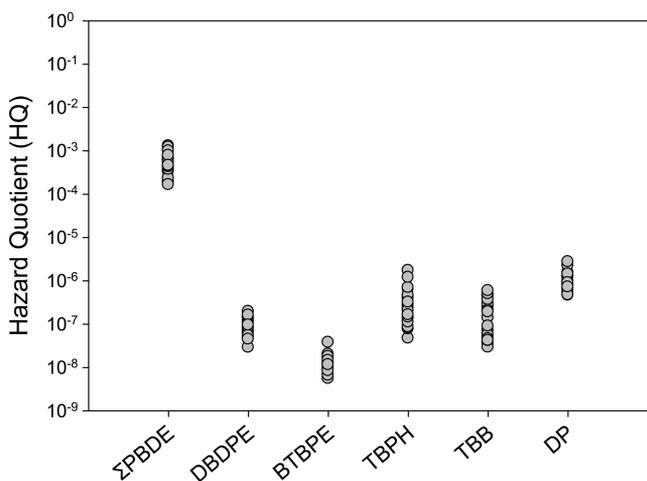
**Figure 3.** Relative abundance (%) of size-fractionated particles at 1.5 m in the e-waste recycling zone (SI Figure S1) to deposition fluxes of halogenated flame retardants in three main regions of the respiratory tract. The black, white, and gray bars represent coarse (aerodynamic diameter ( $D_p$ ) > 1.8  $\mu\text{m}$ ), accumulation mode (1.8  $\mu\text{m}$  >  $D_p$  > 0.1  $\mu\text{m}$ ), and ultrafine ( $D_p$  < 0.1  $\mu\text{m}$ ) particles, respectively. All acronyms are defined in the main text, and  $\Sigma\text{PBDE}$  is the sum of BDE-28, 47, 66, 85, 99, 100, 153, 154, 181, 183, 190, 196, 203, 204, 206, 207, 208, and 209.

fraction (SI Table S3). The majority (73–87%) of the deposition amounts was in the HA, and only a small portion (13–27%) deposited in the deeper respiratory system (i.e., TB and AR). If only the portion deposited into the AR was assumed to be directly hazardous to human health, that fraction constituted only 10–22% of the inhalable fraction, much lower than the empirical value of 75%. For example, the mean inhalation exposure of HFRs estimated from the size-fractionated deposition fluxes at the 1.5 m height within the e-waste recycling zone was 630 pg/kg bw/d (SI Table S4), lower than that estimated from the total concentration (1120 pg/kg bw/d). The daily intake portion that can penetrate deep into the lung estimated using the empirical fraction (0.75) of total concentration was 840 pg/kg bw/d, almost 10 times the fraction deposited in the AR (80 pg/kg bw/d) estimated on the basis of the measured particle size-fractionated deposition fluxes (SI Table S4). Therefore, assessments based on total contaminant concentrations probably may have overestimated exposure risk. Nevertheless, the ICRP model used in the present study also has some limitations, such as uncertainties in model parameters,<sup>24</sup> as well as being high-cost and time-consuming due to the requirement of particle size distribution data.

**Inhalation versus Food Consumption.** Food consumption has also been regarded as the dominant source of daily human exposure to PBDEs for the general population.<sup>42,43</sup> The inhalation intake rate of HFRs determined in the present study was 48 ng/d with a 95% confidence interval (CI) of 33–69 ng/d, and PBDEs were the major contributor with 44 ng/d (95% CI: 30–65 ng/d). In comparison, the inhalation intake rates of PBDEs determined in the present study were similar to intake rates of PBDEs through food consumption in non-e-waste recycling regions, such as Canada (44 ng/d),<sup>44</sup> Spain (82–97 ng/d),<sup>45</sup> Sweden (51 ng/d),<sup>46</sup> the United States (54–76 ng/d),<sup>47</sup> and Shenzhen of China (117 ng/d),<sup>43</sup> assuming an average body weight of 60 kg. These results are somewhat unexpected in that food consumption in non-e-waste recycling regions and inhalation in e-waste recycling areas are equally important as the routes of human exposure to PBDEs, and perhaps also HFRs in non-e-waste recycling regions.

Consumption of local food items around e-waste recycling areas has been shown as a major route of human exposure to PBDEs. For example, consumption of fresh duck eggs (159–5100 ng/d) in Taizhou, Zhejiang Province, another major e-waste recycling site in China,<sup>48</sup> and total dietary intake amounts (including freshwater and marine fish, shellfish, meat, poultry, egg, animal viscera, and vegetables) in Taizhou (2700 ng/d) and Guiyu of Guangdong Province (56000 ng/d)<sup>49</sup> demonstrated the dominance of dietary intake as a source of resident exposure to PBDEs around e-waste recycling areas. However, it appeared that these estimates were based on the assumption that residents consumed only food items produced locally around e-waste recycling sites, which represents the worst-case scenario. In addition, the samples of fresh duck eggs were collected within 10–500 m of an e-waste recycling workshop;<sup>48</sup> resident dietary exposure to PBDEs can be minimized by avoiding these special duck eggs all together. In the second study, freshwater fish were estimated to contribute 98% and 61% to total dietary exposure in Guiyu and Taizhou, respectively, and freshwater fish from a local river contained at least 30 times greater concentrations of PBDEs than those from local markets.<sup>49</sup> If residents consume only fish sold in local markets, which were presumably originated from outside the e-waste recycling areas, dietary exposure can be reduced by 61–98%. Nevertheless, when the local food supplies (including water, vegetables, pulses, rice, hen eggs, fish, pork, and chicken) were sampled, from local grocery stores or residents' families, the total dietary intake of PBDEs was estimated at 196 ng/d,<sup>14</sup> 1–2 orders of magnitude lower than those predicted based on foods produced locally and only slightly higher than those in the non-e-waste recycling regions as discussed above. Therefore, combined with the results from the preceding section (Inhalation Exposure to Polybrominated Diphenyl Ethers), these findings suggest that if residents do not consume foods produced locally, resident exposure to PBDEs around e-waste recycling areas is no worse than that by the general population around the world.

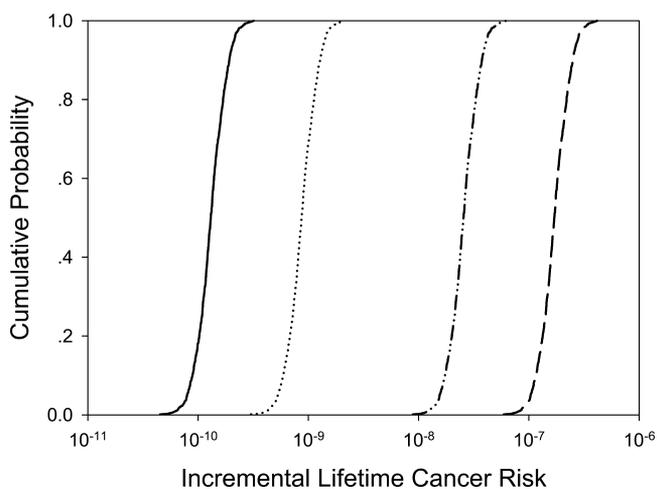
**Health Risk Assessment.** Noncancer risk and incremental lifetime cancer risk were assessed on the basis of the measured levels of resident inhalation exposure of HFRs in e-waste recycling zone. The HQ value of  $\Sigma\text{HFR}$  was  $5.6 \times 10^{-4}$  (95% CI:  $3.8 \times 10^{-4}$ – $8.8 \times 10^{-4}$ ), and those of individual target compounds are presented in the SI Table S4. In comparison, HQ values of ABFRs and DP were 1–3 orders of magnitude lower than those of PBDEs (Figure 4). Even if a high breathing rate of 3 m<sup>3</sup>/h,<sup>24</sup> similar to that under heavy exercise conditions, was assumed, the estimated HQ of  $\Sigma\text{HFR}$  was still far less than 1



**Figure 4.** Hazard quotients (HQ) for particle-bound halogenated flame retardants in the e-waste recycling zone (SI Figure S1). All acronyms are defined in the main text, and ΣPBDE is the sum of BDE-28, 47, 66, 85, 99, 100, 153, 154, 181, 183, 190, 196, 203, 204, 206, 207, 208, and 209.

(SI Figure S3). Thus, particle-bound HFRs, especially ABFRs and DP, within the e-waste recycling zone posed low noncancer risk. Because BDE-209 is the only target congener with reported carcinogenic potency (with a cancer slope factor of  $7 \times 10^{-4}$  (kg d)/mg),<sup>50</sup> the incremental lifetime cancer risk was estimated for BDE-209 only. This cancer risk induced by BDE-209 was  $1.36 \times 10^{-10}$  (95% CI:  $7.3 \times 10^{-11}$ – $2.3 \times 10^{-10}$ ), much lower than the Safe Acceptable Range ( $1.0 \times 10^{-6}$ – $1.0 \times 10^{-4}$ ) established by the USEPA.<sup>25</sup> Even in the worst case scenario, i.e., use of a heavy exercise breathing rate of  $3 \text{ m}^3/\text{h}$ <sup>24</sup> and the cancer slope factor of  $0.137$  (kg d)/mg for benzo[*a*]pyrene,<sup>51</sup> the derived cancer risk (95% CI:  $9.5 \times 10^{-8}$ – $3.0 \times 10^{-7}$ ) was still below the high-end threshold of  $10^{-6}$  (Figure 5).

We further estimated the total resident daily intake of PBDEs from the sum of dust ingestion ( $37 \text{ ng/d}$ ),<sup>27</sup> dietary intake ( $196 \text{ ng/d}$ ),<sup>14</sup> dermal contact, and inhalation ( $44 \text{ ng/d}$  in the present



**Figure 5.** Cumulative probability of incremental lifetime cancer risk induced by BDE-209 via inhalation for residents dwelling in the e-waste recycling zone (SI Figure S1). Solid and dotted curves represent normal exposure and heavy exercise conditions, respectively, while dash-dot-dot and long-dashed curves indicate normal condition and heavy exercise conditions, respectively, but setting the cancer slope factor of BDE-209 as that of benzo[*a*]pyrene (the worst-case scenario).

study). Dermal exposure to particle-bound HFRs was estimated at  $0.33 \text{ ng/d}$  (detailed in the SI), much lower than all other intake routes, and can be neglected. Therefore, the total resident daily intake of PBDEs in the e-waste recycling zone was  $4.6 \text{ ng/kg bw/d}$ , higher than that ( $1.11 \text{ ng/kg bw/d}$ ) in the United States,<sup>52</sup> but below the RfD values ( $1 \times 10^2$ – $7 \times 10^3 \text{ ng/kg bw/d}$ ) for individual BDE congeners suggested by the USEPA Integrated Risk Information System ([www.epa.gov/ncea/iris/index.html](http://www.epa.gov/ncea/iris/index.html)) (SI Table S1). Because no data are available on human exposure pathways for ABFRs and DP in e-waste recycling areas, only the contribution of inhalation, reportedly amounted to 4.6% of the total intake dose for PBDEs,<sup>52</sup> to the total resident daily intake was estimated. The total daily intake doses of ABFRs and DP were thus estimated at  $1.7$  and  $0.31 \text{ ng/kg bw/d}$ , respectively, much lower than RfDs ( $1.02 \times 10^4$ – $3.3 \times 10^5 \text{ ng/kg bw/d}$ ) estimated previously<sup>12,53</sup> (SI Table S1).

The above assessment suggested that the potential noncancer and cancer risks of HFRs for residents within the e-waste recycling zone were low. However, this is not to suggest that the occurrence of HFRs is not an issue around e-waste recycling areas. A better strategy would be to continue monitoring of HFRs in both e-waste recycling and regular residential areas and at the same time enhance efforts in refining RfDs and other health risk assessment parameters.

**Comparison of Potential Health Risk via Exposure to HFRs and Other Contaminants.** Now that HFRs currently have low potential noncancer and cancer risk for human health, it may be sensible to compare potential health risk due to exposure to HFRs and other contaminants such as heavy metals, PAHs, and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) within e-waste recycling areas. In general, HFRs were shown to pose the least health risk compared to other contaminants.<sup>28,54–56</sup> Zheng et al. observed that exposure to heavy metals via food consumption, dust ingestion, and water drinking for residents in e-waste recycling areas led to potential noncancer risk, i.e., HQ was 5.5 for food consumption, 1.9 for dust ingestion, and 21 for groundwater drinking.<sup>54</sup> Cancer risk induced by Pb ( $5 \times 10^{-4}$ )<sup>54</sup> was also higher than the USEPA Safe Acceptable Range ( $1.0 \times 10^{-6}$ – $1.0 \times 10^{-4}$ ).<sup>25</sup> Wang et al. found that parent and halogenated PAHs in air of an e-waste recycling area were associated with high incremental lifetime cancer risk via inhalation up to 1200 per million people.<sup>28</sup> Chan and Wong estimated the total doses ( $5.6$ – $105 \text{ pg WHO-TEQ/kg bw/d}$ ) of exposure to PCDD/Fs in an e-waste recycling area,<sup>56</sup> which exceeded the total daily dietary intake thresholds ( $1$ – $4 \text{ pg WHO-TEQ/kg bw/d}$ ) recommended by the WHO.<sup>57</sup> It is important to realize that, despite the low health risks posed by HFRs as found in the present study, the problems associated with e-waste recycling may be largely related to toxic heavy metals, PAHs, and PCDD/Fs, which may pose more serious threat to the health of residents living around e-waste recycling areas.

The present study demonstrated that inhalation exposure to particle-bound HFRs was size-dependent and that the potential health risk for residents residing within a typical e-waste recycling zone was low from inhalation exposure to particle-bound HFRs, especially PBDEs. In fact, it is no worse than that for the general population around the world if the residents do not consume food items produced locally. In general, heavy metals, PAHs, and PCDD/Fs posed greater health risk than HFRs within e-waste recycling areas. However, this is not to overlook the potential health hazards posed by HFRs to the public; rather, we advocate

an integrated assessment strategy that addresses both indoor and outdoor exposures to HFRs and related health risk.

## ■ 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>.

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### Notes

The authors declare no competing financial interest.

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