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Emissions and Occupational Exposure Risk of Halogenated Flame Retardants from Primitive Recycling of E-Waste

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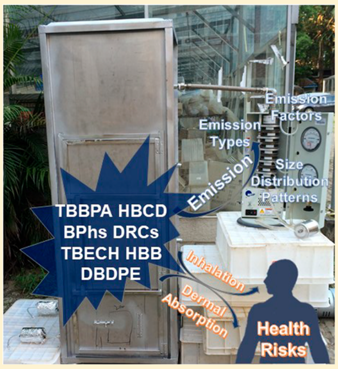
Supporting Information

ABSTRACT: The production and usage of non-polybrominated diphenyl ether (PBDE) halogenated flame retardants (HFRs) have substantially increased after the ban of several PBDEs. This has resulted in widespread environmental occurrence of non-PBDE HFRs, further amplified by emissions from primitive recycling of obsolete electronics (e-waste). The present study conducted chamber experiments to characterize 15 HFRs ($\sum_{15}$HFR) from thermal treatment and open burning of typical e-waste. Emission factors of $\sum_{15}$HFR from thermal treatment were 2.6×10^4−3.9×10^5 ng g^{-1}, slightly higher than those from open burning (8.8×10^3−1.0×10^5 ng g^{-1}). Greater output over input mass ratios of $\sum_{15}$HFR were obtained in thermal treatment than in open burning. Particulate and gaseous HFRs dominated the emissions in thermal treatment and open burning, respectively, largely because of the different temperatures used in the two processes. Particulate HFRs were primarily affiliated with fine particles (D_p < 1.8 μm) peaking at 0.56−1.0 or 0.32−0.56 μm in both thermal treatment and open burning. Occupational exposure to most FRs was relatively low, but several PBDEs may pose potential health risk to workers in e-waste home-workshops. Potentially accruing emissions and health risks of non-PBDE HFRs from primitive recycling of e-waste remain a great concern.



INTRODUCTION

Within the last decades, flame retardants (FRs) have been increasingly used to meet demands for fire safety. Halogenated FRs (HFRs), such as chlorinated and brominated FRs (CFRs and BFRs), are particularly popular as they have high trapping efficiency and low decomposing temperature.[1] Tetrabromobisphenol A (TBBPA), accounting for around 60% of the global total BFR production,[2] along with hexabromocyclododecane (HBCD) and polybrominated diphenyl ethers (PBDEs), have been the most frequently used BFRs.[3,4] Amid the gradual phase-out of PBDEs and HBCDs, alternative HFRs (AHFRs) have been introduced or proposed as replacements.[4,5] For instance, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), bis-(2-ethylhexyl)-tetrabromophthalate (TBPH), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and dechlorane plus (DP) were marketed as alternatives to commercial penta-BDE products,[6] octa-BDE,[7] and deca-BDE,[6,8] respectively. However, some AHFRs have been demonstrated to behave similarly to PBDEs, with high persistence, long-range transport potential, and POPs-like attributes, and thus are unsuitable replacements of PBDEs.[5,9] Toxic effects of not only AHFRs, for example, TBB, BTBPE, DBDPE, and DP,[9] but also TBBPA,[10] have been addressed by *in vitro* and *in vivo* studies, such as acute toxicity, endocrine disruptor activity, reproductive and developmental toxicity, neurotoxicity, and genotoxicity in animals. However, no suitable replacement of these non-PBDE HFRs has been obtained, resulting in continuous usage of these chemicals.

Obsolete electronic/electric devices (e-waste) have been a global concern by virtue of not only its gigantic amounts but also inherent toxic substances. For example, BFRs typically contributed 5.0−10.0% and 19.0% by weight to plastics and printed circuit boards, respectively.[11] Primitive recycling of e-waste in underdeveloped countries, such as China, India, Nigeria, and Vietnam is particularly troubling. Unsafe recycling practices are vital sources of HFRs, such as TBBPA,[12,13] DP,[14] and DBDPE,[15] leading to their frequent occurrences in the atmosphere,[16] rivers,[12] sediment,[17] and soils[18,19] near e-waste recycling zones, but with lower levels than PBDEs within the same e-waste recycling zones.[17,20] For instance, the concentrations of AHFRs (9.6−300 pg m^{-3}) were 1−3 orders of magnitude lower than those of BDE-209 (2600−7900 pg m^{-3}) in the atmosphere of Qingyuan, an important e-waste recycling zone.[21]

Current knowledge about TBBPA and HBCD, as well as AHFRs, mainly centers on their environmental occurrence, geographical distribution, and so-called PBTL (persistence, bioaccumulation, toxicity, and long-range transport).[4,5] Conversely, few studies have been carried out on the emissions of non-PBDE HFRs particularly from primitive recycling processes of e-waste. Chamber experiments are typically used

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in simulating formal recycling processes with high operating temperatures, completed recycling procedures, and pollution controlling facilities,[22−24] which often result in reduced emissions of HFRs compared to uncontrolled recycling practices.[25] Occupational exposure to non-PBDE HFRs during primitive recycling activities is another area of insufficient assessment. Although exposure to PBDEs both for workers in formal e-waste recycling facilities equipped with effective protection and pollution controls[22,23] and for residents in an e-waste recycling zone[16] resulted in low risk, workers at under-equipped workshops may suffer from higher health risk due to higher contaminant emissions and poorer protection measures. Ohajinwa et al.[26] demonstrated that exposure to soil and dust at primitive e-waste recycling sites might pose both adverse noncarcinogenic and carcinogenic health risks for the workers. Lack of data on non-PBDE HFRs also undermines the risk assessment of occupational exposure in primitive e-waste recycling. Our previous studies characterized PBDEs and organophosphate flame retardants (OPFRs) released from primitive treatment of e-waste.[27,28] Further investigation into other non-PBDE HFRs, especially AHFRs, are deemed significant as these chemicals remain in volume production and widespread application, but there is insufficient information about their emission mechanisms and occupational exposure.

To partially fill the above-mentioned knowledge gap, the present study was initiated to accomplish the following tasks: (1) obtain emission factors (EFs) of 20 non-PBDE HFRs, that is, TBBPA, HBCD, brominated phenols (BPhs), and AHFRs, derived from primitive treatment of e-waste; (2) identify the emission types (gaseous phase, suspended particles and ash residues) of HFRs helpful to predict their environmental destinations; (3) elucidate the size distribution patterns of particle-bound HFRs for better health risk assessment; and (4) estimate the occupational exposure to PBDEs, OPFRs, and HFRs for workers engaged in primitive e-waste recycling activities. Chamber tests for thermal treatment and open burning of selected e-waste were applied to acquire needed samples.

■ MATERIALS AND METHODS

Materials. The standards of 11 BFRs, including 4-bromophenol (4-BPh), 2,4-dibromophenol (2,4-DBPh), 2,6-dibromophenol (2,6-DBPh), 2,4,6-tribromophenol (2,4,6-TBPh), tetrabromoethylcyclohexane (TBECH), hexachlorocyclopentadienyldibromo-cyclooctane (HCDBCO), hexabromobenzene (HBB), TBB, tris(2,3-dibromopropyl) phosphate (TDBPP), BTBPE, and DBDPE, along with *α*-, *β*-, and *γ*-HBCD, were purchased from AccuStandard (New Heaven, CT). Five dechlorane-related compounds (DRCs), including dechlorane 602 (Dec-602), dechlorane 603 (Dec-603), and dechlorane 604 (Dec-604), were purchased from Toronto Research Chemicals (Toronto, ON, Canada), and DPs (*anti*- and *syn*-DP) were from AccuStandard. Standard of TBBPA was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Standards of BDE-51, BDE-115, and F-BDE-208 from AccuStandard, along with $^{13}C_{12}$-labeled TBBPA, $^{13}C_{12}$-labeled *α*-, *β*-, and *γ*-HBCD from Wellington Laboratories (Guelph, ON, Canada) were employed as surrogate standards. Additionally, internal standards include BDE-69 and F-BDE-201 from AccuStandard, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate-d_{17} (TBB-d_{17}) from Toronto Research Chemicals, fluorene-d_{10} and pyrene-d_{10} from Cambridge Isotope Laboratories (Andover, MS), TBBPA-d_{10} and *α*-, *β*-, and *γ*-HBCD-d_{18} from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Sample Collection, Extraction, and Analysis. Detailed procedures have been described previously[27,28] and also can be found in Text S1. A brief description is provided herein. Three plastic casings (A1−A3) and three printed circuit boards (B1−B3), cleaned and smashed into pieces (830−1700 μm) beforehand, were applied as raw materials in thermal treatment (at 300 °C; board roasting) and open burning (~800−1350 °C; uncontrolled incineration in open air). These experiments were conducted in a stainless steel chamber (0.5 m length × 0.5 m width × 1.5 m height). Particulate samples in 11 size fractions and gaseous samples were collected on glass microfiber filters by a Micro-Orifice Uniform Deposit Impactor and on a polyurethane foam plug behind, respectively. Residual ash samples were also collected after fume sampling was completed. Altogether, 192 samples were attained and stored at −20 °C prior to treatment.

Spiked with surrogate standards up front, raw e-waste, particulate, and residual ash samples were ultrasonically extracted with different solvents in an ultrasonic extractor, while Soxhlet extraction was applied for PUF plugs. Extracts concentrated to around 1 mL in *n*-hexane were purified on a silica gel column, eluded with *n*-hexane (45 mL), and dichloromethane (50 mL) in sequence. The first fraction containing AHFRs (TBECH, HCDBCO, HBB, TBB, TBPH, BTBPE, DRCs, and DBDPE) was then concentrated to 100 μL and purified by another glass column packed with sulfuric acid silica with an eluate of 1.5 mL of *n*-hexane. Finally, each eluate was concentrated to 100 μL in *n*-hexane or methanol, and corresponding internal standards were spiked prior to instrumental analysis.

The detailed instrumental analysis procedures are described in Text S2.

Quality Assurance and Quality Control. Target HFRs in spiked samples were averagely recovered from 72% to 133% (72 ± 6% to 133 ± 2% in solvent spiked samples, 80 ± 12% to 111 ± 16% in spiked GF/A samples, 80 ± 14% to 105 ± 21% in spiked PUF samples, and 82 ± 4% to 111 ± 6% in spiked residue samples). The mean recoveries of the surrogate standards BDE-51, BDE-115, and F-BDE-208 were 88 ± 15%, 94 ± 17%, and 80 ± 13% and 94 ± 19%, 91 ± 16%, 89 ± 17%, and 106 ± 22% for $^{13}C_{12}$-labeled TBBPA and $^{13}C_{12}$-labeled *α*-, *β*-, and *γ*-HBCD, respectively. Procedural blanks were applied during sampling and extraction procedures to monitor conceivable cross contamination. Field blank samples were collected during both thermal treatment and open burning processes free of e-waste. Only 2,4,6-TBPh and TBBPA were detected in procedural and field blanks with abundances less than 1% of those in related field samples. All measured concentrations were obtained after blank correction but absent from surrogate standard recovery correction.

Data Analysis. The EF of an analyte is defined as the analyte mass emitted from per unit mass of raw e-waste material. The EFs calculated by detection limits for HFRs were 0.08−20 ng g^{-1}. The output over input (O/I) mass ratio is defined as the EF value divided by the analyte concentration in raw e-waste material.

Occupational exposure was estimated utilizing the EFs of 38 PBDEs, 8 OPFRs, and 15 HFRs obtained in the previous[27,28] and present studies, as well as the statistical data about home-workshops in Guiyu, South China (Text S3). A comprehensive comparison of occupational exposure to these three types of

FRs can somewhat distinguish the potential health risks of non-PBDE HFRs from those of PBDEs and OPFRs. Because open burning is often conducted in wide-open atmospheric environments with numerous interfering factors, only emissions from thermal treatment of plastic casings and printed circuit boards were employed in assessing occupational exposure to the target FRs through inhalation and thermal absorption. Deposition fluxes of size-fractioned particulate FRs in the head airway (HA, including nose, mouse, pharynx, and larynx), tracheobronchial region (TB), and alveolar region (AR) in the human respiratory tract were estimated with an International Commission on Radiological Protection model (Text S4). Assuming the average bodyweight of an adult worker is 60 kg, the daily intake dose through inhalation and dermal absorption in home-workshops were calculated.

RESULTS AND DISCUSSION

Occurrence of HFRs in Raw Materials. Among the 20 HFRs, on account of the absence of HCDBCO, TBB, TDBPP, Dec-603, and BTBPE in any sample, the sum of 4-BPh, 2,4-DBPh, 2,6-DBPh, 2,4,6-TBPh, TBBPA, *α*-, *β*-, and *γ*-HBCD, TBECH, HBB, DBDPE, and Dec-602 and 604, *anti*- and *syn*-DP is defined as $\sum_{15}$HFR. Concentrations of $\sum_{15}$HFR in plastic casings (1.71×10^5–5.66×10^5 ng g^{-1}) were slightly higher than those in printed circuit boards (3.69×10^4–1.77×10^5 ng g^{-1}), with different compositional profiles (Table S1). The overwhelmingly dominant HFR was TBBPA in both plastic casings and printed circuit boards, accounting for 65–95% of $\sum_{15}$HFR. The concentration of DBDPE was the second highest in plastic casings contributing an average of 12% to $\sum_{15}$HFR, followed by DP (sum of *anti*- and *syn*-DP; 7.7%), $\sum_4$BPh (sum of 4-BPh, 2,4-DBPh, 2,6-DBPh, and 2,4,6-TBPh; 6.3%), and HBCDs (*α*-, *β*-, and *γ*-HBCD, $\sum$HBCD; 2.7%). Printed circuit boards contained more simplex compositions than plastic casings and were dominated by TBBPA (85%), BPhs (12%), and HBCDs (0.4%), while DBDPE was only detected in B3 with a contribution of 6.1%.

Although HBCD is the most widely used aliphatic cyclic additive BFR globally, it was a minor constituent in plastic casings and printed circuit boards (2.7% and 0.4%, respectively). The primary usage of HBCDs is in construction materials and textiles,[29] and rarely (~1%) as a FR, mainly in high impact polystyrene (HIPS) for moldings and housings of electrical goods, such as computer monitors and CRT-based televisions.[30] Typically, *γ*-HBCD (75–89%) was dominant in commercial HBCD mixtures, followed by the *α* (10–13%) and, then, the *β* isomer (1–12%).[31] However, *α*-HBCD constituted of 75% of $\sum$HBCD in raw e-waste materials in the present study. A previous study also identified *γ*-HBCD as the dominant congener (~40%) in five plastic wastes, which was much lower than that in commercial mixtures.[32] There are two putative reasons for this disparity: (1) the obsolete electronics under investigation were made of recycled plastics,[33] and (2) chemical transformation occurred in the production and use stage. It was demonstrated that *γ*-HBCD can isomerize to *α*-HBCD at temperatures exceeding 100 °C,[34] resulting in decreased fractions of *γ*-HBCD in environmental samples.

Target HFRs mainly serve as additive FRs in consumer products and, therefore, may leach out during usage and recycling processes. The exceptions are BPhs and TBBPA, which are additive/reactive FRs.[3,35] For instance, the majority of TBBPA, as the highest volume BFR on the market, is used reactively in epoxy, phenolic, and polycarbonate resins mainly for manufacturing printed circuit boards, with small amounts used as additive FRs in acrylonitrile butadiene styrene (ABS) resins and HIPS.[36−39] Reactively incorporated TBBPA either becomes an embedded component or grafts onto the polymer backbone and is, thus, more stable than additive TBBPA.[31]

Emission Factors and Mass Balance. The EFs of $\sum_{15}$HFR ranged from 2.6×10^4 to 1.6×10^5 ng g^{-1} for plastic casings and 7.0×10^4 to 3.9×10^5 ng g^{-1} for printed circuit boards in thermal treatment (Table S2). Values of EFs in open burning were slightly smaller, at 8.8×10^3–1.0×10^5 and 2.5×10^4–4.0×10^4 ng g^{-1}, respectively. Remarkably, the higher operating temperatures (~800–1350 °C) and better air flows in open burning may have led to stronger degradation thus underestimated emissions of HFRs compared with field burning activities. These findings suggested that primitive e-waste recycling can result in intensified release of HFRs from both thermal treatment and open burning. The EFs of $\sum_{15}$HFR from thermal treatment and open burning of plastic casings were comparable with those of PBDEs (3.04×10^4–1.60×10^5 and 1.66×10^3–9.14×10^4 ng g^{-1}, respectively)[27] and OPFRs (3.7×10^4–6.8×10^4 and 6.2×10^3–1.6×10^4 ng g^{-1}, respectively).[28] On the other hand, for printed circuit boards, which were relatively newly manufactured (roughly 0–10 years later),[27] the EFs of $\sum_{15}$HFR and OPFRs (5.2×10^3–3.7×10^5 ng g^{-1})[28] were several orders of magnitude higher than those of PBDEs (RL–2.18×10^3 ng g^{-1}).[27] Emissions of most target HFRs decreased in open burning owing to stronger decomposition under higher temperatures compared with thermal treatment. In contrast, BPhs had higher EFs in open burning possibly because of stronger degradation of TBBPA or selected PBDEs, which can be induced by thermal or UV decomposition.[40] Dettmer et al.[41] observed large amount of BPhs (up to 17%) from thermal degradation of TBBPA. Enhanced BPh levels at 1.3–14.5 mg kg^{-1} were observed in the pyrolysis of printed circuit boards with a temperature increase from 300 to 500 °C,[42] 2–3 orders of magnitude lower than pyrolysis at 600 °C (1280 mg kg^{-1}) but comparable with those at 850 °C (4.7 mg kg^{-1}).[43] These reported results are compatible with the data in the present study. Because BPhs are mainly incomplete combustion products, they might present higher emissions in field open burning at lower temperatures and oxidation.[44] The much lower EFs of HBCD than those of TBBPA suggested that e-waste dismantling is a more important source for TBBPA than for HBCD, consistent with the results in riverine and estuarine sediments of the Pearl River Delta.[12] Emissions of DBDPE and DPs also occurred with high EFs, especially from plastic casings, at 2.7×10^3–9.7×10^3 and 370–1.2×10^4 ng g^{-1} from thermal treatment, in comparison with 780–1.2×10^4 and <RL–8.7×10^3 ng g^{-1} from open burning. On the contrary, the EFs of TBECH, HBB, and Dec-602 and 604 seemed to be inappreciable, where the largest value was obtained for HBB at 1.2–290 ng g^{-1}. Similar relative abundance was found in e-waste recycling environments,[21,45] implying discrepant usages of different HFRs in electronic/electrical products.

The O/I mass ratios of $\sum_{15}$HFR (Table S3) from thermal treatment (0.09–2.91) were significantly (*t*-test; $p < 0.05$) higher than those from open burning (0.03–0.69), with the exception of BPhs (0.16–174 and 0.17–312, respectively), probably because of the stronger decomposition of abundant TBBPA in open burning. Plastic casings had significantly (*t*-test; $p < 0.05$) lower O/I mass ratios (0.03–0.36) than printed circuit boards (0.23–2.91), inconsistent with the results of

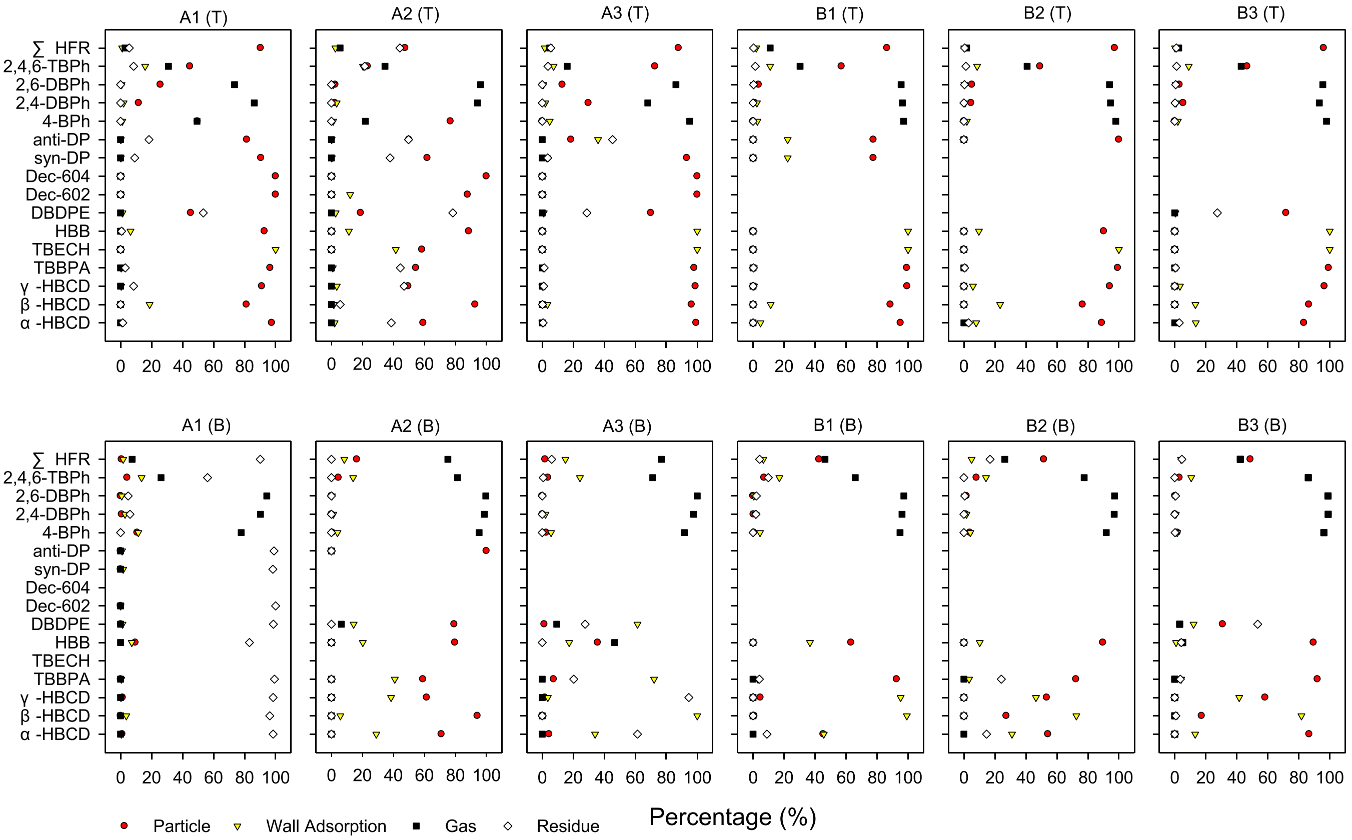

Figure 1. Relative abundances of different emission types for halogenated flame retardants from thermal treatment (T) and open burning (B) of plastic casings (A1−A3) and printed circuit boards (B1−B3).

PBDEs and OPFRs.[27,28] Exceptionally large values were obtained for TBBPA from thermal treatment of printed circuit boards (2.04 to 3.10), which was attributed to different chemical structures of after-treatment products and raw materials. High temperatures could break down various covalent bonds, especially the C−C bonds,[46] enhancing the extraction efficiency of reactive TBBPA from after-treatment products compared to raw materials. The significant higher O/I mass ratios of TBBPA from printed circuit boards than from plastic casings also demonstrated that sample matrices and FR-adding types (additive or reactive) can influence on emissions. Reactive TBBPA in printed circuit boards are chemically bonded to the resins, where TBBPA need to be formed from pyrolyzing brominated epoxy resin first in pyrolysis process,[42] and therefore, are less facile to release[24] and subject to less degradation than additive TBBPA and other additive FRs in ABS and HIPS, which are elementary components of plastic casings. Moreover, several O/I mass ratios for HBCD were larger than 1, implicating for potential formation of HBCD from rearrangement of interisomers and unknown sources during treatment processes.

Emission Types and Compositional Profiles. The emission types for total HFRs were different between thermal treatment and open burning (Figure 1). The emissions of $\sum_{15}$HFR in thermal treatment were predominated by particulate matter with an average contribution of 84%, followed by residues (10%) and gas phase (4.8%). Gaseous HFRs (46%) overwhelmed particulate HFRs (27%) and residual ash (20%) in open burning. These emissions can lead to high levels of HFRs in ambient environments, such as the atmosphere,[16,47] indoor dust,[24] and soils.[17,18] The relatively low vapor pressures of semivolatile organic compounds suggest that adsorption on chamber surfaces may reduce their emissions in air samples. As an example, a long-term chamber test under 60 °C did not detect any TBBPA and HBCD in air samples but found high amounts in wall-rinsed samples.[48] Surface adsorption in the present study only produced low emissions in both thermal treatment (1.3%) and open burning (6.8%). The slightly higher surface adsorption in open burning than in thermal treatment was probably due to different chemical compositions in the airborne particles collected. Apparent differences of particulate matter were observed in open burning with larger amount of black carbon potentially, implying more carbonization than thermal treatment. In-depth mechanisms remain to be investigated.

Different physicochemical properties, such as vapor pressure, volatility, and hydrophobicity, of different HFRs result in large variability in the contributions of each emission type.[48] BPhs were largely detected in the gaseous phase, with an average abundance of 54% in thermal process and 86% in open burning. By contrast, the abundances of TBBPA, HBB, and DBDPE with lower vapor pressures compared to BPhs were low in the gaseous phase, but high in particle matter and residual ash. Similar results were found for PBDEs and OPFRs from primitive recycling of e-waste[27,28] and PBDEs and HBCD derived from open burning of plastic wastes.[32] Noteworthily, discrepancies were observed in that gaseous 2,4,6-TBPh contributed much less to its total emissions during treatment processes compared to other BPhs (Figure 1), possibly because of its higher logarithmic octanol−air partition coefficient (log K_{oa} = 9.968 at 298 K) and lower vapor pressure (0.0404 Pa at 298 K) calculated with EPI suite version 4.1. In addition,

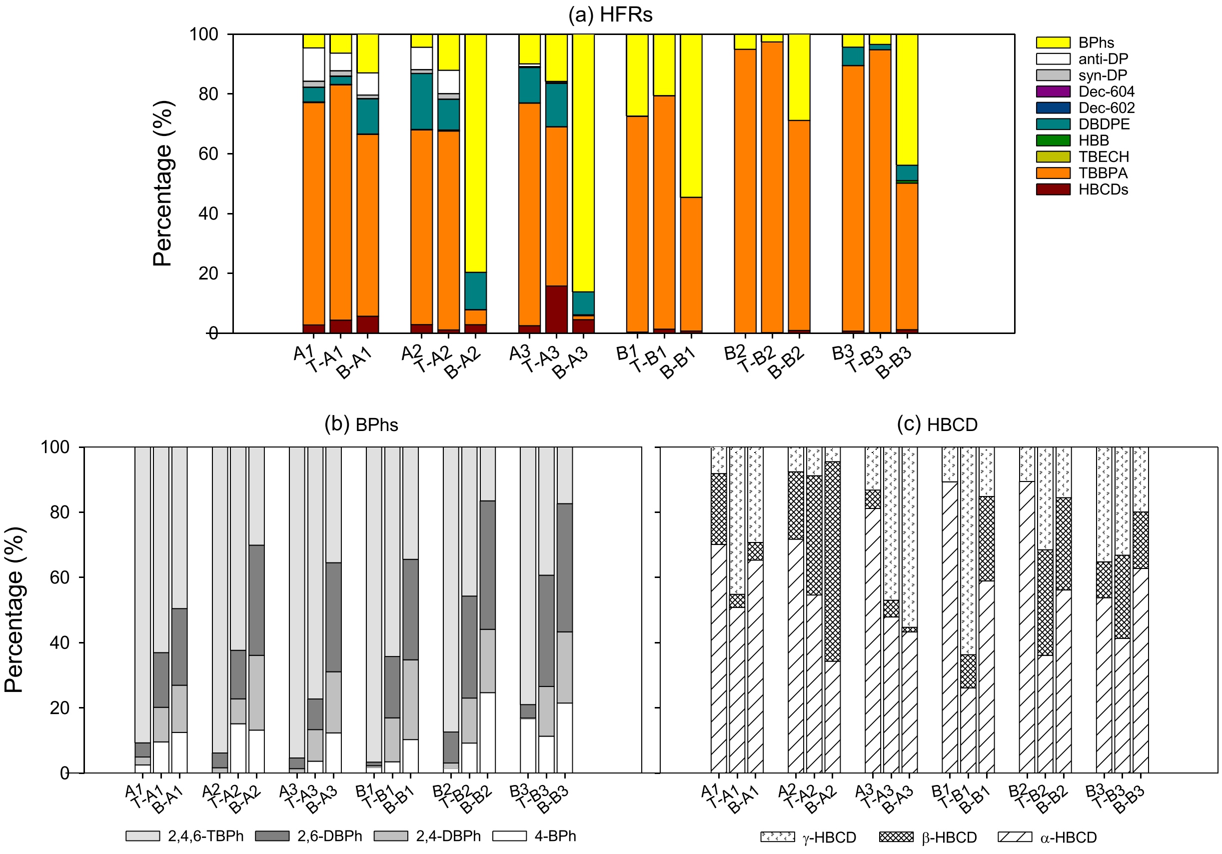

Figure 2. Relative abundances of individual halogenated flame retardants in raw materials and derived from thermal treatment (T) and open burning (B) of plastic casings (A1–A3) and printed circuit boards (B1–B3).

2–4 orders of magnitude higher contents of 2,4,6-TBPh than mono- and di-BPhs in raw materials and O/I mass ratios below 1 indicated that its decomposition overwhelmed formation during thermal treatment and open burning, inducing less gaseous emissions, as TBBPA debrominated and then debromination products volatilized under pyrolysis.[49]

The relative abundances of 15 HFRs (Figure 2a and Table S4) indicated that TBBPA from thermal treatment contributed 78% of $\sum_{15}$HFR on average, consistent with its dominant concentrations in raw materials. Lowered abundance (39%) in open burning indicated greater decomposition of TBBPA compared to thermal treatment. On the contrary, the relative abundance of BPhs increased from raw materials (9.3%) to thermal treatment (10%) and to open burning (51%) in most cases. The total BPh emissions in thermal treatment were dominated by 2,4,6-TBPh (Figure 2b), at an average of 59%, followed by DBPhs (2,4- and 2,6-DBPh; 33%), in contrast to open burning where the contribution of DBPs (54%) overwhelmed that of 2,4,6-TBPh (31%). Similar predominance of DBPhs (2,4- and 2,6-DBPh), followed by 2,4,6-TBPh and 4-BPh, was obtained in pyrolysis and combustion of pure TBBPA at 600 °C.[37] Debromination to lower brominated phenols and further to phenol and HBr,[50] and formation of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) of BPhs could take place under thermal condition,[51] and thus emissions of BPhs were net results after competition of formation, debromination, and transformation. The declined trend of 2,4,6-TBPh in open burning compare with thermal treatment was opposite to those of other BPhs, suggesting 2,4,6-TBPh is less likely to accumulate under high operating temperature than lower brominated phenols. In addition, the higher contributions of lowly brominated phenols indicated stronger decomposition in open burning compared to thermal treatment. Enhanced emissions of BPhs are relevant as BPhs can be precursors in the formation of PBDD/Fs.[41]

Although HBCDs only contributed 3.8% and 2.6% to the total emissions in thermal treatment and open burning, respectively, the isomer rearrangement observed in the present study can be referred to elucidate the relative abundances of HBCDs in the environment. As the most abundant constituent (Figure 2c), *α*-HBCD contributed 43% and 58% to the total emissions of HBCDs in thermal treatment and open burning, respectively. These values were close to those in rural (~65%) and urban (~50%) aerosols.[52] The abundance of *γ*-HBCD in thermal treatment (38% of $\sum$HBCD) was also substantially greater than those in raw materials (14%) and in open burning (23%). Transformation of *γ*-HBCD to *α*-diastereomer can occur under thermal and photolytic conditions,[1,53] but the inverse reaction was possible in the present study as abundant *α*-HBCD in raw materials could partially be transformed to *γ*-diastereomer. In generation of HBCD stereoisomers from pure (+)-*α*-HBCD at 200 °C, reactions, for example, (+)-*α*-HBCD → (+)-*γ*-HBCD and (+)-*α*-HBCD → (+)-*β*-HBCD, were obviously configured.[54] The emissions of individual HBCD may have been the outcome of the competitive processes of formation, transformation, and degradation. Stronger degradation in open burning was ascribed to the higher reaction temperatures employed. The reduced abundance of *γ*-HBCD was obtained in open burning in contrast with thermal treatment (Figure 2c). The decomposition rate was possibly

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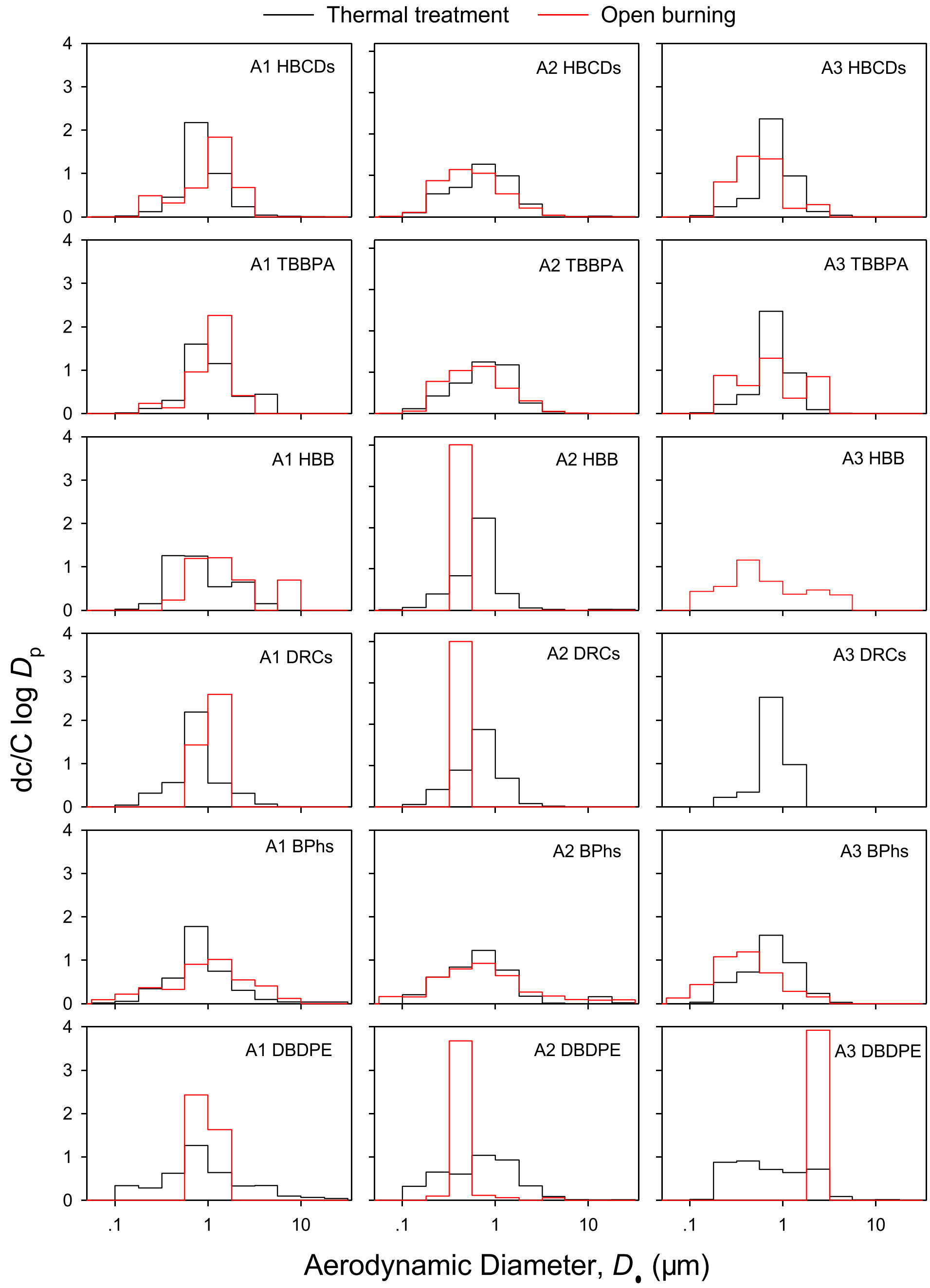

Figure 3. Size distribution patterns of particle-bound halogenated flame retardants by thermal treatment and open burning of plastic casings (A1−A3). dc is the concentration of halogenated flame retardant in each filter, *C* is the sum concentration in all filters, and *d* log D_p is the logarithmic size interval for each impactor stage in aerodynamic diameter (D_p).

higher for γ-HBCD than for α- and β-diastereomers in open burning, and similar results were also obtained for their degradation rates at 170−190 °C.[53]

The fraction of *anti*-DP (f_{anti}; EFs of *anti*-DP divided by those of $\sum$DP) was 0.26−0.81 from thermal treatment, slightly smaller than those in raw e-waste (0.84−0.81) and from open burning (0.86−1). Smaller f_{anti} values were obtained in other ambient media, e.g., 0.59−0.76 in airborne particles[21] and 0.726 ± 0.037 in the air[14] of e-waste recycling areas, and 0.54 ± 0.07 in fine particles from Chinese cities.[15] The anti-isomer is more susceptibly photodegradable and tends to isomerize to the syn-isomer,[55,56] and long-range migration of atmospheric particles may have an important impact on the transformation of DP isomers.[15] For example, the f_{anti} value was found to decline with increasing distance from the source.[56]

Size Distribution of Particulate HFRs. In most cases, a unimodal pattern peaking at 0.56−1.0 or 0.32−0.56 μm was characteristic of particulate HFR conformers in both thermal treatment and open burning (Figures 3 and 4). However, several dominant peaks at 1.0−5.6 μm were observed for the size distributions of particle-bound TBB, TBPH, DP, and DBDPE in the atmosphere of an e-waste recycling zone.[21] Abundant peaks of TBECH, PBT, HBB, and BTBPE were also found in finest particles (< 0.95 μm) in urban and rural atmospheric samples,[52] while trimodal (0.7−1.1, 2.1−3.3, and 9.0−10 μm) and bimodal (4.7−5.8 and 9.0−10 μm) patterns

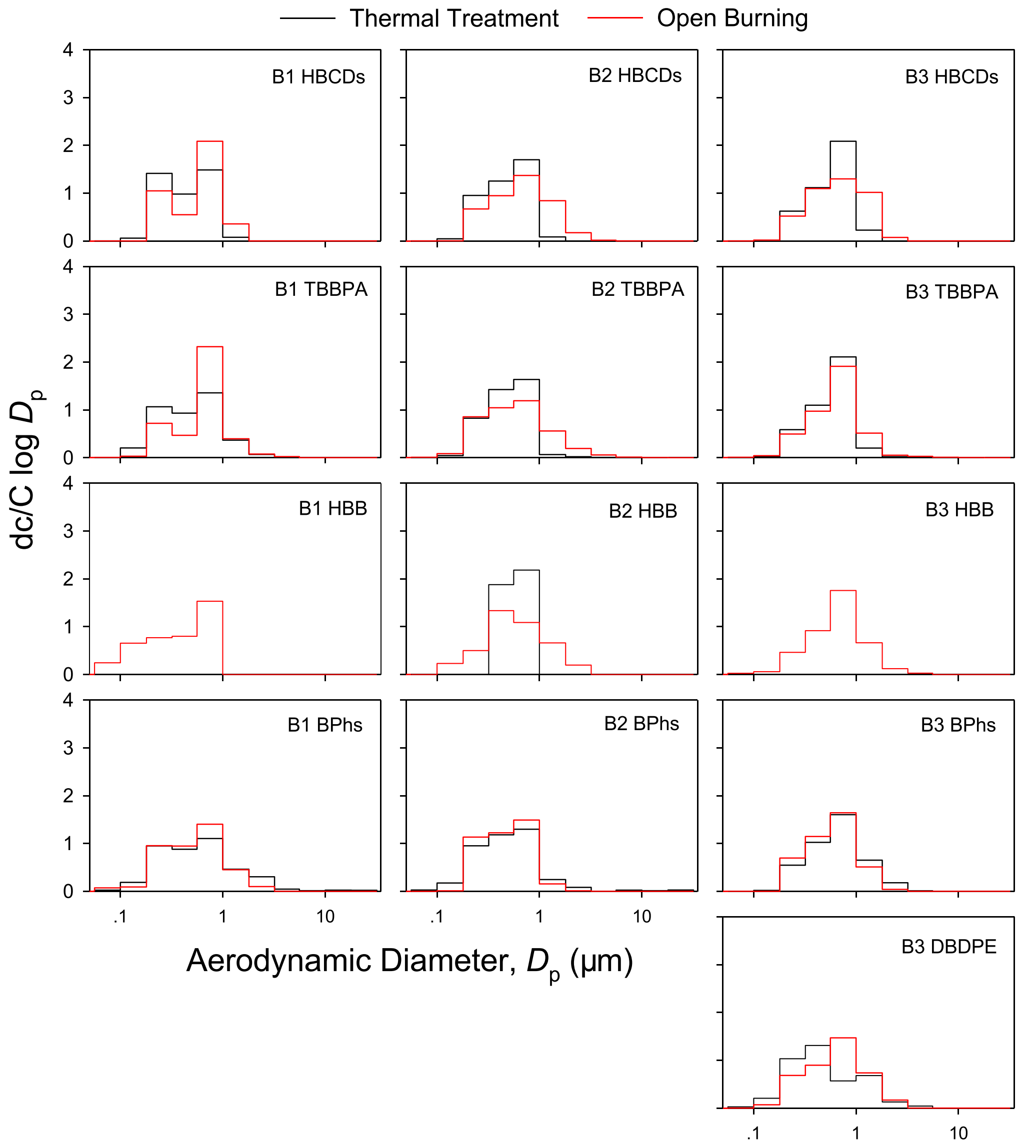

Figure 4. Size distribution patterns of particle-bound halogenated flame retardants by thermal process and open burning of printed circuit boards (B1−B3). dc is the concentration of HFR in each filter, *C* is the sum concentration in all filters, and *d* log D_p is the logarithmic size interval for each impactor stage in aerodynamic diameter (D_p).

were obtained for DPs and NBFRs, respectively, in indoor and outdoor air.[57] The discrepancies may have been reflective of mixed emission sources in the atmospheric environments. Particle-bound HFRs from both thermal treatment and open burning were primarily associated with fine particles ($D_p < 1.8$ μm) (Figure S1). The mean contribution of coarse particles ($D_p > 1.8$ μm) from thermal treatment (11%) of plastic casings was slightly smaller than that from open burning (13%), coincident with the results for printed circuit boards (1% and 4%, respectively). Similar results were found for PBDEs[27] and OPFRs[28] in our previous studies, also for size fraction patterns of PAHs between smoldering and flaming phase.[58] This was probably due to more abundant coarse particles generated from open burning. These values were much smaller than those obtained from an e-waste recycling zone (42%−68%)[21] and indoor and outdoor environments ($D_p > 2.1$ μm; mean, 51.8%).[57] Rearrangement of HFRs on different size fractions or recombination of fine particles may have taken place from emission sources to the surrounding atmosphere, resulting in even distribution on coarse and fine particles. Additionally, dust resuspension has been demonstrated as an important contributor to coarse atmospheric particles.[59−61] The abundances of HFRs in coarse particles from plastic casings were significantly greater than those from printed circuit boards (*t*-test; $p < 0.05$), likely owing to the different chemical compositions of atmospheric particles emitted from plastic casings and printed circuit boards.[62,63]

Geometric mean diameter (GMD) and geometric standard deviation (GSD) of target HFRs are good indicators of size distribution patterns (Tables S5 and S6). No significant difference was found between the GMDs of HFRs from thermal treatment (0.73−1.06 and 0.48−0.56 μm for plastic casings and printed circuit boards, respectively) and open burning (0.47−0.99 and 0.57−0.62 μm, respectively). These results were similar to those for PBDEs and OPFRs in the same chamber experiments,[27,28] but much lower than those from field measurements in an e-waste recycling area.[21] The diverse physicochemical properties of HFRs have important impacts on size distributions. Luo et al.[21] found that the GMDs of HFR congeners with higher vapor pressures and lower K_{oa}

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were significantly higher than those with lower vapor pressures and higher K_{oa}, due to rearrangement on all size fractions. They also obtained significant positive correlations between GMD values and logarithmic subcooled liquid vapor pressures (log P_L/Pa) at 298 K, and between relative abundances of PBDEs in atmospheric coarse particles and log P_L/Pa at 298 K in an e-waste recycling zone.[21] However, similar correlations were not obtained in the present study, potentially due to their different emission mechanisms and rearrangements on particles from sources to the surroundings.

Diverse emission mechanisms may induce different size distribution patterns of HFRs. Ample literatures have identified the main emission mechanisms as vaporization from HFRs-containing products, physical mechanistic processes such as abrasion, miniaturization, or weathering, and combustion.[48,64−66] Theoretically, light FRs in the atmosphere mostly emitted through evaporation and reabsorption, while heavy congeners are largely bond with particles with large surface areas.[62,67] In the present study, most HFRs were affiliated with particles, similar to heavily brominated BDEs and OPFRs.[27,28] The distribution of HFRs in size-fractionated particles did not rest to vapor pressure and probably was not a result of gas-particle partitioning, in light of no significant positive correlation between their GMDs or masses in coarse particles and log P_L at 298 K.[68] The exception was BPhs with high vapor pressures which are predominantly emitted in gaseous phase and tend to evaporate and sorb to airborne particles.[27]

Occupational Exposure Assessment. The daily intake through combined inhalation and dermal absorption of $\sum_{15}$HFR, $\sum_{38}$PBDE, and $\sum_{8}$OPFR was $5.4 \times 10^5 \pm 8.2 \times 10^4$, $4.4 \times 10^5 \pm 7.6 \times 10^4$, and $4.2 \times 10^5 \pm 3.8 \times 10^4$ ng d^{-1}, respectively (Table S7). Airborne particles as the main carriers of FRs contributed overwhelmingly to inhalation, with mean values of 4.0×10^5, 3.6×10^5, and 3.5×10^5 ng d^{-1}, respectively. The mean fluxes of FRs to the HA, TB, and AR of the human respiratory tract (Figure 5) followed the sequence of HA (2.9×10^4−3.4×10^4 ng h^{-1}) > AR (1.1×10^4−1.4×10^4 ng h^{-1}) > TB (2.6×10^3−3.0×10^3 ng h^{-1}). This sequence was compatible to, but the values were 3−5 orders of magnitude higher than those for residents dwelling in an e-waste recycling zone (1600, 300, and 97 pg h^{-1}, respectively).[16] Dermal absorption of particulate FRs also contributed significantly to the overall intake, with mean values of 7.3×10^4−8.7×10^4 ng d^{-1}. Furthermore, inhalation and dermal absorption of gaseous HFRs (mostly BPhs) contributed higher fluxes (mean = 4.3×10^4 and 8.9×10^4 ng h^{-1}, respectively) than those of gaseous PBDEs (mean = 120 and 25 ng h^{-1}, respectively) and OPFRs (mean = 3.5×10^3 and 730 ng h^{-1}, respectively). Among the target HFRs, TBBPA was the dominant component contributing 76% to the total fluxes (Table S7). BDE-180 (24%) and BDE-183 (19%) dominated the total fluxes of $\sum_{38}$PBDE, while BDE-209 only contributed 8%. In the case of $\sum_{8}$OPFR, TCEP (32%), TPHP (30%), and TCIPP (24%) were the significant contributors.

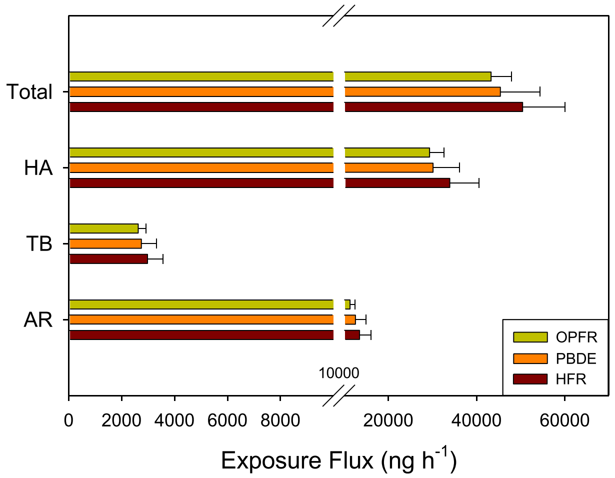

Figure 5. Deposition fluxes of particle-bound flame retardants in the head airway (HA), tracheobronchial region (TB), and alveolar region (AR) of the human respiratory tract.

The estimated daily intake doses of $\sum_{15}$HFR, $\sum_{38}$PBDE, and $\sum_{8}$OPFR were 9.0×10^3 (95% confidence interval (CI) = 7.0×10^3−1.1×10^4), 7.3×10^3 (95% CI = 5.6×10^3−9.6×10^3), and 7.0×10^3 (95% CI = 6.1×10^3−8.2×10^3) ng kg^{-1} d^{-1}, respectively (Table S7). These doses were approximately 3 orders of magnitude higher than inhalation exposure for residents dwelling in an e-waste recycling area (630 pg kg^{-1} d^{-1} for 25 HFRs),[16] as well as for workers in the waste printed circuit boards desoldering workshop (1.46 ng kg^{-1} d^{-1} of $\sum_{8}$PBDE),[22] and 1−2 orders of magnitude higher than those for manual recyclers (8.7−112 ng kg^{-1} d^{-1} of $\sum_{21}$PBDE) in another dismantling workshop,[23] both containing dust removal facilities and negative pressure operating tables. In most cases, the estimated intake doses for FR congers are substantially below the reference dose values (Table S6). The exceptions are the estimated intake doses (mean: 290−1.8×10^3 ng kg^{-1} d^{-1}) of BDE-153, -180, and -183, much higher than the reference dose values (200 ng kg^{-1} d^{-1}). These compounds may pose adverse effects on neurobehavioral development, endocrine systems, and thyroid hormones.[69] Furthermore, PBDEs can pose additional health concerns in light of their facile oxidative transformation into PBDD/Fs.[70] Similarly, the cumulative hazard indice of PBDEs via dermal absorption, inhalation, and ingestion for workers at primitive e-waste recycling sites in Nigeria were several orders of magnitude higher than the safe limits.[26]

The daily intake doses via inhalation and dermal intake of air at illegal workshops in the present study may have been overestimated because rearrangement of particulate FRs potentially leading to higher contribution on coarse particles and indoor−outdoor air exchange were not considered. Finer particles might cause higher health risk and carry more contaminants to human lung because of their deeper penetration in the respiratory tract.[16] Although occupational exposure to HFRs and OPFRs in the present study was well below the reference doses, the emissions of these contaminants potentially accrue due to their increasing and unlimited production and usage in consumer products, thus lead to increasing health risks in the future. Moreover, occupational exposure via other routes also need to be emphasized; for example, dust ingestion was demonstrated to be the main exposure route contrast with inhalation for recyclers.[23,26,71]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b05027.

Experimental setup and sampling, sample extraction, and purification; instrumental analysis; estimation of the concentration of particulate and gaseous FRs in workshop air based on the EFs; exposure and health assessment of flame retardants; concentrations of halogenated flame retardants in plastic casings and printed circuit boards; emission factors of 15 kinds of halogenated flame retardants; output over input mass ratios by thermal process and open burning of plastic casings and printed circuit boards; relative abundance of individual halogenated flame retardant derived from thermal treatment and open burning of plastic casings and printed circuit boards; geometric mean diameter and geometric standard deviations of particle-bound HFRs; daily intake of particle-bound and gaseous flame retardants; and relative abundances of particle-bound halogenated flame retardants (PDF)

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Notes

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