

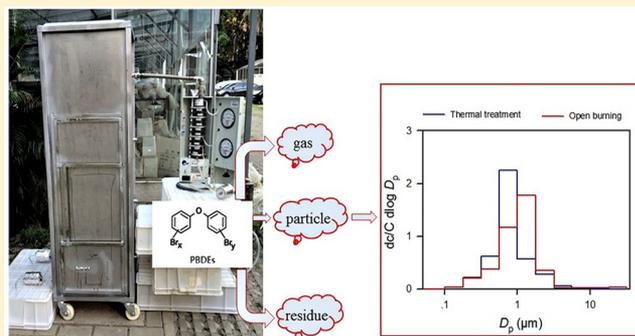
Characteristics of Polybrominated Diphenyl Ethers Released from Thermal Treatment and Open Burning of E-Waste

Ting-Yu Li, Jun-Feng Zhou, Chen-Chou Wu, Lian-Jun Bao,^{1b} Lei Shi, and Eddy Y. Zeng^{*1b}

School of Environment and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, China

Supporting Information

ABSTRACT: Primitive processing of e-waste potentially releases abundant organic contaminants to the environment, but the magnitudes and mechanisms remain to be adequately addressed. We conducted thermal treatment and open burning of typical e-wastes, that is, plastics and printed circuit boards. Emission factors of the sum of 39 polybrominated diphenyl ethers ($\sum_{39}\text{PBDE}$) were $817\text{--}1.60 \times 10^5 \text{ ng g}^{-1}$ in thermal treatment and nondetected- $9.14 \times 10^4 \text{ ng g}^{-1}$, in open burning. Airborne particles (87%) were the main carriers of PBDEs, followed by residual ashes (13%) and gaseous constituents (0.3%), in thermal treatment, while they were 30%, 43% and 27% in open burning. The output–input mass ratios of $\sum_{39}\text{PBDE}$ were 0.12–3.76 in thermal treatment and 0–0.16 in open burning. All PBDEs were largely affiliated with fine particles, with geometric mean diameters at $0.61\text{--}0.83 \mu\text{m}$ in thermal degradation and $0.57\text{--}1.16 \mu\text{m}$ in open burning from plastic casings, and $0.44\text{--}0.56$ and nondetected- $0.55 \mu\text{m}$, from printed circuit boards. Evaporation and reabsorption may be the main emission mechanisms for lightly brominated BDEs, but heavily brominated BDEs tend to affiliate with particles from heating or combustion. The different size distributions of particulate PBDEs in emission sources and adjacent air implicated a noteworthy redistribution process during atmospheric dispersal.



INTRODUCTION

Obsolete electrical and electronic devices (e-waste) with fast-growing quantities have triggered emerging and critical waste management issues. Approximately 30–50 million tons of e-waste were expected to be generated globally each year with a growth rate of 3–5% annually.¹ Global legal and illegal trades from developed countries to developing countries and subsequent recycling of e-waste have been motivated by highly valuable materials such as metals and plastics present in e-waste.^{2–4} A number of environmental issues with primitive e-waste recycling, for example, emission of chlorinated and brominated dioxins and furans (PCDD/Fs and PBDD/Fs) and polybrominated diphenyl ethers (PBDEs), have been raised in some developing countries.^{5–7} Various primitive e-waste recycling techniques include manual dismantling, toner sweeping, plastic chipping and melting, heating, and acid leaching of printed circuit boards and open burning printed circuit boards, cables, and plastics.⁸ Despite the tremendous efforts in promoting environmentally sound management of e-waste worldwide over the past few decades, primitive e-waste dismantling and recycling techniques have remained a significant problem in China, as well as in other developing countries, such as India, Thailand, and Ghana.⁹

As once widely used brominated flame retardants, PBDEs can be derived from e-waste recycling activities and greatly affect both ecosystems and residents living within or near the

recycling zones.^{10–12} A long list of emission sources have been identified for PBDEs,⁸ for example, leachates from waste dumping, fly and bottom ashes from burning events, and wastewater from dismantling and shredding facilities, cyanide leaching, and other leaching sources. Besides, fumes from dismantling activities, mercury amalgamate “cooking”, desoldering, and other burning events may also become emission sources of PBDEs. To optimize e-waste recycling technologies, chamber experiments have been conducted to estimate pollutant emissions from e-waste processing. Combustion or incineration,^{5,6} extrusion process¹³ and thermal treatment^{7,14} are a few examples. These studies have focused on formal recycling approaches employed in e-waste recycling facilities, but data are scarce in the literature on the characteristics of PBDEs emitted from primitive recycling technologies. In addition, PBDEs with low saturated vapor pressures and large octanol–air partition coefficients tend to affiliate to airborne particles.¹⁰ The characteristics of particles therefore largely dictate the fate of PBDEs in the environmental. As such, particle size distribution is a critical factor governing the fate of particle-bound contaminants in the atmosphere and associated

Received: February 9, 2018

Revised: March 28, 2018

Accepted: March 30, 2018

Published: March 30, 2018

human health risk.¹⁵ However, the emission mechanisms and emission factors (EFs) of PBDEs on size-fractionated particles from primitive recycling of e-waste have not been reported in the literature.

To address the above-mentioned issue, the present study simulated two primitive e-waste recycling procedures, that is, thermal treatment (board baking or cooking) and open burning (uncontrolled incineration in open air), and examined the characteristics of PBDEs released during these processes. Closed chamber experiments were used to simulate these processes as they would isolate the input sources from environmental interferences. The proportions of PBDE emitted with the gaseous phase, suspended particles and ash residues were determined. The particle size dependency was also considered in the investigations. The objectives of the present study were to (1) estimate the EFs of PBDEs with different emission types and particle sizes, (2) compare the difference between emission types, and (3) analyze the size distribution patterns of atmospheric particle-bound PBDEs.

MATERIALS AND METHODS

Materials. Thirty-eight individual BDE congeners (BDE-3, -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -184, -191, -194, -195, -196, -197, -198, -199, -200, -201, -202, -203, -204, -205, -206, -207, -208, and -209) were contained in two PBDE standard mixtures (BDE-MXE and OND), along with BDE-180, were purchased from Wellington Laboratories (Guelph, Canada). The sum of the 39 BDE congeners is defined as $\sum_{39}\text{PBDE}$. Additionally, all the surrogate standards, including BDE-51, BDE-115, and F-BDE-208, were obtained from AccuStandard (New Haven, CT). BDE-69 and F-BDE-201 from AccuStandard and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate-*d*₁₇ from Toronto Research Chemicals (Toronto, Canada) were employed as the internal standards. Glass microfiber filters from Whatman International (Maidstone, England) were baked at 450 °C for at least 4 h prior to use.

Experimental Setup and Sampling. Raw materials were collected from e-waste dismantling workshops in Guiyu and a resource utilization company in Foshan, Guangdong Province. One hundred sixty-one e-waste samples, including television sets, computers, air conditioners, refrigerators, wash machines and cell phones, were screened by a portable X-ray fluorescence device (Bruker, S1 TITAN, Germany). Three plastic casings (A1, A2, and A3) and three printed circuit boards (B1, B2, and B3) were chosen in modeling experiments. Detailed information about the e-waste samples is presented in the Table S1. Prior to dismantling tests and extraction, large pieces of e-waste were smashed into small pieces (between 10 and 20 mesh sieves, that is, 830–1700 μm) by a stainless universal high-speed smashing machine (Taisite, FW177, China). Modeling experiments were conducted in a stainless steel chamber (50 × 50 × 150 cm; Figure S1). The inner wall of the apparatus was buffed to reduce adsorption and cleaned between samplings with acetone. The apparatus was ventilated over 12 h after each treatment. Particulate samples were collected with a Micro-Orifice Uniform Deposit Impactor (MOUDI) (MSP Corporation; Shoreview, MN) at the chamber outlet. Each sample was collected on 47 mm diameter glass microfiber filters at a constant flow rate of 30 L min^{-1} . Airborne particles were segregated into 11 size fractions, that is, >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 μm . Polyurethane foam plugs

(PUF; 6.5 cm diameter × 8.0 cm; density = 0.03 g cm^{-3}) were applied to collect gaseous PBDEs behind MOUDI. In addition, an air cleaning unit with desiccant, glass microfiber filter and PUF was installed at the inlet of the apparatus. Thermal treatment experiments were carried out at 300 °C with an electronic hot plate (Ansai, 946C, China) for 150 min. A butane blowtorch was applied in open burning tests, with a temperature range of approximately 800–1350 °C for 3 min. The MOUDI started to collect particles once the treatment was initiated and lasted for another 180 min after the end of disposal. A total of 180 samples at three categories, that is, gas phase, airborne particle, and residual ash, were collected after treatment of all e-wastes and stored in aluminum foil at -20 °C until further treatment.

Sample Extraction and Purification. Each sample was spiked with the surrogate standards. Each e-waste sample was ultrasonically extracted with 20 mL of toluene three times (30 min each). Airborne particle and residual ash samples were also ultrasonically extracted with 20 mL of an hexane, dichloromethane and acetone mixture (2:2:1 in volume). PUF plugs were Soxhlet extracted with 200 mL of hexane, dichloromethane, and acetone mixture (2:2:1 in volume) for 48 h. Each extract was concentrated, solvent exchanged to hexane and further concentrated to 1–2 mL with a pressure blowing concentrator (TurboVap II, Biotage, Sweden). The concentrate was purified with a silica gel column (i.d. = 1.0 cm) consisted of 12 cm neutral silica gel and 1 cm anhydrous sodium sulfate from bottom to top. The column was eluted with 45 mL of hexane and the eluate was then concentrated to 100 μL . The eluate was further purified by another glass column with 0.23 cm i.d. consisted of 5 cm sulfuric acid silica (44% sulfuric acid, w/w) and 1 cm anhydrous sodium sulfate with an eluate of 1.5 mL hexane. Finally, the extract was concentrated to 100 μL under a gentle nitrogen stream and spiked with the internal standards before instrumental analysis.

Instrumental Analysis. All the BDE congeners were measured with a Shimadzu Model QP2010 Ultra GC/MS in the negative chemical ionization mode. A DB-5MS capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness) was used for chromatographic separation for mono- to hepta-BDEs. The column temperature was increased from 110 °C (held for 1 min) to 200 °C (held for 1 min) at 12 °C min^{-1} , ramped to 240 °C at 5 °C min^{-1} (held for 5 min), raised to 280 °C at 2 °C min^{-1} (held for 5 min), and finally programmed to 310 °C at 30 °C min^{-1} (held for 10 min). A DB-5HT capillary column (15 m × 0.25 mm i.d. with 0.1 μm film thickness) was applied for separation of octa- to deca-BDEs, and the column temperature was programmed from 100 °C (held for 2 min) to 255 °C at 25 °C min^{-1} , elevated to 265 °C at 1 °C min^{-1} and finally increased to 325 °C at 25 °C min^{-1} (held for 6 min). Ultrahigh purity helium was used as carrier gas operated at a flow rate of 1.5 mL min^{-1} . The ion source and quadrupole temperatures were maintained at 200 and 150 °C, respectively.

Quality Assurance and Quality Control. The mean recoveries of the surrogate standards (BDE-51, BDE-115, and F-BDE-208) spiked to each sample before the extraction were 88 ± 15%, 94 ± 17%, and 80 ± 13%, respectively. The mean recoveries of the target compounds in 12 spiked samples (one target standards spiked blank sample was analyzed for every batch of 11 field samples) were 78–112%. To verify the efficiency of recovering target analytes from the treated e-waste samples, air-bound particles from thermal treatment of A3 for 150 min were collected with MOUDI for 330 min. In addition,

continuous sampling with MOUDI for another 210 min was conducted after the above-mentioned thermal test and removal of residues. Analyses of these two sets of samples indicated that the percent of residual PBDEs remaining in the second set of samples was less than 0.6% of PBDEs in the first set. Procedural blanks were employed to identify any potential cross contamination from sampling and extraction procedures. In disposal experiments, field blank samples were obtained by sampling without e-waste in both thermal treatment and open burning. All blank samples and field blank samples contained negligible PBDEs with a percentage less than 1%. Concentrations of PBDEs in all samples were corrected by those detected in the corresponding procedural and field blanks within the same batch but not corrected for the surrogate standard recoveries. The EFs calculated by the limits of detection for PBDEs ranged from 0.08 to 5 ng g⁻¹ and the results below the reporting limit were displayed as “<RL”.

RESULTS AND DISCUSSION

Occurrence of PBDEs in Raw Materials. In the present study, all the e-waste samples did not exceed the restriction of the use of certain hazardous substances (RoHS) limit value of $1 \times 10^6 \mu\text{g kg}^{-1}$ for PBDEs.¹⁶ Concentrations of $\sum_{39}\text{PBDE}$ in plastic casings were 1.01×10^5 – $2.57 \times 10^5 \text{ ng g}^{-1}$, 2–5 orders of magnitude higher than those in printed circuit boards (0 – $2.19 \times 10^3 \text{ ng g}^{-1}$). This PBDE level is much lower than those reported in the literature; for example, PBDE contents in PBDEs flameproof plastics typically ranged between 5×10^6 and $3 \times 10^8 \text{ ng g}^{-1}$ (0.5–30%).¹⁷ This may be due to the introduction of regulations on the use of brominated flame retardants in various products in the developed countries in the early 2000s. Hepta- to deca-BDEs dominated the PBDE homologue distribution profiles in plastic casings at an average relative abundance of 97% (Figure S2). Printed circuit board samples contained low levels of PBDEs. The X-ray fluorescence investigations showed high Br contents in these samples (Table S1), which likely contain other alternative brominated flame retardants, such as TBBPA and HBCD. Apparently plastic casings and printed circuit boards are imbedded with different types of flame retardants.

Emission Factors. The EF in the present study is expressed as the mass of emitted PBDEs per unit mass of e-waste treated. The EFs of total PBDEs were 817– 1.60×10^5 and <RL– $9.14 \times 10^4 \text{ ng g}^{-1}$ in thermal treatment and open burning, respectively (Table 1). The EFs with the thermal treatment in the present study were higher than those with many formal e-waste disposal processes. In pyrolytic processes of plastic casings and printed wiring boards, the mean EF values of $\sum_{13}\text{PBDE}$ were $1.04 \pm 1.13 \times 10^4$ and $8.1 \pm 4.6 \times 10^3 \text{ ng g}^{-1}$, respectively.¹⁸ These values were approximately 1 order of magnitude lower than those for plastic casings ($1.14 \pm 0.60 \times 10^5 \text{ ng g}^{-1}$) but slightly higher than those for printed circuit boards ($1.29 \pm 0.63 \times 10^3 \text{ ng g}^{-1}$) obtained in the present study. It was reported that the EFs of deca-BDE per unit weight of PBDE in flue gas ranged from 8 to $5 \times 10^3 \text{ ng g}^{-1}$ (median: 30 ng g^{-1}) for dismantling and crushing of seven home appliance recycling facilities and 100 to $1.8 \times 10^3 \text{ ng g}^{-1}$ for three incineration tests.¹⁹ Although the open burning process diminished a large portion of the emissions of PBDEs compared to thermal degradation in the present study, laboratory results may be underestimated compared to field emissions because of air flow and oxygen deficiency. Nevertheless, informal recycling procedures such as thermal degradation and open burning

Table 1. Emission Factors (EFs) of 39 Individual PBDE Congeners (ng g⁻¹) for Plastic Casings (A1–A3) and Printed Circuit Boards (B1–B3)

	gas	residue	particle	total EFs
thermal process				
A1	17.3	2.63×10^4	1.27×10^5	1.53×10^5
A2	8.4	1.64×10^4	1.40×10^4	3.04×10^4
A3	6.7	7.54×10^3	1.52×10^5	1.60×10^5
B1	18.8	11.6	2.15×10^3	2.18×10^3
B2	2.7	8.9	871	882
B3	5.8	<RL ^a	811	817
open burning				
A1	36.3	9.08×10^4	549	9.14×10^4
A2	28.7	41.6	1.64×10^3	1.71×10^3
A3	34.6	1.38×10^3	245	1.66×10^3
B1	42.4	39.5	50.6	133
B2	14.2	<RL	<RL	14.2
B3	<RL	<RL	<RL	<RL

^aReporting limit. The EFs calculated by the limits of detection for mono- to penta-BDEs were 0.08 ng g^{-1} (plastic casings) and 0.5 ng g^{-1} (printed circuit boards). The values were 0.16 ng g^{-1} and 1 ng g^{-1} for hexa- to hepta-BDEs, 0.33 ng g^{-1} and 2 ng g^{-1} for octa-BDEs, 0.8 ng g^{-1} and 5 ng g^{-1} for nona- to deca-BDEs.

can release large amounts of PBDEs into the surrounding environment and might cause adverse human health risks.⁸ For instance, high levels of PBDEs were found in serum samples of workers in an e-waste recycling region in Guangdong Province of China, with the highest concentration of BDE-209 at 3440 ng/g lipid weight.²⁰ Besides, Yuan et al.²¹ found that the median concentration of total PBDEs in serum samples from e-waste dismantling workers of Guiyu, South China was twice as high as that from a control group.

In thermal degradation experiments, airborne particles were the leading contributor of the total PBDE EFs, except for A2 whose residues were the largest (Table 1). Higher percentage of particles affiliated PBDEs among the three emission types was observed from printed circuit boards than from plastic casings. The emissions of PBDEs were lower in open burning process than in thermal degradation. Strong ashing of e-waste observed during the open burning process indicated that stronger destruction rather than debromination of PBDEs arose due to higher reaction temperature. More complete degradation products such as HBr and Br₂ might be produced. Even though the operational temperatures in the combustion chamber can reach 1350 °C, resulting in high PBDE destruction efficiencies, the residues of PBDEs could still cause some environmental issues. Residues became the most important output source of PBDEs in open burning, similar to other waste incineration results,^{6,22} except for A2. This is because there were dense smoke and black soot in the air with almost no residual ashes left during the burning of A2. Similar findings were also observed in open burning of PS among five types of plastic wastes.¹² Thus, this special case of A2 may have resulted from different matrices from other plastic casings.

In addition, the EFs of PBDEs on size fractions were calculated for the first time (Figure 1). Size-fractionated particles were categorized as coarse ($D_p > 1.8 \mu\text{m}$) and fine ($D_p < 1.8 \mu\text{m}$). The fine fraction includes accumulation mode ($0.10 \mu\text{m} < D_p < 1.8 \mu\text{m}$) and ultrafine ($D_p < 0.10 \mu\text{m}$) particles.²³ Generally, EFs of PBDEs on fine particles were 1–3 orders of magnitude greater than those on coarse particles from

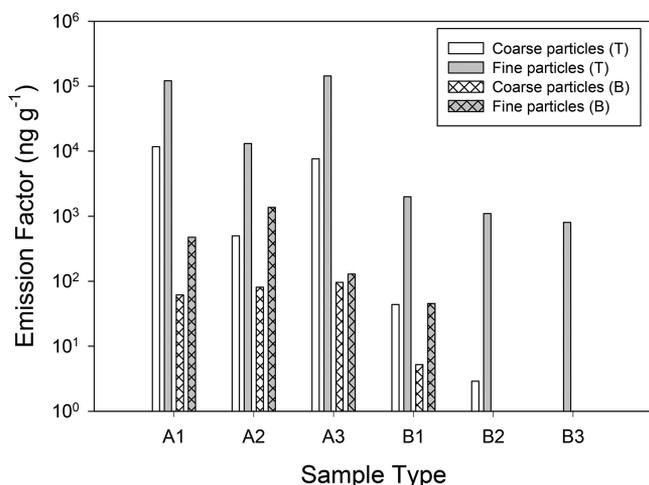


Figure 1. Emission factors of \sum_{39} PBDE by thermal process (T) and open burning (B) of plastic casings (A1–A3) and printed circuit boards (B1–B3).

both thermal treatment and open burning. This implicates adversely for inhalation exposure because fine particles are able to penetrate deep into the human respiratory tract and consequently transport abundant contaminants to the lung.¹⁰

Few PBDEs were detected in the gas phase in the present study (Table 1). This finding indicated that the output of PBDEs to air during the primitive recycling process of e-waste was dominated by airborne particles rather than the gas phase. It was helpful to accurately estimate the emissions and human health risks at the emission source.

The Output over Input Mass Ratios. The output over input (O/I) mass ratios of PBDEs for thermal degradation and open burning of six e-waste samples are summarized in Table 2. The O/I mass ratios of \sum_{39} PBDE ranged from 0.12 to 3.76 in thermal degradation, higher than those in open burning with a range of 0–0.16. No significant difference in the O/I mass ratios of plastic casings and printed circuit boards were found (*t*-test; *p* > 0.05). For plastic casings, the average O/I mass ratios were 0.47 and 0.06 in thermal degradation and open burning, respectively, 1.91 and 0.07 for printed circuit boards. Lower O/I mass ratios for total PBDEs were found in another

report (0.02 and 0.06 for pyrolytic treatments of plastic casings and printed wiring boards, respectively).¹⁸ The results in the present study were also higher than those (0.01–0.05) in open burning of plastic wastes.¹²

Concentrations of several PBDEs were higher in after-treated field samples than in raw materials (*O/I* > 1). Plausible explanation was stated in literature that PBDE decomposition was overwhelmed by formation and survival during the thermal degradation and open burning of PBDE-containing e-wastes.¹² Redfern et al.²² concluded that the competitive effects between formation and destruction determine the fate of PBDEs in combustion. When large amounts of PBDEs are introduced to the combustion system, the destruction of PBDEs is dominant; otherwise the formation of PBDEs is prevailing.²² Apparently PBDEs were formed mostly after thermal treatment of printed circuit boards, which contained few PBDEs before treatment. Previous studies found that PBDEs can be formed in combustion systems even if no commercial PBDE mixtures were added, for example, PBDEs can be generated under the similar conditions for formation of PCDD/Fs in metallurgical facilities and vehicles using bromines-containing fuel.^{24–27} The underlying formation mechanisms have remained unclear and need to be further investigated.

Composition Profiles. The mean output mass fractions of \sum_{39} PBDE in thermal degradation were 87%, 13%, and 0.3%, discharged from the airborne particles, residual ash and gas phase, respectively. The total PBDE amount was emitted mainly by airborne particles, much less by residual ashes and the gaseous constituents in thermal process (Figure S3), similar to the results from open burning of plastic waste at 850–1000 °C.¹² The mean output mass fractions of \sum_{39} PBDE in open burning were 30%, 43%, and 27%, respectively. Ash residues provided the most important output of PBDEs in open burning. The difference in the main emission type of PBDEs derived from thermal degradation and open burning needs to be considered when estimating human health risk of these recycling processes.

The homologue distribution profiles of emitted PBDEs are displayed in Figures S2 and S4. In thermal degradation, hepta- to deca-BDEs still dominated the total emissions of PBDEs. Cai et al.¹⁸ demonstrated that exhaust fumes derived from the pyrolytic process of e-wastes were dominated by lightly and

Table 2. Output over Input Mass Ratio by Thermal Process (T) and Open Burning (B) of Plastic Casings (A1–A3) and Printed Circuit Boards (B1–B3)

	A1		A2		A3		B1		B2		B3	
	T	B	T	B	T	B	T	B	T	B	T	B
mono-BDE	-- ^a											
di-BDE	0.68	0.06	0.15	0.07	3.92	0.50	0.57	0.21	1.82 ^b	9.58 ^b	15.0 ^b	
tri-BDE	5.16	0.46	0.30	0.51	1.91	0.21	0.15	0.02	2.31 ^b	1.57 ^b	1.43 ^b	
tetra-BDE	0.22	0.39	0.21	0.26	1.33	0.10	0.20	0.04	0.40	3.05 ^b	14.4 ^b	
penta-BDE	0.59	0.82	0.11	0.84	13.0	0.35	0.37	0.05	17.0	0.13	15.3 ^b	
hexa-BDE	0.72	0.22	0.37	0.10	7.81	0.01	2.24		84.1 ^b		69.6 ^b	
hepta-BDE	0.26	0.08	0.14	0.00	1.64	0.01	34.0	9.92		570 ^b		
octa-BDE	0.98	0.53	0.21	0.03	20.2	0.37	202 ^b				109 ^b	
nona-BDE	0.65	0.54	0.20	0.01	2.69	0.02	4.82				12.1 ^b	
deca-BDE	0.08	0.17	0.09		0.18		0.11	0.09	0.03		0.05	
\sum_{39} PBDE	0.27	0.16	0.12	0.01	1.03	0.01	0.88	0.06	1.10	0.16	3.76	

^aReporting limits: The emission factors calculated by the reporting limits for mono- to penta-BDEs were 0.08 ng g⁻¹ (plastic casings) and 0.5 ng g⁻¹ (printed circuit boards). The values were 0.16 ng g⁻¹ and 1 ng g⁻¹ for hexa- to hepta-BDEs, 0.33 ng g⁻¹ and 2 ng g⁻¹ for octa-BDEs, 0.8 ng g⁻¹ and 5 ng g⁻¹ for nona- to deca-BDEs. ^bTarget PBDEs were not detected in raw materials and their emission factors (ng g⁻¹) are displayed here.

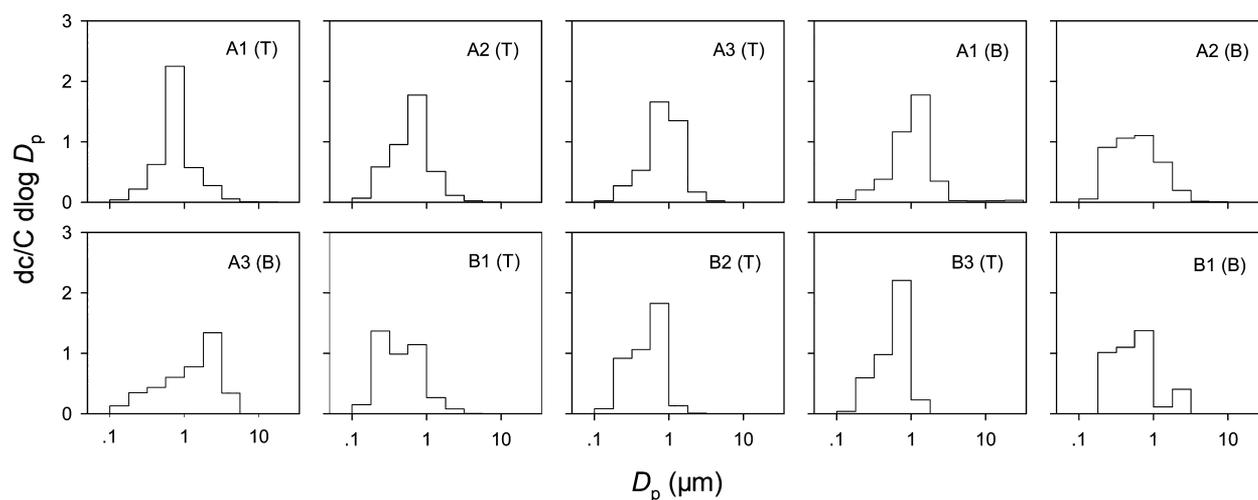


Figure 2. Size distributions of particle-bound Σ_{39} PBDE by thermal process (T) and open burning (B) of plastic casings (A1–A3) and printed circuit boards (B1–B3). The size distributions were invalid for particle-bound PBDEs from open burning of B2 and B3 as their concentrations were below the reporting limits. dc is the concentration of Σ_{39} PBDE 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).

heavily brominated congeners (excluding BDE209). This discrepancy might result from stronger debromination reaction in the electric furnace¹⁸ compared to the plot heating in the present study. The mean mass ratio of mono- to hexa-BDEs increased to $9.3 \pm 3.8\%$ and $41 \pm 38\%$ in thermal degradation and open burning, respectively, compared to $2.0\% \pm 1.7\%$ in the raw materials. The case of B1 was excluded in these results, as the main ingredients in B1 were di- to hexa-BDEs at an extremely high mass ratio of 78% before treatment. The sharp increase in the concentrations of lightly brominated BDEs in open burning products indicated that heavily brominated BDE congeners were destructed in open burning.

The most abundant congeners in raw materials were hepta- and deca-BDEs. The relative abundance of deca-BDE was lower in after-treatment samples than in raw materials, suggesting that degradation occurred during thermal process and open burning. The EFs of deca-BDE and octa-BDE or nona-BDE were positively correlated with each other ($p < 0.05$) (Figure S5a), supporting the view that BDE-209 was degraded (estimated degradation rate $>70\%$). Figure S5(b) displays a significant positive correlation ($p = 0.0001$) between hepta-BDEs and hexa-BDEs. The destruction of hepta-BDE might contribute to the emission of hexa-BDEs during the thermal treatment and open burning of e-waste.

Size Distribution of Particulate PBDEs. The mass ratio of PBDEs in coarse and fine particles (Figure S6) indicated that the vast majority of particulate-bound PBDEs were affiliated with fine particles (57–100%) in both thermal treatment and open burning. The results are consistent with another report indicating that most particulate-phase PBDEs derived from the pyrolysis process preferred in finer particles ($<2.1 \mu\text{m}$), that is, 85% of the total mass.¹⁸ These values are higher than those (47–59%) obtained by a previous study conducted in Qingyuan, an e-waste recycling zone.²³ These results indicated that the mass fraction of PBDEs in the coarse particles was elevated during the diffusion process of particle-bound PBDEs from source to the surrounding environment. It was reported that resuspension of soil particles and dusts induced by wind or traffics can be an additional source for atmospheric particle-bound pollutants, which tends to contribute large particles ($D_p > 10 \mu\text{m}$) and their resuspension capacity decreases with

increasing height due to the large dry deposition velocities of large particles.^{28–30}

Generally, PBDEs affiliated with airborne particulates from both thermal degradation and open burning showed a unimodal distribution with dominant sizes at $0.56\text{--}1.0 \mu\text{m}$ and $1.0\text{--}1.8 \mu\text{m}$ (Figure 2). The size distribution patterns of individual BDE homologues are demonstrated in Figures S7–S9. To succinctly describe the size distribution of PBDEs, geometric mean diameter (GMD) and geometric standard deviation (GSD) were calculated (Tables S2 and S3).³¹ The GMD values of particle-bound PBDEs from plastic casings subjected to thermal treatment and open burning were $0.61\text{--}0.83 \mu\text{m}$ and $0.57\text{--}1.16 \mu\text{m}$, respectively, slightly higher than those from printed circuit boards ($0.44\text{--}0.56 \mu\text{m}$ and nondetected– $0.55 \mu\text{m}$). These values were lower than those in Qingyuan ($0.98\text{--}1.98 \mu\text{m}$) at a height of 20 m ²³ and Guangzhou ($0.85\text{--}1.38 \mu\text{m}$) at the heights of $100\text{--}150 \text{ m}$.³² Furthermore, the GMD values of Σ_{39} PBDE in open burning were greater than those in thermal process. The sizes of particles emitted during the thermal degradation phase were smaller than those during the open burning phase, which may have been the main reason for the difference in the size distribution of particle-bound PBDEs. Similar results were obtained for the difference of size-fractionated PAHs between smoldering and flaming phase.³³ Significant correlations between GSD values and logarithmic subcooled liquid vapor pressures ($\log P_L/P_a$) at 298 K, mass fractions of PBDE congeners in coarse particles and $\log P_L/P_a$ at 298 K were obtained in an e-wastes recycling zone.²³ Neither of these correlative relationships were observed in the present study. No significant difference between the size distribution patterns (t -test; $p > 0.05$ for both GSD and GMD values) of lightly (mono- to hepta-) and heavily (octa- to deca-) brominated BDE congeners were observed even though their octanol–air partition coefficients were substantially different. This suggested that the PBDE distribution pattern in particles may have been substantially altered during atmospheric dispersal. Considering the limitation of instrumental analysis, the RL values were replaced with the assumed value (limit of detection divided by $\sqrt{2}$).³⁴ The mass fractions of PBDE congeners in

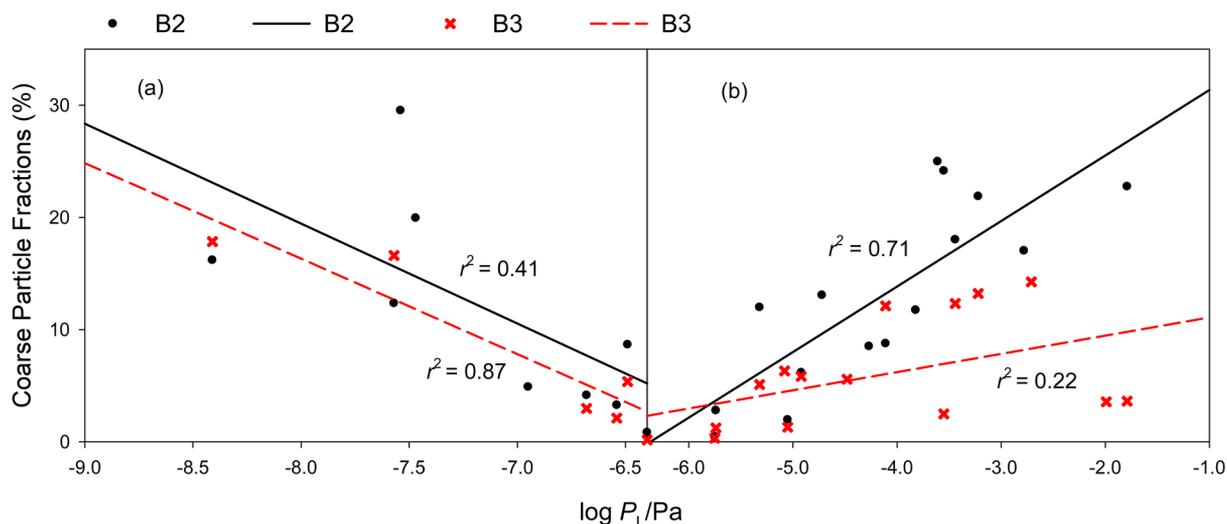


Figure 3. Correlations (a) between heavily brominated BDEs (octa- to deca-BDEs) and their logarithmic subcooled liquid vapor pressures ($\log P_L/P_a$) and (b) between lightly brominated BDEs (mono- to hepta-BDEs) and their $\log P_L/P_a$ values, at 298 K in thermal treatment of printed circuit boards (B2 and B3).

coarse particles and $\log P_L/P_a$ at 298 K upon thermal treatment of B2 and B3 were significantly correlated (Figure 3). BDE-209 was almost the only PBDE congener contained in before-treatment B2 and B3, but abundant PBDEs were identified in the after-treatment samples. Figures 3b show significant positive correlation between di- to hepta-BDE mass fraction in coarse particles and $\log P_L/P_a$ at 298 K ($r^2 = 0.71$ for B2 and $r^2 = 0.22$ for B3), whereas negative correlation between the octa- to deca-BDE mass fraction in coarse particles and $\log P_L/P_a$ at 298 K ($r^2 = 0.41$ for B2 and $r^2 = 0.87$ for B3) was evident (Figure 3a). However, these correlations may not hold if PBDEs are not only formed from the debromination of BDE-209.

The size distribution pattern of particle-bound PBDEs was dependent upon the mechanism of transport to the surrounding environment. PBDEs may be derived from vaporization from PBDE-containing products,³⁵ physical mechanistic processes such as abrasion or weathering³⁶ and combustion.^{6,24,37} Although both lightly and heavily brominated BDEs were largely affiliated with fine particles in the present study, their emission mechanisms may have been different. Luo et al.²³ demonstrated that the main mechanism for lightly brominated BDEs was evaporation and reabsorption, while heavily brominated BDEs were probably emitted in affiliation with particles during the mechanical and combustion processes of e-waste.²³ Physical abrasion may also result from surface damage due to heating,³⁸ with PBDEs remaining bound to particles.³⁹ Particle-bound PBDEs from vaporization may prefer to affiliate with finer particles, due to gas-to-particle partitioning dictated by particle surface areas. The mechanism for partitioning of PBDEs between the gaseous and particulate phases was explained by both adsorption and absorption models.⁴⁰ Absorption by particulate organic carbon rather than surface adsorption was believed to govern gas-particle partitioning of PBDEs during the pyrolysis process, as demonstrated by the negative correlation between the partitioning coefficient (K_p) and the subcooled liquid vapor pressure (P_L^0) of different components.¹⁸ Theoretically, high molecular weight PBDEs with strong hydrophobicity also tend to associate with fine particles with large surface areas.⁴¹ Hence, particle-bound lightly brominated congeners tend to redis-

tribute among particles of different sizes, while heavily brominated congeners may stay in certain specifically sized particles. These explanations can effectually clarify the high mass ratios of both lightly and heavily brominated congeners in fine particles in the present study (Figure S6). However, the mass ratio of particle-bound heavily brominated congeners in coarse particles increased in e-wastes recycling zone compared with the results in the present study.²³ Perhaps heavily brominated congeners were still in the process of approaching steady state rather than reaching equilibrium between the gaseous and particulate phases from emission sources to the surrounding environment due to slow mass transfer.^{42–44} It seems necessary to conduct modeling experiments with e-waste emitted particles and particles from other sources in the atmosphere to better understand this process.

Different emission mechanisms may result in different distribution patterns of PBDEs in individual particles, that is, evaporation leads to adsorption of PBDEs mainly on particle surfaces, while mechanical formation accumulates PBDEs on both inner and external structures of particles. To better describe the emission mechanisms, microanalysis techniques can be applied.^{36,45,46} In addition, the mass fraction of particulate PBDEs in each particle size is size-dependent if PBDEs are derived from the same source and dominated by fine particles, as shown in the present study. It implied that particulate PBDEs may have long atmospheric residence time and they may be capable of reaching the deeper parts of the human respiratory system.⁴⁷

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00780.

Sample information; geometric mean diameters and geometric standard deviations of particle-bound PBDEs calculated for particles; schematic diagram showing the simulation experiment setup; composition profiles of PBDEs in raw materials and products by thermal process and open burning; the distribution of PBDE output mass fractions by the thermal process and open burning;

emission factors of PBDE congeners on coarse and fine particles; relationship of emission factors of deca-BDE and octa-BDEs or nona-BDEs, hepta-BDEs and hexa-BDEs; the distribution of PBDE congeners on coarse and fine particles; and size distribution patterns of PBDE homologues on particles (PDF)

AUTHOR INFORMATION

Corresponding Author

*Phone: 86-20-85226835. E-mail: eddyzeng@jnu.edu.cn.

ORCID

Lian-Jun Bao: 0000-0002-0634-0829

Eddy Y. Zeng: 0000-0002-0859-7572

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The present study was financially supported by the National Natural Science Foundation of China (Nos. 21637001, 41390240, and 21722701). Special thanks go to Jia-Yong Lao, Shan-Yi Xie, Yuan-Jie Hu, and Jia-Li Ge for sample collection and analysis.

REFERENCES

- Cucchiella, F.; D'Adamo, I.; Lenny Koh, S. C.; Rosa, P. Recycling of WEEEs: An economic assessment of present and future e-waste streams. *Renewable Sustainable Energy Rev.* **2015**, *51*, 263–272.
- Lepawsky, J.; Billah, M. Making chains that (un)make things: Waste-value relations and the bangladeshi rubbish electronics industry. *Geografiska Annaler Series B-Human Geography* **2011**, *93* (2), 121–139.
- Chen, W. Q.; Graedel, T. E. Anthropogenic cycles of the elements: A critical review. *Environ. Sci. Technol.* **2012**, *46* (16), 8574–8586.
- Yamasue, E.; Nakajima, K.; Daigo, I.; Hashimoto, S.; Okumura, H.; Ishihara, K. N. Evaluation of the potential amounts of dissipated rare metals from WEEE in Japan. *Mater. Trans.* **2007**, *48* (9), 2353–2357.
- Duan, H. B.; Li, J. H.; Liu, Y. C.; Yamazaki, N.; Jiang, W. Characterization and inventory of PCDD/Fs and PBDD/Fs emissions from the incineration of waste printed circuit board. *Environ. Sci. Technol.* **2011**, *45* (15), 6322–6328.
- Sakai, S.; Watanabe, J.; Honda, Y.; Takatsuki, H.; Aoki, I.; Futamatsu, M.; Shiozaki, K. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* **2001**, *42* (5–7), 519–531.
- Ortuno, N.; Lundstedt, S.; Lundin, L. Emissions of PBDD/Fs, PCDD/Fs and PBDEs from flame-retarded high-impact polystyrene under thermal stress. *Chemosphere* **2015**, *123*, 64–70.
- Sepulveda, A.; Schlupe, M.; Renaud, F. G.; Streicher, M.; Kuehr, R.; Hagelueken, C.; Gerecke, A. C. A review of the environmental fate and effects of hazardous substances released from electrical and electronic equipments during recycling: Examples from China and India. *Environ. Impact Assess. Rev.* **2010**, *30* (1), 28–41.
- Kiddee, P.; Naidu, R.; Wong, M. H. Electronic waste management approaches: An overview. *Waste Manage.* **2013**, *33* (5), 1237–1250.
- Luo, P.; Bao, L. J.; Wu, F. C.; Li, S. M.; Zeng, E. Y. Health risk characterization for resident inhalation exposure to particle-bound halogenated flame retardants in a typical e-waste recycling zone. *Environ. Sci. Technol.* **2014**, *48* (15), 8815–8822.
- Wang, J.; Ma, Y. J.; Chen, S. J.; Tian, M.; Luo, X. J.; Mai, B. X. Brominated flame retardants in house dust from e-waste recycling and urban areas in South China: Implications on human exposure. *Environ. Int.* **2010**, *36* (6), 535–541.
- Ni, H. G.; Lu, S. Y.; Mo, T.; Zeng, H. Brominated flame retardant emissions from the open burning of five plastic wastes and implications for environmental exposure in China. *Environ. Pollut.* **2016**, *214*, 70–76.
- Zennegg, M.; Schlupe, M.; Streicher-Porte, M.; Lienemann, P.; Haag, R.; Gerecke, A. C. Formation of PBDD/F from PBDE in electronic waste in recycling processes and under simulated extruding conditions. *Chemosphere* **2014**, *116*, 34–39.
- Guo, J.; Zhang, R.; Xu, Z. M. PBDEs emission from waste printed wiring boards during thermal process. *Environ. Sci. Technol.* **2015**, *49* (5), 2716–2723.
- Luo, P.; Bao, L. J.; Guo, Y.; Li, S. M.; Zeng, E. Y. Size-dependent atmospheric deposition and inhalation exposure of particle-bound organophosphate flame retardants. *J. Hazard. Mater.* **2016**, *301*, 504–511.
- European Commission. Restriction of Hazardous Substances in Electrical and Electronic Equipment, 2011. http://ec.europa.eu/environment/waste/rohs_eee/legis_en.htm.
- Alaee, M.; Arias, P.; Sjödin, A.; Bergman, Å. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* **2003**, *29* (6), 683–689.
- Cai, C. Y.; Yu, S. Y.; Liu, Y.; Tao, S.; Liu, W. X. PBDE emission from E-wastes during the pyrolytic process: Emission factor, compositional profile, size distribution, and gas-particle partitioning. *Environ. Pollut.* **2018**, *235*, 419–428.
- Sakai, S. I.; Hirai, Y.; Aizawa, H.; Ota, S.; Muroishi, Y. Emission inventory of deca-brominated diphenyl ether (DBDE) in Japan. *J. Mater. Cycles Waste Manage.* **2006**, *8* (1), 56–62.
- Qu, W. Y.; Bi, X. H.; Sheng, G. Y.; Lu, S. Y.; Fu, H.; Yuan, J.; Li, L. P. Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. *Environ. Int.* **2007**, *33* (8), 1029–1034.
- Yuan, J.; Chen, L.; Chen, D. H.; Guo, H.; Bi, X. H.; Ju, Y.; Jiang, P.; Shi, J. B.; Yu, Z. Q.; Yang, J.; Li, L. P.; Jiang, Q.; Sheng, G. Y.; Fu, J. M.; Wu, T. C.; Chen, X. M. Elevated serum polybrominated diphenyl ethers and thyroid-stimulating hormone associated with lymphocytic micronuclei in Chinese workers from an e-waste dismantling site. *Environ. Sci. Technol.* **2008**, *42* (6), 2195–2200.
- Redfern, F. M.; Lee, W. J.; Yan, P.; Mwangi, J. K.; Wang, L. C.; Shih, C. H. Overview and perspectives on emissions of polybrominated diphenyl ethers on a global basis: Evaporative and fugitive releases from commercial PBDE mixtures and emissions from combustion sources. *Aerosol Air Qual. Res.* **2017**, *17* (5), 1117–1131.
- Luo, P.; Ni, H. G.; Bao, L. J.; Li, S. M.; Zeng, E. Y. Size distribution of airborne particle-bound polybrominated diphenyl ethers and its implications for dry and wet deposition. *Environ. Sci. Technol.* **2014**, *48* (23), 13793–13799.
- Wang, L. C.; Wang, Y. F.; Hsi, H. C.; Chang Chien, G. P. Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes. *Environ. Sci. Technol.* **2010**, *44* (4), 1240–1246.
- Chang, Y. C.; Lee, W. J.; Wang, L. C.; Yang, H. H.; Cheng, M. T.; Lu, J. H.; Tsai, Y. I.; Young, L. H. Effects of waste cooking oil-based biodiesel on the toxic organic pollutant emissions from a diesel engine. *Appl. Energy* **2014**, *113*, 631–638.
- Chang, Y. C.; Lee, W. J.; Yang, H. H.; Wang, L. C.; Lu, J. H.; Tsai, Y. I.; Cheng, M. T.; Young, L. H.; Chiang, C. J. Reducing emissions of persistent organic pollutants from a diesel engine by fueling with water-containing butanol diesel blends. *Environ. Sci. Technol.* **2014**, *48* (10), 6010–6018.
- Chen, C. Y.; Lee, W. J.; Wang, L. C.; Chang, Y. C.; Yang, H. H.; Young, L. H.; Lu, J. H.; Tsai, Y. I.; Cheng, M. T.; Mwangi, J. K. Impact of high soot-loaded and regenerated diesel particulate filters on the emissions of persistent organic pollutants from a diesel engine fueled with waste cooking oil-based biodiesel. *Appl. Energy* **2017**, *191*, 35–43.
- Harrison, R. M.; Jones, A. M.; Gietl, J.; Yin, J. X.; Green, D. C. Estimation of the contributions of brake dust, tire wear, and

resuspension to nonexhaust traffic particles derived from atmospheric measurements. *Environ. Sci. Technol.* **2012**, *46* (12), 6523–6529.

(29) Young, T. M.; Heeraman, D. A.; Sirin, G.; Ashbaugh, L. L. Resuspension of soil as a source of airborne lead near industrial facilities and highways. *Environ. Sci. Technol.* **2002**, *36* (11), 2484–2490.

(30) Sabin, L. D.; Lim, J. H.; Venezia, M. T.; Winer, A. M.; Schiff, K. C.; Stolzenbach, K. D. Dry deposition and resuspension of particle-associated metals near a freeway in Los Angeles. *Atmos. Environ.* **2006**, *40* (39), 7528–7538.

(31) Hinds, W. C. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, 2nd ed.; Wiley Interscience: New York, 1999; pp 242–245.

(32) Zhang, B. Z.; Zhang, K.; Li, S. M.; Wong, C. S.; Zeng, E. Y. Size-dependent dry deposition of airborne polybrominated diphenyl ethers in urban Guangzhou, China. *Environ. Sci. Technol.* **2012**, *46* (13), 7207–7214.

(33) Shen, G. F.; Wang, W.; Yang, Y. F.; Ding, J. N.; Xue, M. A.; Min, Y. J.; Zhu, C.; Shen, H. Z.; Li, W.; Wang, B.; Wang, R.; Wang, L.; Tao, S.; Russell, A. G. Emissions of PAHs from indoor crop residue burning in a typical rural stove: Emission factors, size distributions, and gas-particle partitioning. *Environ. Sci. Technol.* **2011**, *45* (4), 1206–1212.

(34) Jin, Y.; Hein, M. J.; Deddens, J. A.; Hines, C. J. Analysis of lognormally distributed exposure data with repeated measures and values below the limit of detection using SAS. *Ann. Occup. Hyg.* **2011**, *55* (1), 97–112.

(35) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46* (5), 583–624.

(36) Webster, T. F.; Harrad, S.; Millette, J. R.; Holbrook, R. D.; Davis, J. M.; Stapleton, H. M.; Allen, J. G.; McClean, M. D.; Ibarra, C.; Abdallah, M. A. E.; Covaci, A. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. *Environ. Sci. Technol.* **2009**, *43* (9), 3067–3072.

(37) Gullett, B. K.; Wyrzykowska, B.; Grandesso, E.; Touati, A.; Tabor, D. G.; Solórzano Ochoa, G. PCDD/F, PBDD/F, and PBDE Emissions from open burning of a residential waste dump. *Environ. Sci. Technol.* **2010**, *44* (1), 394–399.

(38) Holbrook, R. D.; Davis, J. M.; Scott, K. C.; Szakal, C. Detection and speciation of brominated flame retardants in high-impact polystyrene (HIPS) polymers. *J. Microsc.* **2012**, *246* (2), 143–152.

(39) Webster, T. F.; Harrad, S.; Millette, J. R.; Holbrook, R. D.; Davis, J. M.; et al. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. *Environ. Sci. Technol.* **2009**, *43* (9), 3067–3072.

(40) Goss, K. U.; Schwarzenbach, R. P. Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants. *Environ. Sci. Technol.* **1998**, *32* (14), 2025–2032.

(41) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254.

(42) Yu, H.; Yu, J. Z. Polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China: Size distribution characteristics and size-resolved gas-particle partitioning. *Atmos. Environ.* **2012**, *54*, 194–200.

(43) Li, Y. F.; Jia, H. L. Prediction of gas/particle partition quotients of Polybrominated Diphenyl Ethers (PBDEs) in north temperate zone air: An empirical approach. *Ecotoxicol. Environ. Saf.* **2014**, *108*, 65–71.

(44) Li, Y. F.; Ma, W. L.; Yang, M. Prediction of gas/particle partitioning of polybrominated diphenyl ethers (PBDEs) in global air: A theoretical study. *Atmos. Chem. Phys.* **2015**, *15* (4), 1669–1681.

(45) Suzuki, G.; Kida, A.; Sakai, S. I.; Takigami, H. Existence state of bromine as an indicator of the source of brominated flame retardants in indoor dust. *Environ. Sci. Technol.* **2009**, *43* (5), 1437–1442.

(46) Holbrook, R. D.; Davis, J. M.; Scott, K. C. K.; Szakal, C. Detection and speciation of brominated flame retardants in high-

impact polystyrene (HIPS) polymers. *J. Microsc.* **2012**, *246* (2), 143–152.

(47) Mandalakis, M.; Besis, A.; Stephanou, E. G. Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece. *Environ. Pollut.* **2009**, *157* (4), 1227–1233.