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Organophosphate flame retardants emitted from thermal treatment and open burning of e-waste

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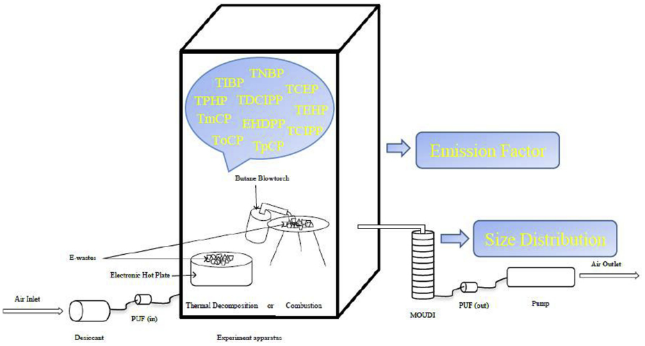
GRAPHICAL ABSTRACT



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ABSTRACT

Organophosphate flame retardants (OPFRs) have been increasingly produced and consumed since the gradual phase-out of polybrominated diphenyl ethers. Primitive recycling of e-waste can be a significant input source of OPFRs to the environment. Thermal treatment and open burning of typical e-wastes were conducted in a closed chamber to examine the emissions and the size distribution patterns of particle-bound OPFRs from these processes. The sum emission factors of OPFRs were 3.70×10^4–3.65×10^5 ng g^{-1} by thermal treatment and 5.22×10^3–9.27×10^4 ng g^{-1} by open burning. The output-input mass ratios of OPFRs for plastic casings were 0.030–116 and 0.012–7.1 by thermal treatment and open burning, respectively, and were 0.11–40 and 0.0014–6.7 for printed circuit boards. The size distribution patterns of OPFRs were characterized by one unimodal peak (0.56–1.0 µm) for thermal treatment and bimodal peaks (0.56–1.0 or 1.0–1.8 and 10–18 µm) for open burning. Particle-bound OPFRs appeared to form in affiliation with particles rather than by adsorption or deposition from the gaseous phase to particulate organic matter. With increasing amounts of OPFRs used in a variety of consumer products, the emissions of OPFRs to the environment are expected to increase continuously in the future.

1. Introduction

In recent years, the environmental impacts of organophosphate flame retardants (OPFRs) have gained increasing attention [1]. The ban on the production and consumption of some brominated flame retardants (BFRs) has substantially stimulated the widespread adoption of

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OPFRs in consumer products [1–3]. The global consumption of OPFRs increased from 0.1 million tons in 1999 [4] to 1.05 million tons predicted in 2018 [5]. The production of OPFRs in China reached 100,000 tons in 2010, with an annual increase of 15% [6,7]. Because OPFRs are only additive to consumer products, they can easily leach to the environment, resulting in widespread occurrence in ambient air [8–11], indoor dust [12–14], water [15–17], sediment [18,19], soil [20,21], and biota [20,22].

Recycling of obsolete electronics (e-waste) has been recognized as an important source of OPFRs to the environment [2], largely due to shorter-than-ever life cycles of electronic products [13]. Bi et al. [23] expounded that organophosphates were the major organic constituents in particulate matter emitted from an e-waste recycling workshop in South China. Crude or primitive recycling processes have remained prevalent for extracting materials and components from e-waste in many developing nations, and poorly-protected workers and the surrounding environments are exposed to chemical hazards [24,25]. Even though OPFRs are less toxic than BFRs [6], most OPFRs can pose infaust biological effects [1,26]. These include hemolytic and reproductive irregularities, and Cl-containing OPFRs may be carcinogenic [1]. The growing use of OPFRs in electronics, which have been undergoing shorter life cycles due to faster turnaround time, has necessitated the consideration of e-waste recycling processes as significant input sources.

Another important attribute of OPFRs is the potential for long-range atmospheric transport due to their persistence in the atmosphere [27], corroborated by their presence in remote regions [28]. The particle size of airborne particle-bound OPFRs can influence their transport process, and hence is a significant factor for the fate and associated with human health risk of OPFRs [11]. Most previous studies have focused on the chemical compositions of airborne particle-bound OPFRs, with only a few on particle size distribution patterns in the office environment [9] and in the atmosphere [10,11]. No study has been conducted on the state of OPFR contamination around e-waste recycling sites, particularly those mostly employing primitive techniques. The emissions and size distribution patterns of OPFRs derived from primitive recycling of e-waste have remained largely unknown, and need to be accounted for in the assessment of contaminated environments and human health risks.

The present study attempted to address this issue by simulating thermal treatment (board baking or cooking) and open burning (uncontrolled incineration) of OPFR-bearing e-waste in a closed chamber. The objectives were to (1) obtain the emission factors (EFs) of OPFRs of varying emission types and particle sizes; (2) examine the relative strengths of different emissions; (3) elucidate the size distribution patterns of atmospheric particle-bound OPFRs; and (4) estimate the emissions of OPFR from thermal treatment and open burning of e-wastes in China.

2. Materials and methods

2.1. Materials

Standards of tri-*n*-butyl phosphate (TNBP), triphenyl phosphate (TPHP), and tris(1, 3-dichloro-isopropyl) phosphate (TDCIPP) were purchased from AccuStandard (New Haven, CT, USA). Tri-*iso*-butyl phosphate (TIBP) was obtained from Chiron AS (Trondheim, Norway). Tris (2-chloroethyl) phosphate (TCEP), tris(chloroisopropyl) phosphate (TCIPP), 2-ethylhexyldiphenyl phosphate (EHDPP), tri(2-ethylhexyl) phosphate (TEHP), tri-*m*-cresyl phosphate (TmCP), tri-*o*-cresyl phosphate (ToCP), and tri-*p*-cresyl phosphate (TpCP) were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). TPHP-d_{15} and TNBP-d_{27} used as surrogate standards were purchased from Toronto Research Chemicals (Toronto, ON, Canada) and Cambridge Isotope Laboratories (Andover, MA, USA), respectively. Fluoranthene-d_{10}, pyrene-$d_{10,}$ and dibenz[a,h]anthracene-d_{14} used as internal standards were obtained from Cambridge Isotope Laboratories (Andover, MA, USA) [11].

2.2. Experimental setup and sampling

A total of 161 e-waste samples were obtained from e-waste dismantling facilities and a resource utilization company in South China. After a quick screening of the raw materials by a portable X-ray fluorescence device (Bruker, Germany), plastic casings (A1–A3) and printed circuit boards (B1–B3) were selected for subsequent simulation experiments. A stainless universal high-speed smashing machine (Taisite, FW177, China) was utilized to smash large e-waste pieces into small ones (830–1700 μm). The testing apparatus was a stainless steel chamber of 50 cm length × 50 cm width × 150 cm height, and the inner walls were polished to minimize surface sorption, based on the 1-m^3 standard VOC-emission test chambers (inner chamber: electropolished, stainless steel) applied in emission tests of selected flame retardants [29]. The inlet air of the chamber was purified by an unit consisted of desiccant, glass microfiber filter, and polyurethane foam plugs (PUF; 6.5 cm diameter × 8.0 cm; density: 0.03 g cm^{-3}). Thermal treatment and open burning experiments were performed with an electronic hot plate (Ansai, China) at 300 °C for 150 min and a butane blowtorch at approximately 800–1350 °C for 3 min, respectively. Particle samples in 11 size fractions, i.e., > 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, were collected at the chamber outlet with a Micro-Orifice Uniform Deposit Impactor (MOUDI) (MSP Corporation; Shoreview, MN, USA), connected to a PUF collecting gaseous samples. The pump provided an air flow at 30 L min^{-1}, equivalent to an air change rate of 4.8 times per hour. Particle and gaseous samples were sampled in cohesion with the progression of the experiments and continued for another 180 min after the experiments were completed. Residual ash samples were also collected at the end of the simulation experiments. A total of 180 samples were obtained and stored at −20 °C until further treatment. More detailed experimental procedures were described in our previous study [30].

2.3. Sample extraction and purification

Raw e-waste materials were extracted ultrasonically three times, each with 20 mL of toluene for 30 min. Airborne particle and residual ash samples were ultrasonically extracted for three times with a mixture of *n*-hexane, dichloromethane, and acetone (2:2:1 in volume). Gaseous OPFRs were Soxhlet extracted from PUF plugs with the above-mentioned solvent mixture for 48 h. A pressure blowing concentrator (TurboVap II, Biotage, Sweden) was employed to concentrate all extracts to approximately 1 mL in *n*-hexane. Each extract was purified on a silica gel column (i.d. = 1.0 cm) packed with neutral silica gel (12 cm) and anhydrous sodium sulfate (1 cm) from bottom to top. The three fractions were eluted with 45 mL of *n*-hexane, 50 mL of dichloromethane, and 45 mL of acetone and dichloromethane mixture (1:1, v:v) consecutively. The first fraction was abandoned, and the second and third fractions containing OPFRs were collected and concentrated to 100 μL in hexane separately, and spiked with the internal standards before instrumental analysis.

2.4. Instrumental analysis

Concentrations of target OPFRs were determined with an Agilent 7890B gas chromatograph interfaced with an Agilent 5977 mass spectrometer in the electron impact ionization mode, with chromatographic separation provided by an HP-5MS capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness). The column temperature was initiated from 60 °C (held for 1 min), increased to 200 °C at 30 °C min^{-1}, ramped to 278 °C at 15 °C min^{-1}, and finally raised to 300 °C at 25 °C min^{-1} (held for 14 min). Ultrahigh purity helium served as the carrier gas at a flow rate of 1.0 mL min^{-1}. The temperatures for the ion source and quadrupole were 230 °C and 150 °C, respectively. Quantitative analysis was performed in both the full-scan and selected ion monitoring modes.

2.5. *Quality assurance and quality control*

The average recoveries of the surrogate standards (TPHP-d_{15} and TNBP-d_{27}) spiked to each sample before the extraction were 112% ± 10% and 94% ± 13% for raw materials, 100% ± 26% and 99% ± 15% for particle samples, 101% ± 7% and 108% ± 13% for gas samples, and 106% ± 11% and 105% ± 12% for ash residues. The average recoveries of the target OPFRs in the spiked samples ranged from 86% to 125%. Two procedural blanks were processed for each batch of 11 samples to determine if any cross contamination occurred from sampling and extraction. Analyses of field blank samples collected in both thermal treatment and open burning experiments without the use of e-waste detected negligible OPFRs in all blank samples, contributing to less than 1% of those in the field samples. TNBP was most frequently detected in the blank samples. TCEP and TCIPP were occasionally detected in blank samples at a low level of concentration. The detection limit in this study is 5 ng g^{-1}. The results were blank corrected but not corrected for surrogate standard recovery.

3. Results and discussion

3.1. *Emission factors*

The EF values are calculated as the mass of OPFRs emitted from one unit mass of treated e-waste. Among the 11 targeted OPFRs, the concentrations of TEHP, TmCP, and TpCP were below the reporting limits in all samples (i.e., size-fractioned particle, gaseous, and residual samples). The sum of TIBP, TNBP, TCEP, TCIPP, TDCIPP, TPHP, EHDPP, and ToCP was designated as Σ_8OPFR. The EFs of Σ_8OPFR ranged from 3.70×10^4 to 3.65×10^5 ng g^{-1} for thermal treatment, and from 5.22×10^3 to 9.27×10^4 ng g^{-1} for open burning (Table 1). These values were higher than the EFs of PBDEs in our previous study [30], and comparable to results obtained from an e-waste recycling zone [11]. Moreover, the average EFs of Σ_8OPFR discharged from plastic casings were approximately one order of magnitude lower than those from printed circuit boards processed by both thermal process and open burning, which was not the case with PBDEs [30]. The EFs of OPFRs were an order of magnitude lower for open burning than for the thermal process, but still suggested high levels of OPFR emissions from open burning. Primitive recycling activities are apparently significant sources of OPFRs in surrounding environments. The laboratory conditions of high temperatures (approximately 800–1350 °C), good air flow, and sufficient oxygen employed in the present study may have led to greater destruction of OPFRs compared to field recycling activities, resulting in underestimated emission factors.

Table 1
Emission factors (EFs) of eight OPFRs (ng g^{-1}) for plastic casings (A1–A3) and printed circuit boards (B1–B3).

	A1	A2	A3	B1	B2	B3
Thermal Process						
TIBP	< RL[a]	< RL	< RL	< RL	< RL	653
TNBP	68	6.1	115	242	177	143
TCEP	2.4×10^4	2.2×10^4	4.9×10^4	9.8×10^3	2.0×10^4	1.3×10^4
TCIPP	326	225	< RL	2.3×10^5	2.7×10^4	1.4×10^5
TDCIPP	< RL	< RL	< RL	3.6×10^3	RL	2.1×10^5
TPHP	4.1×10^4	1.4×10^4	6.3×10^3	1.6×10^3	1.5×10^5	3.4×10^3
EHDPP	1.2×10^3	403	1.3×10^3	< RL	< RL	< RL
ToCP	830	177	69	< RL	< RL	< RL
Σ_8OPFR	6.8×10^4	3.7×10^4	5.7×10^4	2.4×10^5	2.0×10^5	3.7×10^5
Open Burning						
TIBP	< RL	530	< RL	< RL	< RL	90
TNBP	96	2.4	306	154	90	113
TCEP	2.6×10^3	2.0×10^3	2.1×10^3	1.6×10^3	1.0×10^3	1.5×10^3
TCIPP	3.6×10^3	1.9×10^3	4.4×10^3	2.3×10^3	570	3.7×10^3
TDIPP	675	< RL	< RL	580	< RL	1.4×10^3
TPHP	9.5×10^3	1.7×10^3	550	620	9.1×10^4	2.3×10^3
EHDPP	< RL	< RL	< RL	< RL	< RL	< RL
ToCP	< RL	< RL	< RL	< RL	< RL	< RL
Σ_8OPFR	1.6×10^4	6.2×10^3	7.4×10^3	5.2×10^3	9.3×10^4	9.1×10^3

[a] Reporting limits. The emission factors calculated by the reporting limits were 0.12 ng g^{-1} (thermal treatment) and 0.71 ng g^{-1} (open burning).

Generally, TCEP and TCIPP were the most abundant chlorinated OPFRs, and TPHP was the most abundant nonchlorinated OPFRs (Fig. S1 of the Supplementary Data; "S" indicates tables and figures in the Supplementary Data afterwards). The average mass ratios of TCEP, TCIPP, and TDCIPP derived from thermal treatment of plastic casings were 60%, 0.4%, and 0, respectively, and 6%, 49%, and 19% for printed circuit boards. These values were 26%, 38%, and 1% for plastic casings, and 16%, 28%, and 9% for printed circuit boards processed by open burning, respectively. Similar concentration profiles for the three compounds (TCIPP > TECP > TDCIPP) were also observed in atmospheric fine particles of selected Chinese cities [31]. Nonchlorinated TPHP contributed 37% and 26% of the Σ_8OPFR emissions from the thermal processing of plastic casings and printed circuit boards, respectively, and 31% and 45% in open burning. In the atmosphere of an e-waste recycling zone in South China, TBOEP was the dominant OPFR, followed by TNBP [11], while TCIPP and TPHP were the major OPFRs in indoor dust from several e-waste recycling sites in South China [13]. The dominance of TPHP was also found in soils and sediments around e-waste recycling workshops in northern Vietnam [21]. These differences may have been reflective of different types and amounts of OPFRs used in these regions.

Particulate matter appeared to be an important carrier of emitted OPFRs. The size fractioned EFs of particulate Σ_8OPFR were categorized by their aerodynamic diameter (D_p) as coarse ($D_p > 1.8\,\mu m$) and fine ($D_p < 1.8\,\mu m$) (Fig. 1). The average EFs of Σ_8OPFR on coarse and fine particles derived from thermal treatment of plastic casings were 5.03×10^3 and 4.75×10^4 ng g^{-1} respectively, while those from open burning were 1.96×10^3 and 4.58×10^3 ng g^{-1}. For printed circuit boards, the EFs were 3.27×10^4 and 2.30×10^5 ng g^{-1} from the thermal process, and 2.84×10^3 and 2.60×10^4 ng g^{-1} from open burning. The EF values for coarse particles were up to one order of magnitude lower than those for fine particles. The mass ratios of size-fractioned OPFRs (Table S1) indicate that the amounts of OPFRs released from coarse particles were significantly greater for open burning than for the thermal process (*t*-test; $p < 0.01$). Greater emissions of OPFRs in fine particles may penetrate deeper in the lung region and induce higher risks [9,11].

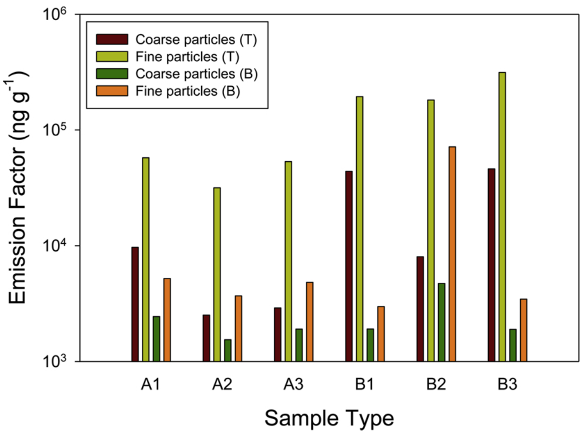

Fig. 1. Emission factors of Σ_8OPFR by the thermal process (T) and by open burning (B) of plastic casings (A1–A3) and printed circuit boards (B1–B3).

Table 2

Output over input mass ratio by thermal treatment (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
TIBP	–[a]	–	–	–	–	–	–	–	–	–	–	–
TNBP	0.47	0.67	0.03	0.01	0.78	2.1	0.5	0.32	0.36	0.19	0.31	0.25
TCEP	52.2	5.58	77.4	7.11	116	5.02	9.68	1.58	–	–	–	–
TCIPP	0.22	2.4	0.27	2.31	$<$ RL[b]	6.3	0.14	1.4×10^{-3}	40.4	0.84	0.17	4.6×10^{-3}
TDCIPP	–	–	–	–	–	–	0.11	0.02	–	–	0.22	1.5×10^{-3}
TPHP	0.2	0.05	0.19	0.02	0.18	0.02	0.4	0.15	0.21	0.13	9.8	6.71
EHDPP	0.49	$<$ RL	0.28	$<$ RL	0.72	$<$ RL	–	–	–	–	–	–
ToCP	0.75	$<$ RL	0.26	$<$ RL	0.28	$<$ RL	–	–	–	–	–	–

[a] Invalid. The concentrations are below the reporting limits in raw materials and the output over input mass ratio therefore could not be calculated.

[b] The concentration of OPFRs in after-treatment products were below reporting limits.

3.2. *Mass balance*

The output over input (O/I) mass ratios of OPFRs were calculated as EFs from thermal treatment or open burning divided by OPFR concentrations in raw e-waste materials (Table 2). For plastic casings, the O/I mass ratios of OPFRs from thermal treatment ranged from 0.030 to 116, higher than those from open burning (0.012–7.1). Similarly, these values for printed circuit boards were higher from thermal treatment (0.11–40) than from open burning (0.0014–6.7). The open burning process, with high operational temperatures (˜ 800–1350 °C), reduced a large portion of the emitted OPFRs, thus leading to high OPFR destruction efficiencies. It is noteworthy that TCIPP derived from plastic casings was the only exception, with O/I mass ratio enhanced by open burning. Larger OPFR emission was observed for a lower-density sample treated at 60 °C [29]. However, the O/I mass ratios between plastic casings and printed circuit boards were not significantly different (*t*-test; $p > 0.05$) in the present study. Moreover, the O/I mass ratios varied widely among different OPFR analogs (Table 2). For instance, TCEP had O/I mass ratios ranging from 1.6 to 116, while TDCIPP had much lower values (0.0015–0.22). An O/I mass ratio well exceeding 1 was obtained several times, indicating the formation of some OPFR analogs during the treatment process. These OPFRs may have derived from the degradation or transformation of other OPFR analogs with similar molecular structures, e.g., TCEP, TCIPP and TDCIPP have similar molecular structures. More data should be collected in future studies to ratify this hypothesis.

3.3. *Emission types*

Different emission types may result in diverse distribution patterns of OPFRs in the environment around e-waste recycling cites. Coarse particles, along with dust and ashes, can enter the soil or water systems and further leach into groundwater or react with biota, while fine particles and fumes can be transported over long distances [32]. High concentrations of OPFRs (include range of concentrations) have been reported in airborne particles in e-waste processing facilities [23,33], as well as soils and sediments around e-waste recycling areas [21], raising severe exposure concerns for nearby residents.

Particulate matter was the dominant carrier of OPFRs emitted, accounting for 99% and 81% of the total emissions by thermal treatment and open burning, respectively (Fig. 2). Residues made up 0.6% and 17%, respectively, with gas phase OPFRs comprising 0.4% and 2%, respectively (Fig. 2). Similarly, OPFRs were mainly associated with particles rather than the gas phase at an electronics recycling plant and its work environments [33], as well as in the atmosphere of an urban city of east China [8]. However, there might be minuscule differences in the output mass fractions for some OPFR analogs (Fig. S2). Intake of OPFRs via inhalation exposure route was reported to be an important route, especially via suspended particulate matter, which should be taken into consideration in health risk assessments [9,34]. It is worth noting that open burning produced more abundant residual OPFRs than the thermal process in the present study. Similarly, pilot-scale incineration experiments (destruction efficiencies greater than 99.999%) conducted by Matsukami et al. [35] suggested that all OPFRs partitioned into ash rather than into final exhausted gases. Apparently, greater destruction of OPFRs due to higher reaction temperatures in open burning led to lower emissions of gaseous and particulate OPFRs to the atmosphere, as observed in the present study.

3.4. *Size distribution patterns of particle bound OPFRs*

The size distribution of Σ_8OPFR in the present study was characterized by a unimodal peak from 0.56 to 1.0 μm for thermal treatment, or bimodal peaks with a dominant one ranging from 0.56 to 1.0 μm or from 1.0 to 1.8 μm and a secondary peak from approximately 10 to 18 μm for open burning (Fig. 3). Similarly, unimodal and bimodal peaks were observed for OPFRs in suspended particulate matter collected from offices [9]. However, Luo et al. observed no modal peaks of particulate OPFRs in an e-waste recycling zone and in urban Guangzhou, possibly due to multiple emission sources in the outdoor atmosphere [11]. The present study found different size distribution patterns of chlorinated and nonchlorinated OPFRs (Figs. S3 and S4). Particulate TCEP and TCIPP exhibited bimodal and unimodal patterns for open burning and for thermal treatment, respectively, while TPHP was unimodal-distributed for these two recycling processes. Different size distribution patterns of particle-bound OPFRs may have resulted from the difference in the physiochemical properties of OPFRs, i.e., OPFR analogs with low vapor pressures tend to sorb on small-sized particles [9].

Particulate OPFRs were primarily associated with fine particles (Table S1), which was similar to the case for PBDEs [30]. However, the abundances of OPFRs on coarse particles were higher than those of PBDEs. These abundances were higher for open burning than for thermal treatment, likely because open burning generated more abundant coarse particles [36]. The geometric mean diameter (GMD) and geometric standard deviation (GSD) of particulate-associated OPFRs were calculated to describe their distribution patterns (Tables S2 and S3). The GMD values for thermal treatment (range: 0.45–1.05 μm; median: 0.77 μm) and open burning (range: 0.55–2.05 μm; median: 1.05 μm) were smaller than those at an e-waste recycling zone (0.87–1.77 μm) and in urban Guangzhou (0.50–1.82 μm) [11]. The mass median aerodynamic diameter values of suspended particulate TCEP, TCIPP, TNBP, and TPHP in offices were greater than 2.5 μm, while they were ≤ 2.5 μm for TnPP, TBEP, and EHDPP, and ≤ 1 μm for TDCIPP, TCrP, and TEHP [9].

The means by which particle-bound OPFRs were generated are mechanical abrasion, vaporization, and resuspension of soil and dust [11,37]. Cao et al. [37] deduced that OPFR-containing coarse dust particles were mostly generated from abrasion fragments, as they were similar in geometrical shapes and had low organic content. The mass

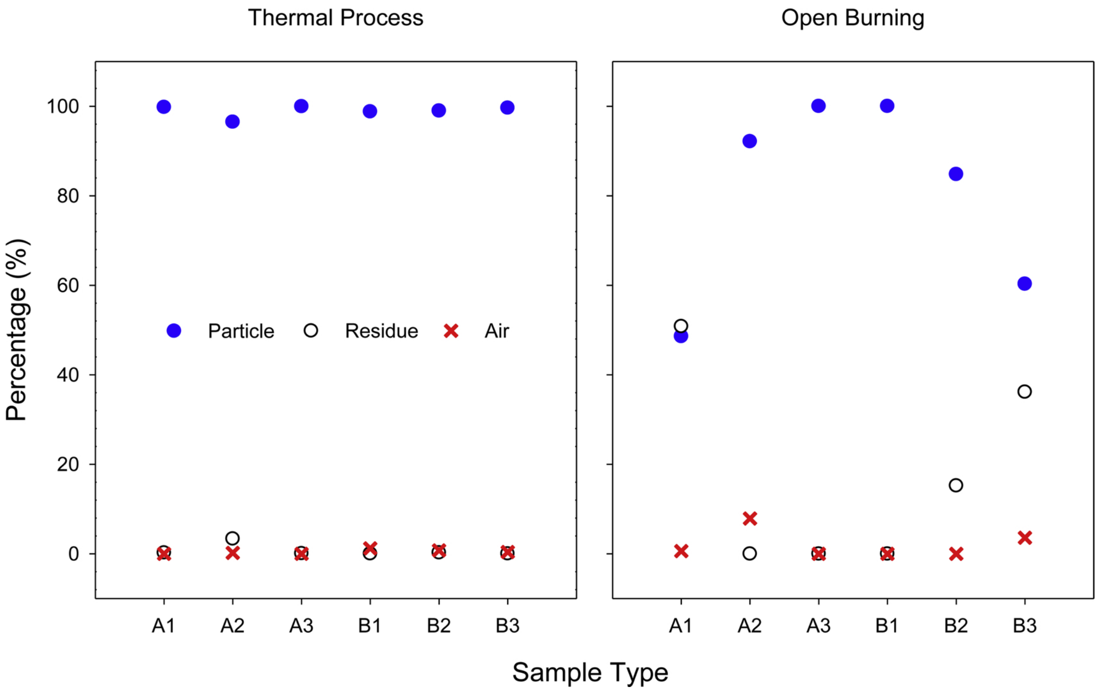

Fig. 2. The distribution of OPFR output mass fractions by the thermal process (T) and by open burning (B) of plastic casings (A1–A3) and printed circuit boards (B1–B3).

median aerodynamic diameter values of particle-bound OPFRs were positively and significantly correlated with their logarithmic subcooled liquid vapor pressures (log P_L/Pa), suggesting that OPFRs with low vapor pressure tend to sorb to small-sized particles [9]. In contrast, GMDs or mass ratios of OPFRs in coarse particles were not significantly correlated with log P_L at 298 K in the present study (Fig. 4). This may suggest that the size distribution of particle-bound OPFRs was not affected by either vapor pressure or gas-particle partitioning. Sources of particle-bound OPFRs other than gas-particle partitioning might exist [11]. During the rapid and violent reaction processes of the present

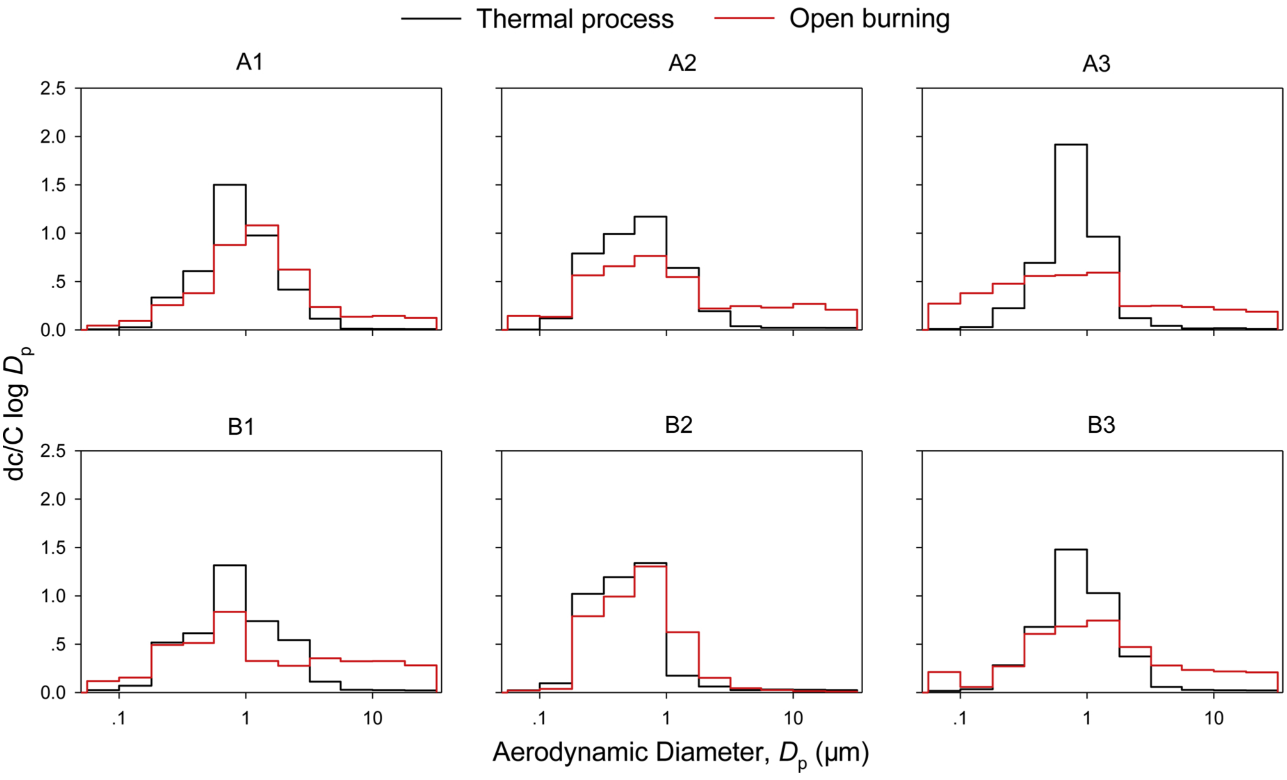

Fig. 3. Size distributions of particle-bound Σ_8OPFR by the thermal process (T) and open burning (B) of plastic casings (A1–A3) and printed circuit boards (B1–B3). dc is the concentration of Σ_8OPFR in each filter, C is the sum concentration in all filters, and d log D_p is the logarithmic size interval for each impactor stage in aerodynamic diameter (D_p).

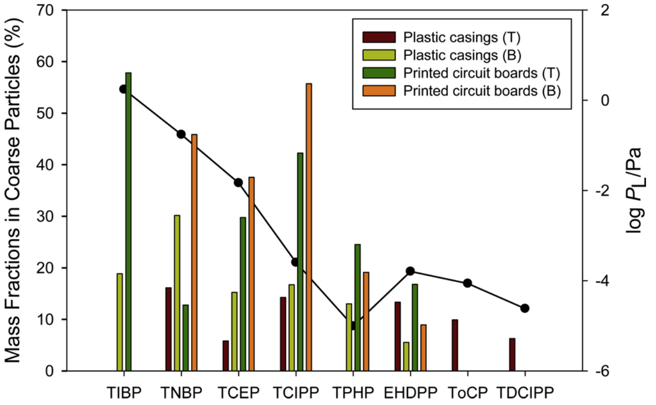

Fig. 4. Correlations between the mass fractions of OPFR in coarse particles and their logarithmic subcooled liquid vapor pressures (log P_L/Pa) at 298 K derived from thermal treatment and open burning of plastic casings and printed circuit boards.

Table 3
Emissions (kg year^{-1}) of OPFRs from thermal process and open burning of e-waste in China in 2018.

	Thermal Treatment				Open Burning			
	Air		Land		Air		Land	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
TIBP	6.1	8.5	–[a]	–	26	40	–	–
TNBP	14.1	6.3	–	–	22	17	0	–
TCEP	4.8×10^3	1.7×10^3	–	–	352	36	0	–
TCIPP	3.7×10^3	2.3×10^3	0.55	0.49	507	146	17	24
TDCIPP	2.0×10^3	2.7×10^3	–	–	50	48	–	–
TPHP	4.3×10^3	2.9×10^3	72	77	876	899	534	575
EHDPP	137	57	–	–	–	–	–	–
ToCP	50	48	–	–	–	–	–	–
Σ_8OPFR	1.5×10^4	4.8×10^3	72	77	1.8×10^3	913	551	575

[a] Invalid. Because measured concentrations were below the reporting limits, the emission values could not be calculated.

study, OPFRs were suspected to discharge directly in association with particles, similar to mechanical abrasion, rather than sorb or deposit to the organic matter phase of particles from the gaseous phase.

3.5. Total OPFR emissions from thermal treatment and open burning

The contributions of e-wastes processed by thermal treatment and open burning to the total OPFR emissions were estimated from the EFs acquired in the present study and the national e-waste recycling activity data of China (Supplementary data Text S1). Among the various e-waste categories in China, televisions and computers were dominant [38] and contained abundant FRs, especially in their plastic parts and printed circuit boards [39]. The emissions of Σ_8OPFR to the air and land from thermal treatment were 1.5×10^4 and 72 kg year^{-1}, respectively. These values were 1.8×10^3 and 551 kg yr^{-1} for open burning (Table 3), which may have been underestimated owing to the underrated EF values of open burning in the present study. The OPFR emissions to air were much greater than those to land for both thermal process and open burning. Presently, no other data are available for comparison with our OPFR data.

A similar estimate was made for PBDEs based on our previously reported data (Table S4). The emissions of PBDE to air and land were 1.4×10^4 and 2.3×10^3 kg year^{-1} for thermal treatment, and 118 and 4.3×10^3 kg year^{-1} for open burning. It is clear that the thermal process contributed greater amounts of PBDEs to the air than to the land, but the opposite was the case for open burning. The large emissions of PBDEs from residual ash implied it as an important source of land pollution. Coincidently, Ni et al. [40] obtained a PBDE emission of 105 kg year^{-1} to the air from open burning of plastic waste, and suggested that residual ash released 7124 kg of PBDEs to the land of China in 2015. Redfern et al. [41] also estimated that combustion and illegal open burning of e-waste contributed 6.75 and 0.255–5.56 tons yr^{-1}, respectively, to the global emissions of PBDEs in 2016, while evaporative and fugitive sources contributed 2.43–14.9 tons yr^{-1} [41].

Although the estimated emissions of OPFRs were less than those of PBDEs in the present study (Tables 3 and S4), they are expected to rise steadily due to continuous production growth since the ban on some PBDEs [1]. In the United States and Europe, the levels of OPFR consumption are close to or slightly higher than those of BFRs due to early commercialization of OPFRs. Conversely, the levels of OPFR consumption have remained substantially lower than those of BFRs in Asia. For instance, BFRs made up 51.7% and 49.6% of all flame retardants in 2005 and 2008, respectively, while OPFRs only accounted for 5.2% and 4.4% [42]. As the replacement of BFRs by OPFRs is imminent, the production and consumption of OPFRs are anticipated to increase continuously in China for years to come [43]. It should be noted that the present study estimated emissions from thermal treatment and open burning of televisions and computers only, based on limited data. Broader and more quantitative analyses of all primitive e-waste recycling processes are desirable to acquire a better estimation of OPFR emissions.

4. Conclusions

Large amounts of OPFRs were released during thermal treatment and open burning of e-waste. The EFs of OPFRs derived from thermal treatment of e-waste were much higher than those from open burning, and were lower for coarse particles than for fine particles. Particulate matter was an important carrier of OPFRs, which are suspected to be emitted in association with particles rather than to be sorbed or deposited to the particle organic phase from the gaseous phase. This was perhaps because the reaction processes were fast and violent, similar to those for mechanical abrasion. Overall, the emissions of OPFRs are expected to rise steadily with ever-growing production and application of OPFRs since the ban on the use of some PBDEs, although they are currently lower than those of PBDEs, based on our estimation.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2018.12.041.

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