



Size-dependent atmospheric deposition and inhalation exposure of particle-bound organophosphate flame retardants



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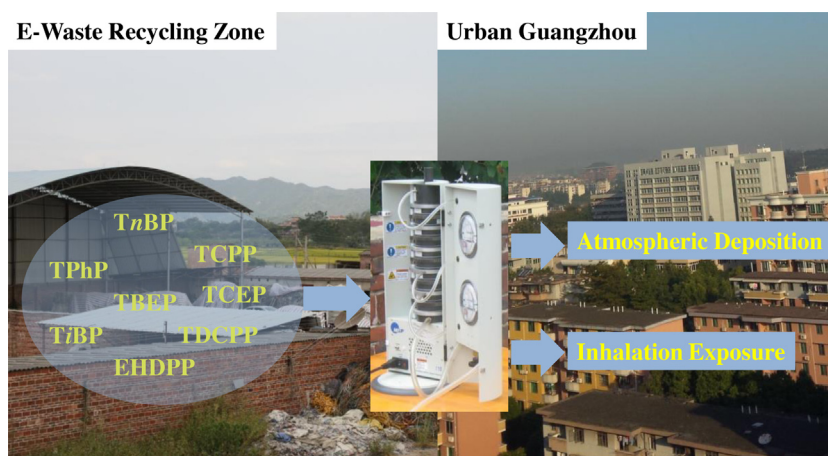
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HIGHLIGHTS

- Particle size distributions of OPFRs were studied in outdoor settings.
- The most abundant OPFR at both study sites was TBEP.
- The abundances of OPFRs in coarse and fine particles were roughly equal.
- Dry and wet deposition fluxes of particle-bound OPFRs were size-dependent.
- Inhalation exposure risk to particle-bound OPFRs at both sites was low.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric size-fractionated particles were collected at different heights in an e-waste recycling zone (QY) and urban Guangzhou (GZ), China and analyzed for organophosphate flame retardants (OPFRs). The total air concentrations of eight OPFRs were 130 ± 130 and $138 \pm 127 \text{ ng m}^{-3}$ in QY and GZ, respectively. Compositional profiles of chlorinated OPFRs were different between QY and GZ, but the size distribution patterns of all OPFRs were not significantly different at different heights. Estimated atmospheric deposition fluxes of OPFRs were 51 ± 67 and $55 \pm 13 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ in QY and GZ, respectively, and the coarse particles ($D_p > 1.8 \text{ } \mu\text{m}$) dominated both the dry and wet deposition fluxes. Moreover, not all particle-bound OPFRs were inhalable and deposited in the human respiratory tract. The calculated inhalation doses of OPFRs were much lower than the reference doses, suggesting that potential health risk due to inhalation exposure to particle-bound OPFRs in the e-waste recycling zone and urban site was low.

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1. Introduction

Atmospheric particle sizes may range over four orders of magnitude from nanometers to microns in diameter, and influence

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the atmospheric processes of particles [1]. As such, size distribution of particle-bound pollutants is a critical factor governing their fate in the atmosphere and associated human health risk. For example, coarse and fine particles contributed the most to the dry and wet deposition fluxes of particle-bound polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs), respectively [2–4]. Smaller particles can penetrate into the deeper regions of lung and hence pose higher risk to human health than larger particles [4–6].

Since the restriction and gradual phase-out of PBDEs due to their persistent, bioaccumulative, and toxic properties, the production and use of organophosphate flame retardants (OPFRs) have substantially increased in recent years [7,8]. The annual global consumption volume of OPFRs increased from ~102,000 tons in 1992 to ~300,000 tons in 2004 [9]. Abundant OPFRs can be released to the environment because they are only additives to consumer products. As a result, OPFRs have been widely detected in air [10–12], water [13,14], sediment [15], indoor dust [16,17], and biota samples [18–20]. Most OPFRs pose adverse biological effects, such as hemolytic and reproductive effects [7]. OPFRs were thought to be persistent in the atmosphere due to their relatively slow OH radical oxidation rates [21], as such they have been detected in remote regions [22]. Hence, understanding the transport processes of atmospheric particle-bound OPFRs, which depend on their particle sizes, is critical for gauging the atmospheric residence time and the potential health effects of OPFRs. Currently published studies have mainly reported on the chemical composition of OPFRs in total suspended particles, and only one peer-reviewed study focused on the particle size distribution of OPFRs in office environment [10]. However, atmospheric transport processes are different in outdoor environments from indoor settings because of different meteorological conditions, such as different strengths of air turbulence in indoor and outdoor environments. Therefore, further research on particle size distribution of OPFRs in the outdoor ambient air is necessary for better understanding the fate and human inhalation exposure risk of OPFRs.

The widespread use of OPFRs-added electronic devices and commercial products, as well as e-waste recycling activities, increases the chance of fugitive emissions of OPFRs into the atmosphere. It has been reported that concentrations of particulate OPFRs were high in air in e-waste processing facilities [23,24]. Less is known about ambient air OPFR concentrations in populated regions, especially in China. In 2007, China produced more than 70,000 tons of OPFRs, accounting for 35% of the global production, and the amount was expected to increase by approximately 15% annually [9]. Therefore, it is important to assess the human health risks for residents dwelling in e-waste recycling zones and the general population living in urban areas from inhalation exposure to particle-bound OPFRs during usage and waste treatment processes of OPFRs-containing products.

To address the above-mentioned need, a study was conducted at an e-waste recycling zone (Qingyuan) and an urban site (Guangzhou) in southern China (Fig. S1 of the Supplementary material; “S” represents figures and tables in the Supplementary material afterwards), which represent the potentially most serious and the general human exposure scenarios, respectively, except for the occupational population exposure. The study objectives were (1) to examine the particle-size distributions of OPFRs in the atmosphere and related atmospheric deposition fluxes and (2) to evaluate the potential health risk of OPFRs from inhalation exposure for residents living within an e-waste recycling zone and a major urban center.

2. Materials and methods

2.1. Chemicals

A standard of tri-*iso*-butyl phosphate (TIBP) was purchased from Chiron AS (Trondheim, Norway). Tri-*n*-butyl phosphate (TNBP), triphenyl phosphate (TPHP), and tris(1,3-dichloropropyl) phosphate (TDCPP) were obtained from AccuStandard (New Haven, CT, USA). Tris (2-chloroethyl) phosphate (TCEP), tri (chloropropyl) phosphate (TCIPP), tributoxylethyl phosphate (TBOEP), 2-ethylhexyl diphenyl phosphate (EHDPP), tri(2-ethylhexyl) phosphate (TEHP), and tricresyl phosphate (TMPP) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isotope-labeled surrogate standards, TNBP-*d*₂₇ and TPHP-*d*₁₅, and internal standards, fluoranthene-*d*₁₀, pyrene-*d*₁₀, and dibenzo[*a,h*]anthracene-*d*₁₄, were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). More information on the physicochemical properties of these OPFRs is provided in Table S1.

2.2. Sample collection and analysis

Particle samples were collected in two sampling regions, i.e., an e-waste recycling zone in Qingyuan and a typical urban site in Guangzhou, both in southern China (Fig. S1). The procedures for field sampling and sample analysis were similar to those described previously [3–5], and only a brief description is presented herein. Sampling time for each sample was approximately 12 h (sampling volume was 21.6 m³) in Qingyuan in October–November and 24 h (sampling volume was 43.2 m³) in Guangzhou in September 2012. Particle samples collected with a Micro-Orifice Uniform Deposit Impactor (MSP Corporation, Shoreview, MN, USA) were separated into 11 fractions: >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 on 47-mm diameter glass microfiber filters (Whatman International, Maidstone, England) at a constant flow rate of 30 L min⁻¹ with a conventional vacuum pump. Sampling was made at different heights, at 1.5, 5, and 20 m in the e-waste recycling zone and at 1.5 and 20 m in Guangzhou. Overall, 24 and 11 sets of size-fractionated samples (a total of 385 field particle samples) were collected in the e-waste recycling zone and Guangzhou, respectively.

The filter samples were spiked with 50 ng of surrogate standards, and then extracted three times with 30 mL of *n*-hexane, dichloromethane and acetone mixture using ultrasonic extraction. Water was removed from the extracts with ~1 g of anhydrous sodium sulfate. A known amount of internal standards (50 ng) was added to each sample extract before instrumental analysis. The OPFRs were analyzed using a gas chromatography coupled to mass spectrometry (Shimadzu QP2010 Plus; Shimadzu, Kyoto, Japan) with a 30 m TG-5MS column (0.25 mm id, 0.25 μm film thickness; Thermo Scientific, West Palm Beach, FL, USA) in the electron ionization mode. Carrier gas was ultrahigh purity helium at a flow rate of 1.0 mL min⁻¹. The oven temperature was programmed from 60 °C for 1 min, increased to 200 °C at a rate of 6 °C min⁻¹ (held for 2 min), and ramped to 300 °C at 8 °C min⁻¹ (held for 20 min). The injector, ion source and interface temperatures were set at 290, 200 and 290 °C, respectively. Signals were scanned from 50 to 500 mass units in the full-scan mode. Quantitative and qualitative ions of the target compounds for mass spectrometry analysis are present in Table S1. A library (National Institute of Standards and Technology) search on the full-scan chromatograms was used to confirm the presence of target compounds.

2.3. Quality assurance and quality control

One procedural blank and one matrix blank samples were analyzed for every batch of 11 field samples. Only TIBP, TNBP and

TCIPP were detected in the blank samples, and their amounts in the blank samples were less than 10% of those in the field samples. Concentrations of OPFRs in all field samples were corrected by the corresponding procedural blanks in the same batch, but not corrected for the surrogate standards recoveries. The recoveries of surrogates TNBP-*d*₂₇ and TPHP-*d*₁₅ were $116 \pm 17\%$ and $108 \pm 16\%$ in field samples ($n = 385$), and $111 \pm 17\%$ and $105 \pm 14\%$ in blank samples ($n = 70$), respectively. The lowest calibration concentrations divided by the actual sample volume were used as the reporting limits for target compounds. In the present study with an average air sampling volume of 21.6 m^3 and a final concentrated volume of $50 \mu\text{L}$, the reporting limits were $0.012\text{--}0.023 \text{ ng m}^{-3}$ for individual OPFRs (Table S1). For samples with target compound concentrations below its reporting limits, zero was used for the calculations for atmospheric deposition fluxes and inhalation exposure risk assessment.

2.4. Estimation of atmospheric deposition fluxes

Dry and wet deposition fluxes (F_{dry} and F_{wet}) of particle-bound OPFRs were estimated following the same approach as our previous studies [3,25], i.e.,

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

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

where C_i is the size-fractionated concentration of OPFRs; V_i and η_i are dry deposition velocity and wet removal efficiency of a special size fraction, respectively; W_T is the wet washout ratio; and Q is the monthly precipitation amount. The values of these parameters are summarized in Table S2.

The sum of dry and wet deposition flux is defined as total deposition flux herein. The overall dry deposition velocity (V_d) and wet removal efficiency (η) of particle-bound OPFRs were estimated by:

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

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

2.5. Estimation of human inhalation exposure

The particle size distributions of OPFRs were used to calculate the fractions of OPFRs that can be inhaled through the nose and/or mouth during breathing (i.e., the inhalable fraction), that can penetrate progressively into the lung below the larynx (i.e., the thoracic fraction), and that can reach deeper into the gas exchange region in the lung (i.e., the respirable fraction) [26]. The fractions of deposition of the particle-bound OPFRs in the human respiratory tract were estimated by the simplified equations from the International Commission on Radiological Protection (ICRP) model [26]. More details about calculation methods are provided in the Supplementary material.

The non-cancer risk from inhalation exposure can be evaluated by hazard quotient (HQ) [27]:

$$\text{HQ} = \frac{C_{\text{OPFR}} \times V}{\text{BW} \times \text{RfD}} \quad (5)$$

where C_{OPFR} is the concentration of a specific OPFR; V is the inhalation rate with $15 \text{ m}^3 \text{ d}^{-1}$ for an average adult; BW is the body weight which was assumed to be 60 kg for adults; and RfD is inhalation reference dose for the OPFR which is shown in detail in Table S1. Because the RfD data of OPFRs from inhalation exposure was scarce, we selected oral RfD values to estimate health risk in the present study. The bulk concentration, derived from the sum of all OPFR in

all size fractions, and the modeled fractions of the bulk concentration deposited in the three regions of the human respiratory tract, were selected as C_{OPFR} in the present study for inhalation exposure assessment. Detailed calculation procedures are provided in the Supplementary material. Values of HQ greater than 1 suggest potential health risk [27].

2.6. Statistical analysis

All statistical analyses were performed with PASW Statistics 18 (Chicago, IL, USA). The Kolmogorov–Smirnov test was used to check for normal distribution of the OPFR concentrations, and all OPFRs concentrations (except for TBOEP at the 20-m height in the e-waste recycling zone) followed the normal distributions. The independent-samples *t*-test was used to observe the significant difference in the concentrations of OPFRs between different heights or different sampling sites. Pearson correlation analysis was applied to explore the correlations between the concentrations of two OPFR compounds.

3. Results and discussion

3.1. Concentrations and profiles of particle-bound OPFRs

Of the 12 OPFR compounds, TMPP (including the three isomers: ortho, meta, and para-TMPP) and TEHP were below the reporting limits in all size-fractionated samples at both sampling sites. The concentration of the sum of TIBP, TNBP, TCEP, TCIPP, TDCPP, TPHP, TBOEP, and EHDPP (designated as $\sum_8 \text{OPFR}$) was 130 ± 130 and $138 \pm 127 \text{ ng m}^{-3}$ in the e-waste recycling zone and Guangzhou, respectively (Fig. 1 and Table S3). There are two noteworthy findings from the measurements. First, the concentrations of particle-bound OPFRs were higher than those of PBDEs in the e-waste recycling zone [3]. Second, the difference of $\sum_8 \text{OPFR}$ concentrations between the e-waste recycling zone and urban Guangzhou was largely negligible compared to particle-bound PBDEs, unexpected and inconsistent with the prevailing perception that primitive processing of e-waste may have been a remarkable source of OPFRs in the environment as with PBDEs [23,24]. Both findings point to the plausible explanation that OPFRs have been applied not only as flame retardants, but also widely used in many other commercial and consumer products such as plasticizers in plastics, foams, textiles, floor polishes, waxes, and furniture, resulting in much higher usage compared to PBDEs due to the increasing restrictions on PBDEs usage in recent years and a more widespread distribution of OPFRs sources than that of PBDEs [7]. In addition, the concentrations of individual OPFRs were not significantly different (*t*-test; $p > 0.05$) among different heights at both sampling sites except for TDCPP (*t*-test; $p = 0.029$) and TBOEP (*t*-test; $p = 0.013$) between 1.5 and 5 m in the e-waste recycling zone, suggesting a well-mixed surface layer in these zones.

The TBOEP was the most abundant OPFR, following by TNBP. Nonchlorinated TBOEP contributed 80% and 85% of the $\sum_8 \text{OPFR}$ concentrations in the e-waste recycling zone and urban Guangzhou, respectively. Again, the similarities of the OPFR chemical composition at both locations suggested the presence of sources not related to e-waste recycling activities; e.g., large amounts of TBOEP are known to be used in floor polish and waxes [17]. High levels of TBOEP were also reported in indoor dust [17,28], further indicating the presence of these sources.

The mean concentration of the sum of three chlorinated OPFRs (TCEP, TCIPP, and TDCPP) was 5.4 and 5.2 ng m^{-3} in the e-waste recycling zone and Guangzhou, respectively, accounting for only 3.9% and 4.9% of the $\sum_8 \text{OPFR}$ concentrations. These concentrations were much lower than those in indoor environments, such as offices

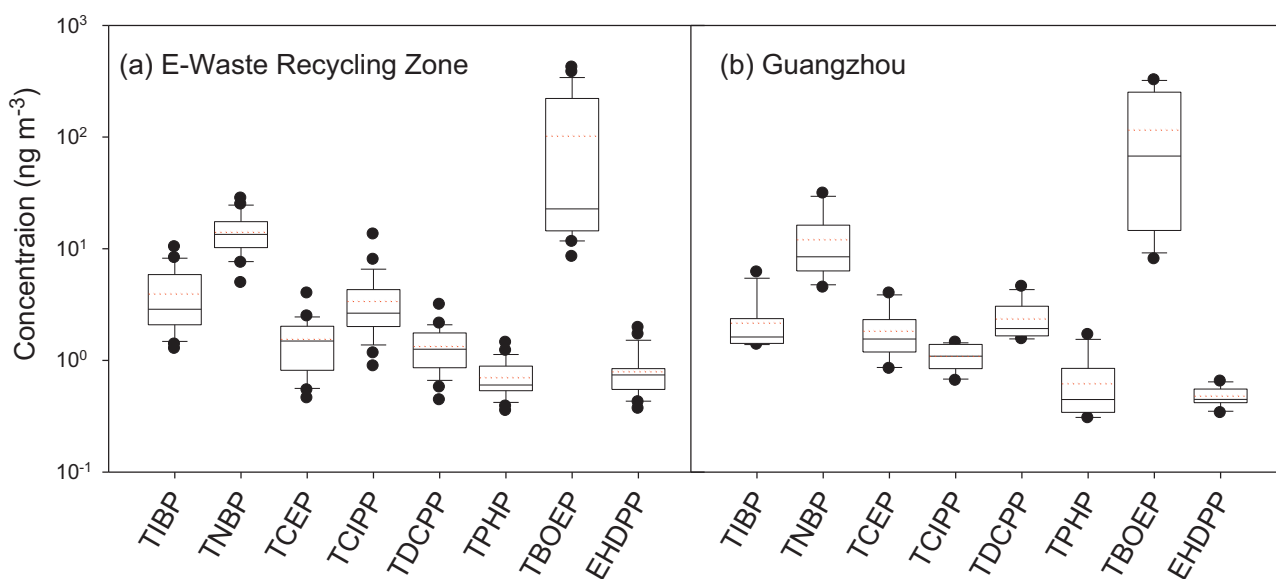


Fig. 1. Concentrations of particle-bound organophosphate flame retardants in the atmosphere of (a) an e-waste recycling zone and (b) Guangzhou, South China (Fig. S1). Solid and dashed horizontal lines represent the median and mean values, respectively. The box represents the 25–75th percentiles, and the whiskers represent the 5th and 95th percentiles.

in China (mean: 31 ng m^{-3}) [10] and Sweden (mean: 155 ng m^{-3}) [29], homes in Sweden (mean: 26 ng m^{-3} [29] or 53 ng m^{-3} [30]), and daycare centers in Sweden (mean: 197 ng m^{-3}) [29]. But they are substantially higher than those in the atmosphere of the Great Lakes (mean: $0.017\text{--}1.4 \text{ ng m}^{-3}$) [31], over the remote Northern Pacific and Indian Oceans (mean: $0.21\text{--}1.51 \text{ ng m}^{-3}$) [11], and a semi-urban location in Toronto, Canada (mean: 1.51 ng m^{-3}) [32].

The TCIPP was the highest of the chlorinated OPFRs in the e-waste recycling zone, while TDCPP was the highest in Guangzhou. This difference could be derived from different product use and sources in the two regions. In addition, TCIPP concentration in the e-waste recycling zone was higher (t -test; $p < 0.01$) than that in Guangzhou, while the opposite was true for TDCPP (t -test; $p < 0.01$). No significant difference (t -test; $p > 0.05$) of TCEP concentrations exists between the e-waste recycling zone and Guangzhou.

Generally, the urban Guangzhou results reflect the present OPFR-containing product mix in the marketplace, while the e-waste recycling zone results were largely influenced by the use histories dating at least several years back. The production volume of TCIPP was higher than that of TDCPP in the last few years; the worldwide production and usage volumes of TCIPP and TDCPP were 40,000 and 8,000 tons in 1997, respectively [7], while the use of TDCPP has increased significantly since the phase-out of PentaBDE [33]. Therefore, the present study documented the historical use patterns of TDCPP and TCIPP. Similarly, significantly higher TCIPP concentration was also observed in a 9-year-old car (260 ng m^{-3}) than in a new car (23 ng m^{-3}) [12]. Pearson correlation analyses (Table S4) suggested that TCIPP, TCEP, and TDCPP were significantly correlated with each other in the e-waste recycling zone but not in Guangzhou, probably indicating different input sources for these three chlorinated OPFRs between the two sites. On the other hand, a significant positive correlation between TBOEP and TNBP was observed at both sites, implying similar input sources for these two compounds. There was another possibility that these two OPFRs were applied to different consumer products but for the same purpose.

3.2. Particle size distribution of OPFRs

The size distribution profiles of OPFRs were not significantly different among different heights at both sites, and no modal peaks

were observed (Figs. S2–S6). This was different from our previous findings that airborne PBDEs displayed an unimodal peak in $1.0\text{--}1.8 \mu\text{m}$ at 20 m height in the e-waste recycling zone [3] and $0.56\text{--}1.0 \mu\text{m}$ at the heights of 100 and 150 m in urban Guangzhou [25]. The different size distribution profiles of OPFRs and PBDEs may be attributed to the widespread use of OPFRs as plasticizers, which disperses OPFRs into all sized particles more evenly compared to PBDEs. On the other hand, Yang et al. [10] observed that airborne OPFRs showed an unimodal or bimodal distribution pattern in particulate matter of an office environment. However, the lack of a clearly defined modal distribution for particle-bound OPFRs in the present study is difficult to interpret. One possible reason is the different sources of OPFRs in the indoor and outdoor environments. The vaporization process was the main source of OPFRs in the indoor office [10] and further partitioning to the existing indoor particles likely follows the particle surface area size distribution; while multiple emission sources might be responsible for OPFRs in the outdoor atmosphere.

The abundances of OPFRs in coarse (aerodynamic diameter $>1.8 \mu\text{m}$) and fine (aerodynamic diameter $<1.8 \mu\text{m}$) particles were roughly equal (Fig. 2), which is different from two previous studies on PBDEs and PAHs in urban Guangzhou that PBDEs and PAHs were largely affiliated with fine particles [25,34]. In addition, the geometric mean diameters (GMDs) ranged from 0.50 to $1.82 \mu\text{m}$ (Table S5) and most GMDs were approximately $1.8 \mu\text{m}$, near the cutoff point between coarse and fine particles. The geometric standard deviations (GSD) were similar for all OPFRs, with a slightly low value for TBOEP at the 20 m height in Guangzhou (Table S5), indicating a well-mixed boundary layer of OPFRs.

A previous study [10] reported a significant positive correlation between the mass median aerodynamic diameters of OPFRs and logarithmic subcooled liquid vapor pressures ($\log P_L/\text{Pa}$). However, no significantly positive correlation between GMDs or masses of OPFRs in coarse particles and $\log P_L$ at 298 K was observed in the present study, suggesting that the distribution of OPFRs in size-fractionated particles was not dependent on vapor pressure and probably not a result of gas-particle partitioning. These results implied the presence of other sources of particle-bound OPFRs at both sites in addition to gas-particle partitioning. Webster et al. [35] used scanning electron microscopy to confirm the transfer of BDE-209 into dust via physical processes such as abrasion or

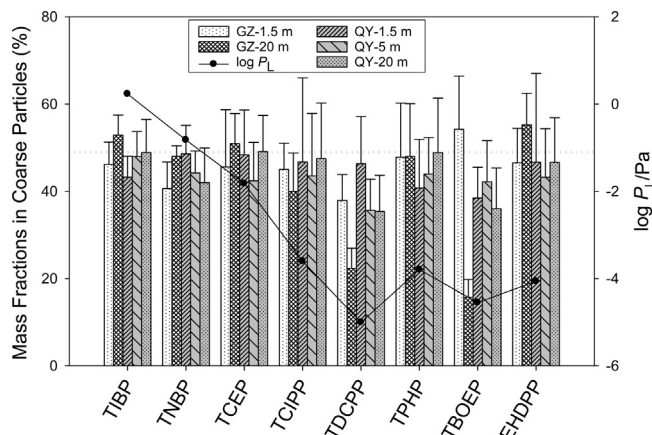


Fig. 2. Logarithmic subcooled liquid vapor pressures ($\log P_L/\text{Pa}$) at 298 K [7] and mass fractions of organophosphate flame retardants in coarse particles (aerodynamic diameter $>1.8 \mu\text{m}$) in the atmosphere at different heights of the e-waste recycling zone (QY) and Guangzhou (GZ) (Fig. S1).

weathering. Cao et al. [16] also deduced that some coarse dust particles containing OPFRs were derived from abrasion fragments because these coarse particles had similar geometrical shapes and low organic contents. As speculated in our previous study on PBDEs [3], particle-bound OPFRs may be derived from various processes including vaporization, mechanical abrasion, and resuspension of soil and dust at both sites. Nevertheless, further studies are desirable to elucidate detailed source profiles and relative contributions.

3.3. Estimation of dry and wet deposition fluxes

The total deposition fluxes of particle-bound OPFRs were 51 ± 67 and $55 \pm 13 \mu\text{g m}^{-2} \text{d}^{-1}$ in the e-waste recycling zone and Guangzhou, respectively (Table 1), estimated using the data for the 20-m height and our previous method [3]. The dry deposition fluxes of OPFRs were 37 ± 53 and $21 \pm 6 \mu\text{g m}^{-2} \text{d}^{-1}$ in the e-waste recycling zone and Guangzhou, much greater than those reported for the German North Sea ($0.009\text{--}0.24 \mu\text{g m}^{-2} \text{d}^{-1}$) [36], the Mediterranean Sea ($0.071\text{--}0.88 \mu\text{g m}^{-2} \text{d}^{-1}$) and Black Sea ($0.30\text{--}1.07 \mu\text{g m}^{-2} \text{d}^{-1}$) [37], whereas the wet deposition fluxes were 13.9 ± 15.3 and $34 \pm 7 \mu\text{g m}^{-2} \text{d}^{-1}$, respectively. It is interesting to note that dry deposition fluxes were greater than wet deposition fluxes in the e-waste recycling zone while the opposite was observed in Guangzhou (Table 1). Such a difference between the e-waste recycling zone and Guangzhou could be explained by different rainfall amounts for the different sampling periods, i.e., dry season in the e-waste recycling zone and wet season in Guangzhou, because rainfall amount was a vital parameter in influencing wet deposition flux [38,39].

The total deposition fluxes of OPFRs were size-dependent (Fig. 3), with coarse particles contributing the most to total deposition fluxes at both sites except for TBOEP (mean: 28%) and TDCPP (mean: 35%) in Guangzhou. In addition, coarse particles also dominated both the dry and wet deposition fluxes of OPFRs (except for TBOEP and TDCPP) in the e-waste recycling zone and Guangzhou (Figs. S7–S8). This result was different from our previous findings that dry and wet deposition fluxes of both PAHs and PBDEs were dominated by coarse and fine particles, respectively [3,4,25,34], which is attributed to the difference in size distributions of OPFRs and PAHs/PBDEs. PAHs and PBDEs were mainly associated with fine particles in the atmosphere [3,4,25,34]. It is notable that the contributions of the $>18 \mu\text{m}$ coarse particles to deposition fluxes in the e-waste recycling zone were higher than those in Guangzhou. The proportions of OPFRs in the $>18 \mu\text{m}$ particles were higher in the e-waste recycling zone than those in Guangzhou, which can be

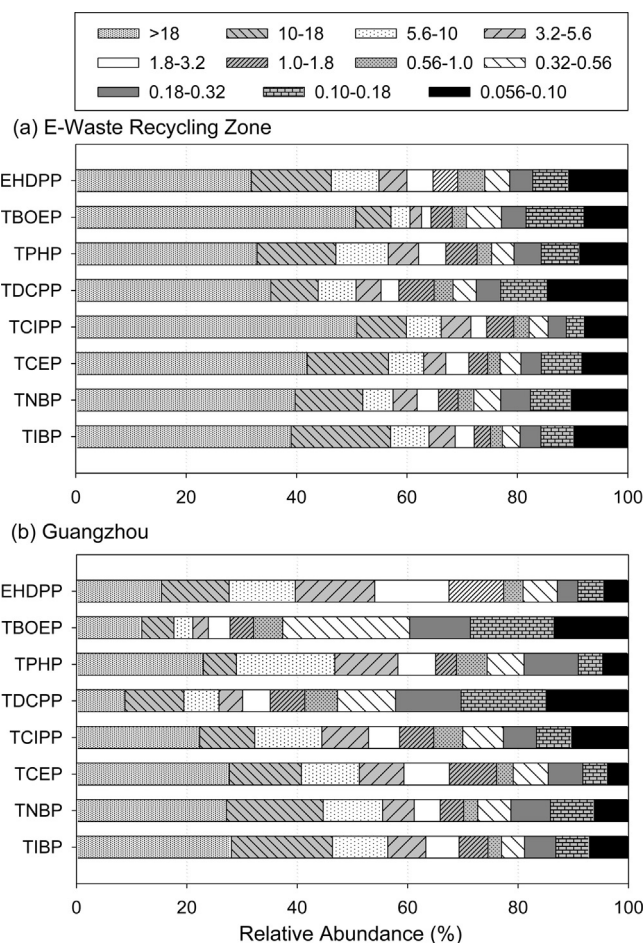


Fig. 3. Estimated relative abundance (%) of atmospheric deposition fluxes of size-fractionated particle-bound organophosphate flame retardants at the 20-m height in (a) the e-waste recycling zone and (b) Guangzhou. The particle sizes in the legend are expressed in μm .

attributed to more mechanical abrasion and resuspension of soil and dust in the e-waste recycling zone.

The mean dry deposition velocities of OPFRs were $0.31\text{--}0.38 \text{ cm s}^{-1}$ and $0.23\text{--}0.37 \text{ cm s}^{-1}$ in the e-waste recycling zone and Guangzhou, respectively (Table 1). These values were higher than the proposed values (0.2 cm s^{-1}) for estimating the deposition of OPFRs over the open seas [37]. However, there was no previous report of the dry deposition velocity of particle-bound OPFRs in the atmosphere of urban or e-waste recycling areas. The wet removal efficiencies (mean: 67–73%) of OPFRs in the e-waste recycling zone were slightly higher than those (mean: 56–69%) in Guangzhou (Table 1), both of which were similar to those (65–72%) of PBDEs in the e-waste recycling zone [3] but higher than those reported (approximately 50%) for PAHs on the campus of the University of Bayreuth in northeastern Bavaria, characterized as a regional background site [2].

3.4. Human health risk assessment

The inhalable, thoracic, respirable, and total deposition fractions of OPFRs in the entire respiratory tract and related health risk were estimated based on the data acquired at the 1.5-m height of both sampling sites. The inhalable, thoracic, respirable, and deposition fractions were estimated to be 90–92%, 78–84%, 64–74%, and 48–54% in the e-waste recycling zone and 89–92%, 78–84%, 65–72%, and 47–58% in Guangzhou, respectively (Table S6). Apparently, not

Table 1

Calculated dry deposition fluxes (F_{dry} ; $\mu\text{g m}^{-2} \text{d}^{-1}$), velocities (V_d ; cm s^{-1}), wet deposition fluxes (F_{wet} ; $\mu\text{g m}^{-2} \text{d}^{-1}$) and removal efficiencies (η ; %) and total deposition fluxes (F_{total} ; $\mu\text{g m}^{-2} \text{d}^{-1}$) of particle-bound OPFRs at 20-m height in the e-waste recycling zone and urban Guangzhou, South China.

	E-waste recycling zone					Guangzhou				
	F_{dry}	V_d	F_{wet}	η	F_{total}	F_{dry}	V_d	F_{wet}	η	F_{total}
TIBP	1.61 ± 0.95	0.38 ± 0.06	0.63 ± 0.34	71.8 ± 3.9	2.2 ± 1.3	0.95 ± 0.77	0.37 ± 0.03	1.28 ± 0.96	68.8 ± 1.4	2.2 ± 1.7
TNBP	5.2 ± 3.0	0.34 ± 0.06	2.1 ± 0.95	68.8 ± 3.9	7.3 ± 3.9	2.0 ± 0.6	0.37 ± 0.04	2.8 ± 0.7	68.0 ± 1.1	4.8 ± 1.2
TCEP	0.64 ± 0.46	0.35 ± 0.10	0.25 ± 0.14	71.6 ± 3.5	0.89 ± 0.59	0.46 ± 0.16	0.32 ± 0.08	0.72 ± 0.23	68.0 ± 0.9	1.18 ± 0.36
TCIPP	1.82 ± 1.76	0.36 ± 0.12	0.69 ± 0.51	71.6 ± 5.3	2.5 ± 2.3	0.24 ± 0.17	0.28 ± 0.08	0.38 ± 0.16	62.6 ± 4.1	0.62 ± 0.33
TDCPP	0.43 ± 0.24	0.32 ± 0.04	0.19 ± 0.10	67.1 ± 3.6	0.62 ± 0.34	0.66 ± 0.29	0.25 ± 0.02	1.1 ± 0.5	57.6 ± 1.3	1.81 ± 0.76
TPHP	0.21 ± 0.08	0.31 ± 0.07	0.10 ± 0.04	72.7 ± 6.3	0.31 ± 0.11	0.150 ± 0.063	0.28 ± 0.03	0.27 ± 0.14	65.0 ± 4.6	0.42 ± 0.20
TBOEP	27 ± 54	0.34 ± 0.13	9.76 ± 15.2	67.5 ± 4.3	37 ± 68	15.9 ± 5.5	0.23 ± 0.04	28 ± 6	56.2 ± 0.6	43 ± 12
EHDPP	0.26 ± 0.16	0.31 ± 0.10	0.13 ± 0.06	70.6 ± 4.7	0.39 ± 0.21	0.090 ± 0.023	0.23 ± 0.06	0.20 ± 0.06	67.0 ± 1.7	0.29 ± 0.07
$\Sigma_8\text{OPFR}$	37 ± 53	0.36 ± 0.11	13.9 ± 15.3	69.3 ± 4.1	51 ± 67	21 ± 6	0.25 ± 0.03	34 ± 7	57.9 ± 0.6	55 ± 13

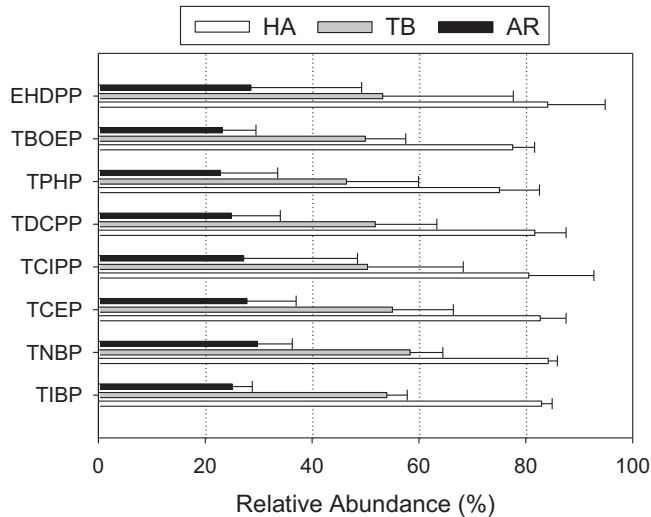


Fig. 4. Relative contributions (%) of coarse particles (aerodynamic diameter >1.8 μm) to deposition concentrations of organophosphate flame retardants in the head airway (HA), tracheobronchial region (TB) and alveolar region (AR) of the human respiratory tract at the 1.5-m height in the e-waste recycling zone (Fig. S1).

all particle-bound pollutants can be inhalable into lung and deposit in the deep parts of respiratory tract.

The deposition fractions of OPFRs were variable in the different regions of the human respiratory tract (Table S7). Deposition fractions of OPFRs in the head airway, tracheobronchial region, and alveolar region were 36–43%, 2.5–3.1%, and 8.1–9.2% in the e-waste recycling zone and 34–50%, 2.4–3.1%, and 7.0–9.7% in Guangzhou, respectively. Deposition in the head airway generally posed lower potential health risk than that in the alveoli region, although the majority of OPFRs was deposited in the head airway. Deposition

fractions of OPFRs in the different regions of the human respiratory tract were particle size-dependent. Coarse particle-bound OPFRs were mainly deposited in the head airway, while fine particle-bound OPFRs were deposited in the tracheobronchial and alveoli regions (Figs. 4 and S9), a finding similar to our previous results with PBDEs [5] and PAHs [40].

Bulk and deposition concentrations of OPFRs used in health risk assessment denote the least and most conservative scenarios, respectively. Assuming an inhalation rate of $15 \text{ m}^3 \text{ d}^{-1}$ for an average adult, the mean daily inhalation dose of OPFRs in the e-waste recycling zone and Guangzhou were 0.17–6.8 and 0.13–35 $\text{ng kg}^{-1} \text{ bw d}^{-1}$ (based on bulk concentrations) or 0.091–3.2 and 0.067–18.8 $\text{ng kg}^{-1} \text{ bw d}^{-1}$ (based on deposition concentrations) in the e-waste recycling zone and Guangzhou, respectively (Table 2). All daily inhalation doses at both sites were much lower than the reference doses from a previous study (13,000–80,000 $\text{ng kg}^{-1} \text{ bw d}^{-1}$; Table S1) [28]. The HQ values of OPFRs were $(0.26\text{--}45) \times 10^{-5}$ and $(0.22\text{--}230) \times 10^{-5}$ based on bulk concentrations or $(0.14\text{--}21) \times 10^{-5}$ and $(0.13\text{--}126) \times 10^{-5}$ based on deposition concentrations in the e-waste recycling zone and Guangzhou, respectively. The total HQ values, 61×10^{-5} and 260×10^{-5} based on bulk concentrations or 30×10^{-5} and 136×10^{-5} based on deposition concentrations in the e-waste recycling zone and Guangzhou, were several orders of magnitude lower than 1, suggesting that inhalation exposure to particle-bound OPFRs in the e-waste recycling zone and Guangzhou was associated with low risk. Nevertheless, it should be noted that uncertainties on the health risk assessment results would be produced by the use of oral RfD values in the present study. According to the United States Environmental Protection Agency (http://www.popstoolkit.com/tools/HHRA/SF_USEPA.aspx), the oral RfD values of most semi-volatile organic compounds were 1–2 orders of magnitude higher than inhalation RfD. In the worst case scenario, i.e., the inhalation RfD values of OPFRs were assumed to be three orders of magnitude

Table 2

Daily inhalation dose (ID; $\text{ng kg}^{-1} \text{ bw d}^{-1}$) and hazard quotients (HQ; 10^{-5}) of particle-bound OPFRs at 1.5-m height in the e-waste recycling zone and urban Guangzhou, South China.

	E-waste recycling zone				Guangzhou			
	ID _{C-Total} ^a	ID _{D-Total} ^b	HQ _{C-Total} ^a	HQ _{D-Total} ^b	ID _{C-Total}	ID _{D-Total}	HQ _{C-Total}	HQ _{D-Total}
TIBP	0.87 ± 0.60	0.44 ± 0.31	c	c	0.44 ± 0.12	0.23 ± 0.07	c	c
TNBP	2.85 ± 0.59	1.54 ± 0.38	11.9 ± 2.4	6.4 ± 1.6	3.9 ± 2.3	1.88 ± 1.16	16.2 ± 9.4	7.8 ± 4.8
TCEP	0.33 ± 0.20	0.178 ± 0.107	1.51 ± 0.90	0.81 ± 0.49	0.49 ± 0.31	0.25 ± 0.15	2.2 ± 1.4	1.14 ± 0.7
TCIPP	0.64 ± 0.28	0.33 ± 0.15	0.79 ± 0.35	0.42 ± 0.19	0.30 ± 0.04	0.16 ± 0.03	0.38 ± 0.05	0.19 ± 0.03
TDCPP	0.25 ± 0.12	0.130 ± 0.068	1.64 ± 0.78	0.87 ± 0.45	0.50 ± 0.12	0.23 ± 0.03	3.3 ± 0.8	1.51 ± 0.23
TPHP	0.18 ± 0.06	0.095 ± 0.037	0.26 ± 0.09	0.14 ± 0.05	0.15 ± 0.12	0.091 ± 0.088	0.22 ± 0.17	0.13 ± 0.13
TBOEP	6.8 ± 4.1	3.2 ± 1.9	45 ± 28	21 ± 13	35 ± 37	18.8 ± 19.1	230 ± 250	126 ± 127
EHDPP	0.172 ± 0.049	0.091 ± 0.034	c	c	0.125 ± 0.022	0.067 ± 0.016	c	c
$\Sigma_8\text{OPFR}$	12.1 ± 4.1	5.9 ± 1.9	61 ± 28	30 ± 13	41 ± 39	22 ± 20	260 ± 260	136 ± 132

^a Calculated based on total concentration of particle-bound OPFRs in the atmosphere.

^b Calculated based on deposition concentration of particle-bound OPFRs in the human respiratory tract.

^c Not available due to lack of reference dose data.

lower than the oral RfD, the total HQ values of OPFRs at both sites were still lower than 1.

Our previous study [5] also found low health risk from inhalation exposure to particle-bound halogenated flame retardants (HFRs) in the e-waste recycling zone. Therefore, inhalation exposure to these flame retardants in the e-waste recycling zone would lead to low health risk based on existing toxicological data of OPFRs and HFRs. As a result, further studies are needed to focus on other more toxic pollutants such as PAHs, PCDD/Fs, and heavy metals [5]. It is notable that the production volumes of OPFRs are likely to rise substantially due to the recent restrictions on the use of PBDEs, leading to increasing human health risk. Chronic toxicity caused by OPFRs in long-term exposure and the collective effects of flame retardants should be investigated in future research.

4. Conclusions

The total air concentrations of eight OPFRs were almost the same in the e-waste recycling zone and urban Guangzhou, suggesting that e-waste recycling activities are not a significant source of OPFRs probably because these OPFRs are used as both flame retardants and plasticizers in consumer products. The dominance of TBOEP at both sites is attributed to the widespread use of TBOEP-containing products. The concentrations of OPFRs distributed in coarse and fine particles were almost equal at different heights at both sites. Estimated atmospheric deposition fluxes of particle-bound OPFRs were size-dependent, and coarse particles dominated both the dry and wet deposition fluxes. The potential inhalation exposure risk of particle-bound OPFRs assessed with hazard quotient was low for residents dwelling in the e-waste recycling zone and urban sites.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.09.014>.

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