Organophosphorus esters (OPEs) in PM$_{2.5}$ in urban and e-waste recycling regions in southern China: concentrations, sources, and emissions

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ABSTRACT

Organophosphate esters (OPEs) are novel ubiquitous contaminants that are attracting growing concern, but their emissions into the environment are still poorly understood. In this study, 12 OPEs were measured in fine particulate matter (PM$_{2.5}$) at 20 industrial sites in an urban region and four e-waste recycling facilities in a rural region in southern China. There was no significant difference in the concentrations of ΣOPEs between the urban region (519–62,747 pg/m^3, median = 2854 pg/m^3) and the rural e-waste region (775–13,823 pg/m^3, 3321 pg/m^3). High OPE concentrations in urban PM$_{2.5}$ were generally associated with the electrical, electronic, plastic, and chemical industries. There were no significant correlations between most OPEs in these two regions, suggesting different emission mechanisms. The average emissions of ΣOPEs estimated using a simplified dispersion model were 73.0 kg/yr from the urban industrial point sources and 33.2 kg/yr from the e-waste recycling facilities. The estimated emission inventory from industrial activities in the whole city (3228–4452 kg/yr) was approximately 30-fold higher than that from the e-waste recycling (133 kg/yr) facilities because urban region has a much larger industrial scale. To the best of our knowledge, this is the first effort to model the emissions of OPEs from industrial and e-waste recycling activities to the atmosphere.

1. Introduction

Organophosphate esters (OPEs) are a group of chemicals that are used as flame retardants and plasticizers in various consumer and industrial products such as electronic equipment, plastics, textiles, furniture, and building materials (Ma et al., 2017; Van der Veen and De Boer, 2012). Some OPEs are also used in hydraulic fluids, floor polish, extractants for metal complexes, and glues (Van der Veen and De Boer, 2012). OPEs are considered suitable alternatives for brominated flame retardants (BFRs) and have exhibited increasing demand and production especially after some BFRs have been restricted under the Stockholm Convention (Su et al., 2016). In 2008, the US, Europe, and Asia (excluding Japan) consumed 72,000, 83,000, and 22,000 metric tons of OPEs, respectively (Ou and Lang, 2010). However, some of these chemicals are suspected to be carcinogenic, mutagenic, or neurotoxic as suggested in numerous studies (Van der Veen and De Boer, 2012; Wei et al., 2015). Tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) can easily enter the bloodstream and is listed as a known carcinogen by the state of California (ATSDR, 2009; Butt et al., 2014). Tris(1-chloro-2-propyl) phosphate (TCIPP) accumulates in the liver and kidneys of animals and

is potentially carcinogenic (Leisewitz et al., 2000). Meeker and Stapleton (2010) found that house dust concentrations of OPEs were correlated with hormone levels and semen quality parameters for men.

Most OPEs are additives and not chemically bonded to polymer products and are easily released to the environment during the processes of production, application, and disposal of related products (Ma et al., 2017). Consequently, there has been an increasing number of reports of OPEs occurrence in various environmental compartments and humans (Cao et al., 2017; Ding et al., 2016; Guo et al., 2017; Khan et al., 2016a, 2016b; Kim et al., 2014; Z. Lu et al., 2017; Ren et al., 2016; Vojta et al., 2017; Yadav et al., 2018, 2017; Zhao et al., 2016). OPEs were also detected in both urban and remote atmospheres (He et al., 2018; Lai et al., 2015; Okeme et al., 2018; Vykoukalova et al., 2017). The results indicate a primary emission source of these chemicals from urban regions and long-range atmospheric transport to remote regions (Castro-Jimenez et al., 2014). Air emission of toxic organic pollutants from urban regions has attracted considerable research interest in recent years. The emissions of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) from Toronto were 18 and 17 kg/yr, respectively (Csiszar et al., 2014), which were

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comparable to that for PCBs in Zurich, Switzerland (13 kg/yr) (Diefenbacher et al., 2016). An annual PCB emission rate of 203 kg/yr from the legacy stocks in Chicago has been estimated (Shanahan et al., 2015). These studies also revealed important emissions from legacy sources (e.g., transformers, buildings, and soils) for these chemicals in these cities. However, little is known about the emissions of currently used chemicals from industrial activities.

In this study, atmospheric concentrations of 12 OPEs were investigated in fine particulate matter with aerodynamic diameters less than 2.5 µm ($PM_{2.5}$) around industrial parks from an industrial megacity (Guangzhou City) and around electronic waste (e-waste) recycling facilities from a rural area in southern China. These organic pollutants tend to closely bind to particles with small size (Okonski et al., 2014), and these particles are able to remain in ambient air for a long time and to be transported over long distances (Kurokawa et al., 1998). We aim to i) determinate the importance of these potential emission sources of OPEs to the ambient air, ii) examine the industry sector-specific compositions of OPEs associated with the industrial activities in this region, and iii) estimate, for the first time, emissions of these chemicals to the air from industrial and e-waste activities. In addition, polycyclic aromatic hydrocarbons (PAHs), an indicator of combustion or thermal treatment sources, were also analyzed around these point sources. We aimed to explore potential associations between OPEs and PAHs, which may help elucidate their sources.

2. Materials and methods

2.1. Sampling

Sampling was conducted in an urban area and a rural e-waste recycling area. The urban area, Guangzhou, is a megacity and an important industrial base in southern China. It has a population of approximately 15 million and an area of 2083 km^2 (the main six districts) (GMSB, 2017). There are more than 100 industrial parks within this city, which involve various industries including electrical/electronic products, furniture, chemicals, automobiles, clothing, leather, plastics, metals, and machinery. The e-waste area is one of the largest e-waste sites in China, which is located in the rural area of Qingyuan and is approximately 70 km north of the Guangzhou center (Fig. 1). $PM_{2.5}$ was sampled in the vicinity of 20 potential point sources (18 industrial parks, one electronics shopping center, and one furnishings shopping center) and one downtown site, located in different districts in Guangzhou from January 2015 to April 2016. In the e-waste area, $PM_{2.5}$ was collected in the vicinity of the four e-waste recycling parks. The samples were collected on Whatman quartz fiber filters for 24 h using active large-volume air samplers (TE-6001, Tisch Environment Inc., US) at a flow rate of 1.13 m^3/min. At each site, the sampler was deployed for two and five days in the urban and e-waste areas, respectively, on the rooftop of a building near and downwind the parks. The loaded filter was wrapped in aluminum foil, sealed in a small polyethylene zip bag and stored at −20 °C until extraction.

2.2. Chemicals

Target compounds of 12 OPEs, including tris(ethyl) phosphate (TEP), tris(butyl) phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate (TEHP), tris(chloroethyl) phosphate (TCEP), tris[(2 R)-1-chloro-2-propyl] phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), 2-ethylhexyl diphenyl phosphate (EHDPP), triphenyl phosphate (TPHP), tris(propyl) phosphate (TPP), tris(4-isopropylphenyl) phosphate (TIPPP), and tricresyl phosphate (TMPP), were purchased from Wellington Laboratories (Ontario). Recovery standards (TPP-d_{21}, TNBP-d_{27}, and TCIPP-d_{18}) and internal standards (TCEP-d_{12} and TDCIPP-d_{15}) were purchased from Cambridge Isotope Laboratories, Inc.

2.3. Sample preparation and analysis

The detailed analytical method used in this study is provided in the Supplementary Material (SM). Briefly, $PM_{2.5}$ samples were Soxhlet extracted with a mixture of hexane and acetone (1:1) for 48 h. Prior to the extraction, recovery standards (TPP-d_{21}, TNBP-d_{27}, and TCIPP-d_{18} for OPEs) were added to monitor the recoveries during the procedure. The extracts were concentrated to 1 mL and then purified with a solid-phase extraction cartridge (Supelclean ENVI-Florisil, 3 mL, 500 mg). The column was eluted with 5 mL of hexane and 5 mL of 1:1 hexane: dichloromethane (v/v), and this mixed fraction was analyzed for PAHs. The second fraction containing OPEs was obtained by elution with 8 mL of ethyl acetate. This fraction was concentrated to near dryness under a gentle nitrogen stream then dissolved in 300 µL of isooctane. Internal standards (TCEP-d_{12} and TDCIPP-d_{15}, 60 ng respectively) were added into the extracts before instrumental analysis. OPEs were analyzed by an Agilent 7890 gas chromatograph coupled with an Agilent 5975 mass spectrometer with electron impact ionization (GC-EI-MS). The analytes were separated using a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) (J&W Scientific). The analytical procedures for PAHs and organic and elemental carbons (OC and EC) are given in the SM.

2.4. Quality control and quality assurance

Several OPEs and PAHs were found in the field samples and procedural blanks, but their amounts contributed < 5% of those in the field sample extracts. The concentrations in the sample extracts were blank-corrected. The recoveries of the recovery standards were 125.4 ± 23.7% for TPP-d_{21}, 80.8 ± 10.4% for TNBP-d_{27}, and 98.0 ± 9.4% for TCIPP-d_{18}, and reported concentrations were not recovery corrected. The method detection limits (MDLs) were assigned as the average method blank mass plus three times the standard deviation, or as five times the signal to noise ratio for compounds that were not found in the blanks, which ranged from 0.04 to 1.10 pg/m^3.

2.5. Air emission estimation

We employed a simplified Gaussian dispersion model to estimate the emissions of OPEs from the industrial and e-waste dismantling parks to the atmosphere, which is expressed by:

$$e = c * u * \Delta y * \Delta z \tag{1}$$

where e is the emission rate of target compounds (g/day), c is the concentration of compounds (pg/m^3) (mean concentrations were used here), u is the mean wind speed on the sampling day (m/s), Δy and Δz are the distance from the source to the sampling place (m) and height of the sampler above the ground surface (m), respectively. We assume that the OPEs in the $PM_{2.5}$ around each site were all from the source, and emissions attributed to urban diffuse sources were not considered. This model has been used in several previous studies (Ahrens et al., 2011; Shoeib et al., 2016).

3. Results and discussion

3.1. Concentrations and compositions

Of the 12 target OPEs, the concentrations of TIPPP and TPP were below the MDLs and TDCIPP was not quantified because of interference with an unknown peak in the GC. The total concentrations of OPEs (ΣOPEs) were wide-ranging, from 519 to 62,747 pg/m^3, with a median of 2854 pg/m^3 (Table 1) in the urban $PM_{2.5}$. The concentrations of individual OPEs are given in Table S1 in the SM.

TEP is mainly used as a flame retardant in building/construction materials (Table S2), and was found in 90% of the samples with concentrations ranging from nondetectable (nd) to 132 pg/m^3 (median =
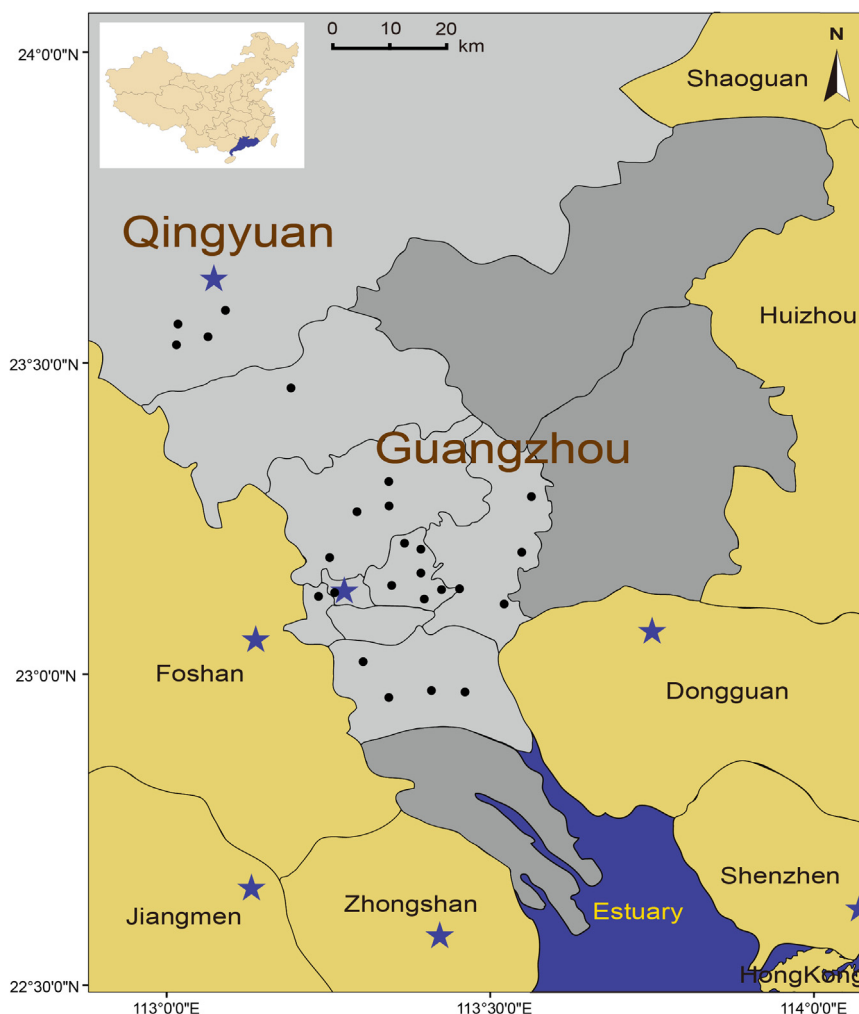
Fig. 1. Map of sampling sites in southern China.

Table 1
Concentrations of OPEs in PM$_{2.5}$ (pg/m^3) in the urban and e-waste regions.

	Urban region			E-waste region		
	Range	Mean	Median	Range	Mean	Median
TEP	nd-132	17.9	8.39	nd-24.0	4.54	3.50
TNBP	12.3–16845	978	237	nd-540	124	72.2
TCEP	39.0–975	206	174	nd-519	98.2	59.5
TCIPP	103–4386	1219	1059	34.7–3727	1008	424
TBOEP	nd-98.2	8.19	nd	nd		
TPHP	39.6–1923	397	298	185–10744	1895	1143
EHDPP	21.5–2176	198	72.8	10.5–438	138	85.9
TEHP	13.3–1902	228	111	6.26–1463	301	84.8
TMPP	22.2–59975	2564	465	37.9–3013	781	322
ΣOPEs	519–62747	5815	2854	775–13823	4350	3321

8.39 pg/m^3). The highest TEP concentration was observed at a site that is close to the largest electronics shopping center in a business zone, where this chemical could be emitted from the electronic products or building materials. The second highest concentration (average = 57.4 pg/m^3) was found at the wastewater treatment plant (WWTP) site. TNBP is usually used as an adhesive, sealant, and flame retardant in building/construction materials. This pollutant showed the highest average concentration (15,002 pg/m^3) in PM$_{2.5}$ at an industrial zone (XP) in southwestern Guangzhou, which is known for manufacturing household products, plastic and rubber products, and electronics. TNBP concentrations at other sites were reduced substantially (12.3–1602 pg/

m^3 and median = 215 pg/m^3), and higher levels were found at two industrial zones (means = 943 and 769 pg/m^3) where chemical industry and electronics manufacturing were dominant, respectively. These results suggest that the XP industrial zone is a significant emission source of TNBP in ambient air.

The PM$_{2.5}$ concentrations of TCEP ranged from 39.0 to 975 pg/m^3, with a median of 174 pg/m^3. Somewhat higher concentrations were observed at several industrial zones related to the automotive, leather, textile, and electronics industries. The applications of this chemical are as flame retardants for industry uses and as paints and coatings for consumer uses. TCIPP has wide applications including adhesives, sealants and flame retardants in building/construction materials, electrical/electronic products, and foam seating and bedding products. Thus, this pollutant showed generally the highest levels in the urban region, with a median of 1059 pg/m^3 (103–4386 pg/m^3). Higher concentrations were found in industrial zones associated with the chemical industry, leather and textile manufacturing, and business. TBOEP is mainly used in lubricants, greases, paints, coatings, and plastic and rubber products. This compound was detected only at four sites, with the highest mean concentration of 90.6 pg/m^3 at an industrial zone for leather processing, followed by a concentration of 50.4 pg/m^3 at the WWTP.

TPHP, used as a flame retardant and plasticizer in electrical and electronic products, foam seating and bedding products, and furniture and furnishings, showed the highest concentration (1581 pg/m^3) at an industrial zone related to the metal, electrical and electronic industries. Higher average concentrations (550–620 pg/m^3) were also found in

other industrial zones related to the electrical and electronic industries, leather and textile processing, and waste recycling industries. The concentrations of EHDPP were between 21.5 and 2176 pg/m^3. Its median concentration (72.8 pg/m^3) was only higher than that of TEP. EHDPP is mainly used as a flame retardant in indoor products such as floor coverings, furniture, and plastic and rubber products. The highest concentrations were found at a waste recycling factory, followed by concentrations at industrial zones of leather and textile processing. Higher concentrations (383–412 pg/m^3) were also observed at a waste incineration power plant. TEHP, used as a chemical intermediate, lubricant and lubricant additive, and agricultural product (non-pesticidal), had a median concentration of 111 pg/m^3. Higher concentrations were associated with the leather and textile industry (208–1619), waste recycling (112–1902 pg/m^3), and waste incineration (265–365 pg/m^3). TMPP displayed the second highest concentration between 22.2 and 59975 pg/m^3 (median = 465 pg/m^3). Its main applications are in polyvinyl chloride (PVC), cellulosic polymers, thermoplastics and synthetic rubber (Van den Eede et al., 2011). The extremely high concentrations (average = 43,602 pg/m^3) were found at an industrial zone (SB) related to the electrical, electronic, plastic, foam, and metal industries. This indicated that the industrial activities in this zone are especially relevant for emission of TMPP. Other potentially significant sources of TMPP included the leather and textile processing (1117 pg/m^3), waste recycling (1088 pg/m^3), and automotive (817 pg/m^3) industries.

Overall, high concentrations of ΣOPEs were generally associated with electrical, electronic, and plastic manufacturing industries, the waste recycling industry, and certain chemical industries (coating and printing ink). This is not surprising because OPEs are commonly used as flame retardants and plasticizers in these products. Low concentrations were associated with the machinery manufacturing, papermaking, clothing, and furnishing industries. The spatial distribution of the concentrations ΣOPEs in PM$_{2.5}$ predicted by ArcGIS mapping software is shown in Fig. 2. Generally, PM$_{2.5}$-associated OPE concentrations were higher outside of the downtown area, consistent with the spatial

distribution of industrial activities in Guangzhou. Nevertheless, different spatial distributions were observed for some individual OPEs as shown in Fig. S1 suggesting industry type-dependent emissions. Based on the modeled spatial distribution of atmospheric OPE levels and population distribution in the urban area, we estimated that about two million people in this city have the highest quartile of OPEs exposure via inhalation. PM$_{2.5}$ can travel deeply into the respiratory tract and reach the lungs and is hazardous to respiratory, pulmonary, and cardiovascular function (Wang et al., 2017). This study has implications for concerns about the potential adverse effects of PM emitted from the industrial activities in these areas.

In most samples, TCIPP and TMPP were the primary compounds, which accounted for 35.7% and 19.6% on average, respectively. The dominance of TCIPP in air has been reported in worldwide locations (Castro-Jimenez et al., 2014; R. Liu et al., 2016; Moller et al., 2011; Salamova et al., 2013), consistent with its widespread applications in a variety of commercial products. Despite this, however, OPE compositions varied among the sites (Fig. S2). For instance, more TPHP (accounting for 32.3–54.1% of the total OPEs) is likely released from the machinery and clothing industries, and household product and furniture manufacturing may result in increased emissions of TNBP (16.7–88.0%). Increased emissions of EHDPP were likely associated with the waste disposal, resource recovery, and leather industries, where EHDPP contributions of 11.2–31.8% were observed.

OPE concentrations in the rural e-waste recycling region ranged from 775 to 13,823 pg/m^3, with a median of 3321 pg/m^3. There was no statistically significant difference in the total OPE concentrations between the e-waste and urban regions. Nevertheless, there were obvious differences in the concentrations between the four e-waste recycling facilities, with mean concentrations of 7156, 1150, 2768, and 6325 pg/m^3, respectively. Varying OPE compositions were also observed at the four e-waste recycling facilities (Fig. S3). The variations in the OPE concentrations as well as compositions may depend on the quantities and types of e-waste being recycled. However, TPHP, TCIPP, and TMPP were the dominant compounds in this region; these three pollutants
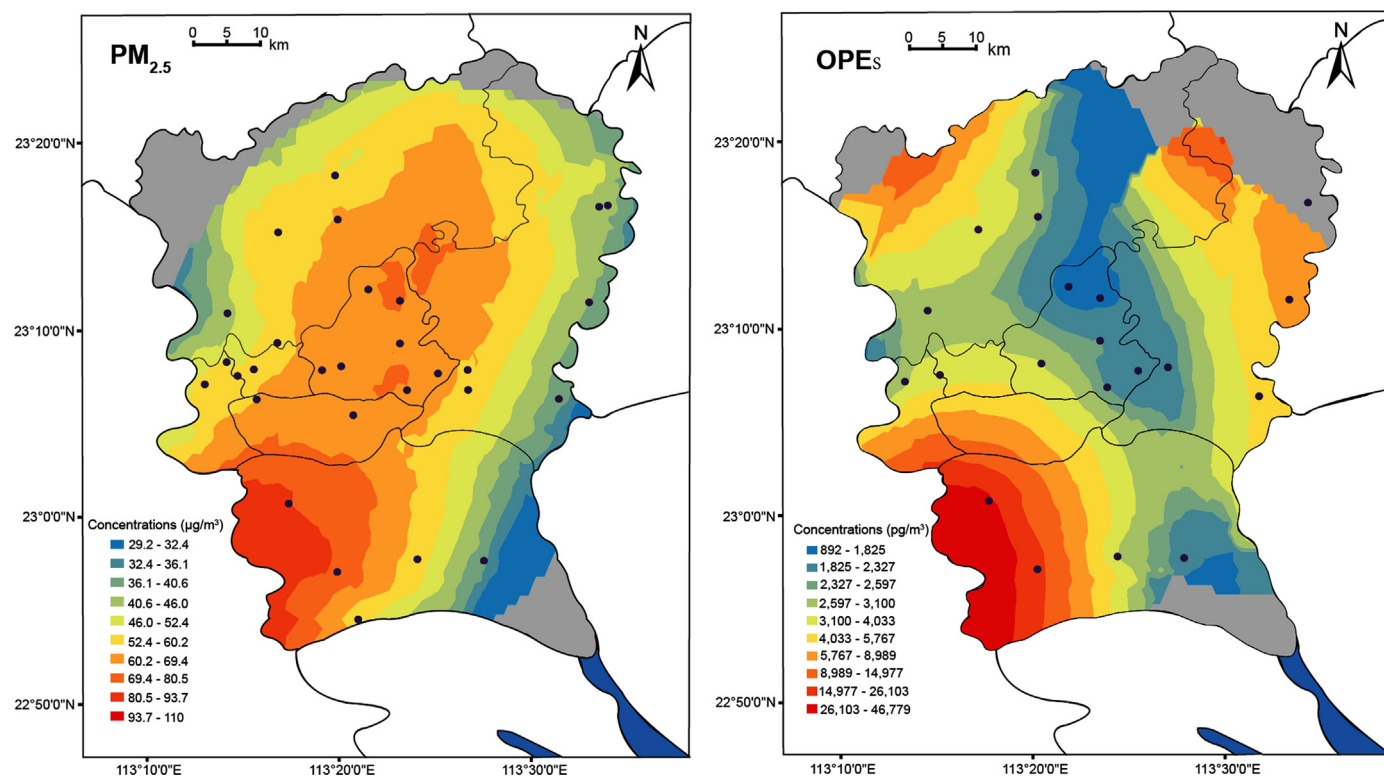

Fig. 2. Spatial distributions of PM$_{2.5}$ and PM$_{2.5}$-bound OPEs in the urban region constructed by the Kriging interpolation method.

constituted on average 83.7% of the total OPEs (41.4%, 25.9%, and 16.5%, respectively). The compositions in the e-waste region were different from those in the urban region, in which they together accounted for 68.9% (13.6%, 35.7%, and 19.6%, respectively). The dominance of TPHP was in line with its widespread application in electrical and electronic products and with previous observations on atmospheric particles and indoor dust from e-waste sites in China (Bi et al., 2010; He et al., 2015). It was reported that TPHP is used as one of important alternatives for technical decabrominated diphenyl ether (deca-BDE) product (S.Y. Lu et al., 2017), which is typically used as a flame retardant in electrical and electronic products. The lower concentrations and contributions of TPHP in the urban region may be because technical deca-BDE has not yet been replaced by TPHP in southern China. However, TPHP is suspected to be carcinogenic, mutagenic, and neurotoxic (Wei et al., 2015). Thus, residents in the e-waste region, especially the recycling workers, have a high health risk for exposure to this pollutant.

Little research has been conducted on OPEs in $PM_{2.5}$. Chlorinated OPEs (TCIPP, TCEP, and TDCIPP) were detected in $PM_{2.5}$ collected in 10 Chinese cities. The most abundant compound, TCIPP, had a mean of 410 pg/m^3 (D. Liu et al., 2016), lower than that in our study (1219 pg/m^3) (Table S3). The median concentrations of Σ_{12}OPEs were 978 and 1046 pg/m^3 in the urban air of the Great Lakes (Salamova et al., 2016), which were approximately 3-fold lower than those in the present study. Comparable mean concentrations of Σ_9OPEs in the air (3250 pg/m^3, gas + particle phases) of Beijing, China have been reported (R. Liu et al., 2016). Σ_{14}OPEs occurred at concentrations ranging from 360 to 4400 pg/m^3 (median = 1800 pg/m^3) in aerosols across the Atlantic, Pacific, and Indian Oceans and higher levels were found at locations close to the coast, suggesting a continental source (Castro-Jimenez et al., 2016). The median concentrations of Σ_8OPEs in remote Arctic sites were 50–334 pg/m^3, providing evidence of their global occurrence associated mainly with long-range atmospheric transport (Salamova et al., 2014; Suhring et al., 2016).

3.2. Correlations and sources

Correlation analysis between individual OPEs (Table 2) shows that significant correlations were not observed for most of them in the urban region. In general, moderate but statistically significant correlations exist between TNBP, TCEP, TCIPP, and TMPP (r = 0.35–0.58,

$p < 0.025$). EHDPP and TEHP had a strong correlation (r = 0.82, $p < 0.001$). The correlations were also weak for OPEs in the e-waste region, where TNBP, TCEP, and TCIPP (r = 0.75–0.87, $p < 0.001$) have strong correlations, as do EHDPP, TEHP, and TMPP (r = 0.87–0.95, $p < 0.001$). The lack of significant correlations for those OPEs in both regions suggests their different emission sources possibly because of the diverse industrial or e-waste recycling activities involved in the complexes. OC and EC are important carbonaceous components of aerosols and play a significant role in the behaviors of semi-volatile organic compounds in the atmosphere given their physicochemical properties. OC may be emitted directly through various combustion sources or formed through atmospheric oxidation of gaseous organic precursors, while EC is produced from incomplete combustion processes such as biomass burning, vehicle exhaust, and coal combustion (Zhang et al., 2016). The concentrations of OC and EC were within the ranges of 3.16–18.7 $\mu g/m^3$ and 0.93–6.94 $\mu g/m^3$ with medians of 7.63 and 2.89 $\mu g/m^3$, respectively. There was a good linear relationship between OC and EC (r = 0.692, $p < 0.001$), implying that approximately half (r^2 = 0.48) of the OC in $PM_{2.5}$ in the urban region were derived from primary emissions. OPEs had no significant correlations with OC and EC, except for TEHP (r = 0.577, $p < 0.001$) and EHDPP(r = 0.310, $p < 0.049$) with OC and TEHP (r = 0.345, $p < 0.025$) with EC. In the e-waste region, a strong correlation existed between OC and EC (r = 0.850, $p < 0.001$), and approximately 72% of the $PM_{2.5}$ OC originated from primary emissions. EHDPP, TEHP, and TMPP were significantly correlated with OC (r = 0.474–0.584, $p < 0.035$) and EC (r = 0.648–0.706, $p < 0.002$). We hypothesize that the emissions of these OPEs may be related to e-waste combustion or thermal processing, during which OPEs and OC/EC are released simultaneously. However, there was a negative dependence (r = -0.543 −-0.374, $p < 0.104$) for the concentrations of TNBP, TCEP, and TCIPP with the increasing OC and EC contents, although the correlations were statistically significant only for TNBP ($p < 0.036$). This could be a reflection of different emission mechanisms or atmospheric processes as these three compounds have high water solubilities relative to others. PAHs are a class of ubiquitous organic pollutants in the atmosphere that are largely from various combustion sources. The concentrations of PAHs ranged from 674 to 39,186 pg/m^3 (median = 4974 pg/m^3) in the urban $PM_{2.5}$. In this region, PAHs had good correlations with OC and EC except for volatile two-ring PAHs, and the correlations with OC (r = 0.341 −0.747, $p < 0.03$) were more

Table 2
Pearson correlations (r-values) between OPEs and OC and EC in the urban and e-waste areas.[a]

| Urban area									
	EC	TEP	TNBP	TCEP	TCIPP	TPHP	EHDPP	TEHP	TMPP
OC	0.69**	0.10	0.05	− 0.30	− 0.04	0.06	0.31*	0.58**	0.23
EC		− 0.14	− 0.06	− 0.15	− 0.17	0.25	0.22	0.34*	0.10
TEP			− 0.16	− 0.32*	0.04	− 0.27	0.14	0.26	− 0.07
TNBP				0.58**	0.56**	0.15	− 0.11	− 0.01	0.47**
TCEP					0.57**	0.16	− 0.17	− 0.24	0.35*
TCIPP						− 0.09	− 0.06	0.08	0.23
TPHP							0.36*	0.25	0.23
EHDPP								0.82**	0.30
TEHP									0.28
E-waste area									
OC	0.85**	− 0.17	− 0.54*	− 0.39	− 0.42	0.17	0.58**	0.47*	0.54*
EC		− 0.20	− 0.47*	− 0.37	− 0.38	0.28	0.71**	0.65**	0.69**
TEP			0.27	0.30	0.20	0.11	0.27	0.28	0.27
TNBP				0.87**	0.86**	0.01	0.14	0.22	0.03
TCEP					0.75**	− 0.21	0.18	0.26	0.03
TCIPP						< 0.01	0.11	0.22	0.04
TPHP							0.33	0.34	0.51*
EHDPP								0.95**	0.93**
TEHP									0.87**

[a] *p < 0.05, **p < 0.01.
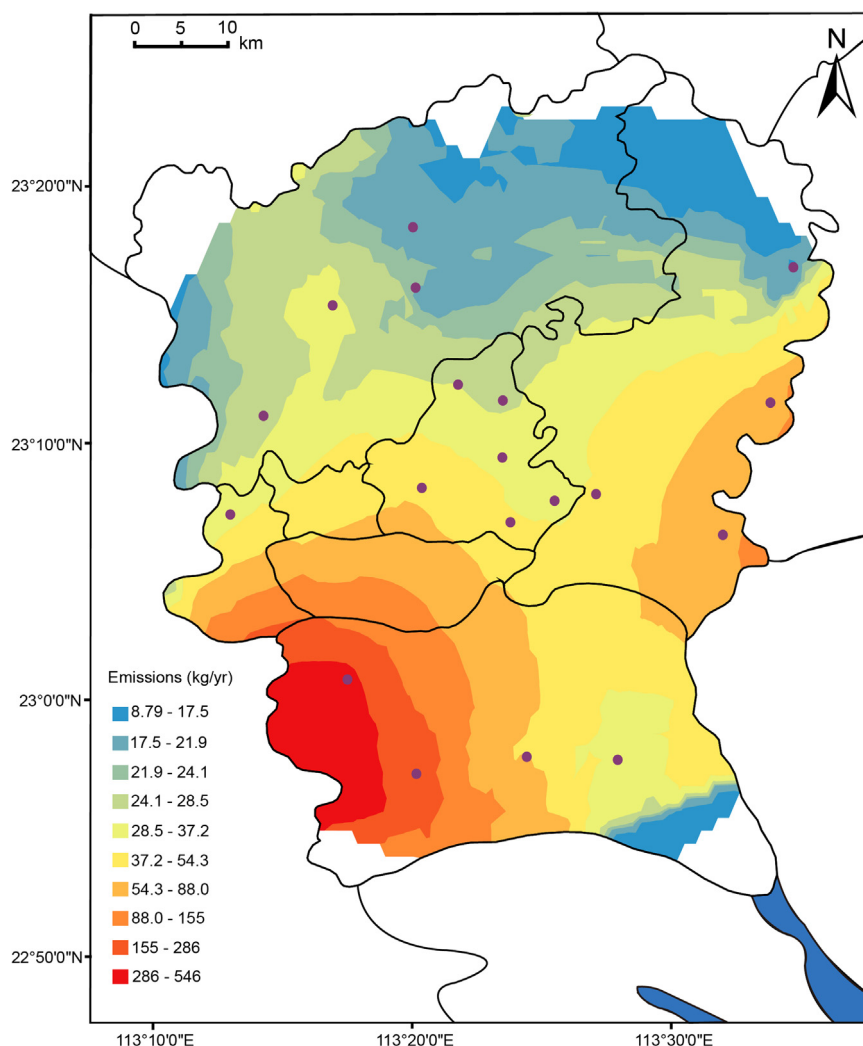
Fig. 3. Spatial distributions of yearly emission of PM$_{2.5}$-bound OPEs in the urban region constructed by the Kriging interpolation method.

significant than those with EC ($r = 0.276 - 0.505$, $p < 0.04$), indicating a similar source. We observed different correlations between OPEs and PAHs (Table S4). TEP correlated with most three- and four-ring PAHs (such as PHE, PYR and, CHR) which are thought to be derived mainly from biomass or coal burning (Ma et al., 2018; Peng et al., 2016; Singh et al., 2013). As discussed above, there is a high likelihood that diffuse sources (such as buildings) play an important role in the occurrence of TEP in the air of this city. The correlations were a result of the partitioning of this compound into particles from biomass and coal burning, which constitute a significant source of urban PM$_{2.5}$ in southern China (Zhou et al., 2018). TNBP, TCEP, and TMPP had negative correlations with some low-molecular weight (2–4 ring) PAHs, suggesting distinct emission sources and/or atmospheric processes. This is also supported by the PAH concentrations at these sites, which were even lower than those (medians = 8060–21,650 pg/m^3) previously measured in PM$_{2.5}$ from non-point sources (Gao et al., 2012). Positive correlations with PAHs (except for a few 2–3 ring-compounds) were found only for EHDPP and TEHP, similar to the correlations with OC and EC.

In the e-waste region, the total PAH concentrations ranged from 2671 to 7473 pg/m^3, with a median of 4610 pg/m^3, which were not significantly different from the levels in the urban region. It is very surprising that significant correlations were not found between most PAHs and OC and EC. The aforementioned correlations between OPEs and OC/EC indicated an e-waste recycling source for OC and EC. This finding suggests that e-waste recycling may be not the primary source

of PAHs in PM$_{2.5}$ in this rural region. PAH molecular diagnostic ratios of FLA/(FLT + PYR) (0.43–0.60, median = 0.48) in the urban area suggest sources of coal/biomass burning and liquid fuel combustion, while in the e-waste area, the ratios (0.48–0.55, median = 0.52) indicated more robust coal/biomass burning source. The IPY/(IPY + BghiP) ratios in the e-waste area also indicated a more significant impact by coal/biomass burning sources in this rural area (Fig. S4). Only a few OPEs (EHDPP, TEHP, and TMPP) showed significant correlations with some PAHs, similar to the observation in the urban region.

Overall, the correlations revealed that around the sites involving industrial/business activities, most OPEs and PAHs in the PM$_{2.5}$ in the study regions had different origins. However, in both regions, EHDPP and TEHP (and TMPP in the e-waste region) were likely associated with combustion or thermal sources.

3.3. Emissions to the air

The yearly emission rates of ΣOPEs from the 20 point source sites in the urban region were estimated between 8.8 and 546 kg/yr, with an average of 73 kg/yr, assuming a constant daily emission rate for a certain site (Table S5). The OPE emissions from these industrial sources were not dependent on the covering areas of the sources. This is probably because the industrial parks in the urban region are usually a complex of various industries, and some are not a significant emission source of OPEs. Estimated total emissions were highest at SB and XP industrial parks, the two industrial parks that showed the highest

atmospheric OPE concentrations. The high emissions were predominantly contributed by TNBP (84%) and TMPP (93%) from these two industrial parks, respectively, in which manufacturing of household products, plastics, or electronics are primary industries. The emissions of TEP (2.9 kg/yr) and TCIPP (6.2 kg/yr) (both are used in building/construction materials) were highest at the electronics shopping center in the business zone. TCEP emissions (15 kg/yr) near an automobile factory and TPHP emission (12 kg/yr) at an industrial park related to metals and electronics were pronouncedly higher than other sites (0.4–3.6 kg/yr for TCEP and 0.5–11 kg/yr for TPHP). High emissions of EHDPP (22 kg/yr) and TEHP (20 kg/yr) were found at the waste recycling enterprise relative to other sources, but this was not found at the waste incineration plant and the e-waste region. The emission rates of OPEs from the four e-waste recycling parks were between 27 and 45 kg/yr with an average of 33 kg/yr.

The total OPE emissions from the 20 investigated industrial sites were 1460 kg/yr. There are approximately 100 comparable industrial parks in Guangzhou. Thus, emission estimates for these sources can be extrapolated to emission inventories for the whole city. The 25th and 50th percentiles of the emission rates of the 20 sites were used, given that a considerable number of uninvestigated industrial parks are of a smaller scale than those investigated. We estimated that the industrial activities in Guangzhou release approximately 3228–4452 kg OPEs into the air each year. The four e-waste recycling parks emit approximately 133 kg OPEs into the air every year, which was much lower than those in the urban region, because the magnitude of the industries in the urban region was much larger than that in the e-waste region. The spatially specific emission inventories of OPE emissions (Fig. 3) indicated that industrial activities in southern Guangzhou apparently emitted more of these pollutants.

Here, we estimated only the emissions associated with the PM$_{2.5}$ fraction. Because the particle size distributions of OPEs are unknown, emissions associated with larger size particles cannot be estimated. Wolschke et al. (2016) investigated the gas/particle partitioning of OPEs and found that the individual gas-phase OPEs accounted for approximately 10–90%. Based on these proportions, individual gas-phase emission rate at each site was estimated. The average gaseous emission rates of ΣOPEs were estimated to be 118 kg/yr (11–556 kg/yr) in the urban region and 46 kg/yr (38–51 kg/yr) in the e-waste region. The total atmospheric (PM$_{2.5}$ + gas) emission inventories from these sources were 3930 and 362 kg/yr in the two regions, and gas contributed to approximately 60% of the emissions.

It should be noted that the emission results contain large uncertainties. They can be attributed to the temporal variations in the emissions and changing weather conditions due to the small sample size, in addition to measurement of the concentrations and diffuse sources around sampling sites. This study probably overestimates the emissions without considering the potential urban non-point emissions (e.g., from indoors). The gaseous emission seems to be overestimated on the basis of applied gas/particle partitioning coefficients (in equilibrium). However, there was a large uncertainty in the coefficients for emissions from these point sources (depending on the releasing mechanisms), leading to substantial uncertainty in the gaseous emission results.

4. Conclusion

The PM$_{2.5}$-bound OPE concentrations displayed great variations among the industrial point sources and the e-waste recycling facilities in southern China. High concentrations were associated with the electrical/electronics, plastics, waste recycling, and certain chemical industries, and lower concentrations were found for the machinery, paper, clothing, and furnishing industries. Varying OPE compositions were also observed at these sites, depending on the industrial activities. There were no significant correlations between most OPEs, and these pollutants generally showed weak correlations with OC, EC, and PAHs

in both regions, suggesting different emission mechanisms or atmospheric processes. The estimated amount of atmospheric OPEs emitted from the industrial sources in the urban region was one order of magnitude higher than that from the e-waste recycling. To the best of our knowledge, this is the first effort to model the emissions of OPEs from industrial and e-waste recycling activities to the atmosphere.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envres.2018.08.015.

References

Ahrens, L., Shoeib, M., Harner, T., Lee, S.C., Guo, R., Reiner, E.J., 2011. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. Environ. Sci. Technol. 45, 8098–8105. https://doi.org/10.1021/es1036173.

Agency for Toxic Substances and Disease Registry, 2009. Draft toxicological profile for phosphate ester flame retardants. Prepared for: US Public Health Service, Agency for Toxic Substances and Disease Registry.

Bi, X.H., Simoneit, B.R.T., Wang, Z.Z., Wang, X.M., Sheng, G.Y., Fu, J.M., 2010. The major components of particles emitted during recycling of waste printed circuit boards in a typical e-waste workshop of South China. Atmos. Environ. 44, 4440–4445. https://doi.org/10.1016/j.atmosenv.2010.07.040.

Butt, C.M., Congleton, J., Hoffman, K., Fang, M., Stapleton, H.M., 2014. Metabolites of organophosphate flame retardants and 2-ethylhexyl tetrabromobenzoate in urine from paired mothers and toddlers. Environ. Sci. Technol. 48, 10432–10438. https://doi.org/10.1021/es5025299.

Cao, D., Guo, J., Wang, Y., Li, Z., Liang, K., Corcoran, M.B., Hosseini, S., Bonina, S.M., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Liu, J., Li, A., Jiang, G., 2017. Organophosphate esters in sediment of the Great Lakes. Environ. Sci. Technol. 51, 1441–1449. https://doi.org/10.1021/acs.est.6b05484.

Castro-Jimenez, J., Berrojalbiz, N., Pizarro, M., Dachs, J., 2014. Organophosphate ester (OPE) flame retardants and plasticizers in the open Mediterranean and Black Seas atmosphere. Environ. Sci. Technol. 48, 3203–3209. https://doi.org/10.1021/es405337g.

Castro-Jimenez, J., Gonzalez-Gaya, B., Pizarro, M., Casal, P., Pizarro-Alvarez, C., Dachs, J., 2016. Organophosphate ester flame retardants and plasticizers in the global oceanic atmosphere. Environ. Sci. Technol. 50, 12831–12839. https://doi.org/10.1021/acs.est.6b04344.

Csiszar, S.A., Diamond, M.L., Daggupaty, S.M., 2014. The magnitude and spatial range of current-use urban PCB and PBDE emissions estimated using a coupled multimedia and air transport model. Environ. Sci. Technol. 48, 1075–1083. https://doi.org/10.1021/es403080t.

Diefenbacher, P.S., Gerecke, A.C., Bogdal, C., Hungerbuhler, K., 2016. Spatial distribution of atmospheric PCBs in Zurich, Switzerland: do joint sealants still matter? Environ. Sci. Technol. 50, 232–239. https://doi.org/10.1021/acs.est.5b04626.

Ding, J., Xu, Z., Huang, W., Feng, L., Yang, F., 2016. Organophosphate ester flame retardants and plasticizers in human placenta in Eastern China. Sci. Total Environ. 554–555, 211–217. https://doi.org/10.1016/j.scitotenv.2016.02.171.

Gao, B., Guo, H., Wang, X.M., Zhao, X.Y., Ling, Z.H., Zhang, Z., Liu, T.Y., 2012. Polycyclic aromatic hydrocarbons in PM2.5 in Guangzhou, southern China: spatiotemporal patterns and emission sources. J. Hazard. Mater. 239–240, 78–87. https://doi.org/10.1016/j.jhazmat.2012.07.068.

Guangzhou Municipal Statistics Bureau, Guangzhou Survery Office of National Bureau of Statistics, 2017. Guangzhou Statistical Yearbook. China Statistics Print, China. IBSN: 978-7-5037-84567-8.

Guo, J.H., Romanak, K., Westenbroek, S., Hites, R.A., Venier, M., 2017. Current-use flame retardants in the water of Lake Michigan tributaries. Environ. Sci. Technol. 51, 9960–9969. https://doi.org/10.1021/acs.est.7b01294.

He, C.T., Zheng, J., Qiao, L., Chen, S.J., Yang, J.Z., Yuan, J.G., Yang, Z.Y., Mai, B.X., 2015. Occurrence of organophosphorus flame retardants in indoor dust in multiple microenvironments of Southern China and implications for human exposure. Chemosphere 133, 47–52. https://doi.org/10.1016/j.chemosphere.2015.03.043.

He, M.J., Lu, J.F., Ma, J.Y., Wang, H., Du, X.F., 2018. Organophosphate esters and phthalate esters in human hair from rural and urban areas, Chongqing, China: concentrations, composition profiles and sources in comparison to street dust. Environ. Pollut. 237, 143–153. https://doi.org/10.1016/j.envpol.2018.02.040.

Khan, M.U., Li, J., Zhang, G., Malik, R.N., 2016a. First insight into the levels and distribution of flame retardants in potable water in Pakistan: an underestimated

problem with an associated health risk diagnosis. Sci. Total Environ. 565, 346–359. https://doi.org/10.1016/j.scitotenv.2016.04.173.

Khan, M.U., Li, J., Zhang, G., Malik, R.N., 2016b. New insight into the levels, distribution and health risk diagnosis of indoor and outdoor dust-bound FRs in colder, rural and industrial zones of Pakistan. Environ. Pollut. 216, 662–674. https://doi.org/10.1016/j.envpol.2016.06.030.

Kim, J.W., Isobe, T., Muto, M., Tue, N.M., Katsura, K., Malarvannan, G., Sudaryanto, A., Chang, K.H., Prudente, M., Viet, P.H., Takahashi, S., Tanabe, S., 2014. Organophosphorus flame retardants (PFRs) in human breast milk from several Asian countries. Chemosphere 116, 91–97. https://doi.org/10.1016/j.chemosphere.2014.02.033.

Kurokawa, Y., Takahiko, M., Matayoshi, N., Satoshi, T., Kazumi, F., 1998. Distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in various sizes of airborne particles. Chemosphere 37, 2161–2171.

Lai, S., Xie, Z., Song, T., Tang, J., Zhang, Y., Mi, W., Peng, J., Zhao, Y., Zou, S., Ebinghaus, R., 2015. Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea. Chemosphere 127, 195–200. https://doi.org/10.1016/j.chemosphere.2015.02.015.

Leisewitz, A., Kruse, H., Schramm, E., 2000. Substituting environmentally relevant flame retardants: assessment fundamentals. Environment research plan of the German Federal Ministry for the environment, nature conservation and nuclear safety (research, report).

Liu, D., Lin, T., Shen, K., Li, J., Yu, Z., Zhang, G., 2016a. Occurrence and concentrations of halogenated flame retardants in the atmospheric fine particles in Chinese cities. Environ. Sci. Technol. 50, 9846–9854. https://doi.org/10.1021/acs.est.6b01685.

Liu, R., Lin, Y., Liu, R., Hu, F., Ruan, T., Jiang, G., 2016b. Evaluation of two passive samplers for the analysis of organophosphate esters in the ambient air. Talanta 147, 69–75. https://doi.org/10.1016/j.talanta.2015.09.034.

Lu, S.Y., Li, Y.X., Zhang, T., Cai, D., Ruan, J.J., Huang, M.Z., Wang, L., Zhang, J.Q., Qiu, R.L., 2017a. Effect of e-waste recycling on urinary metabolites of organophosphate flame retardants and plasticizers and their association with oxidative stress. Environ. Sci. Technol. 51, 2427–2437. https://doi.org/10.1021/acs.est.6b05462.

Lu, Z., Martin, P.A., Burgess, N.M., Champoux, L., Elliott, J.E., Baressi, E., De Silva, A.O., de Solla, S.R., Letcher, R.J., 2017b. Volatile methylsiloxanes and organophosphate esters in the eggs of european starlings (Sturnus vulgaris) and congeneric gull species from locations across Canada. Environ. Sci. Technol. 51, 9836–9845. https://doi.org/10.1021/acs.est.7b03192.

Ma, W.L., Liu, L.Y., Jia, H.L., Yang, M., Li, Y.F., 2018. PAHs in Chinese atmosphere part I: concentration, source and temperature dependence. Atmos. Environ. 173, 330–337. https://doi.org/10.1016/j.atmosenv.2017.11.029.

Ma, Y., Xie, Z., Lohmann, R., Mi, W., Gao, G., 2017. Organophosphate ester flame retardants and plasticizers in ocean sediments from the North Pacific to the Arctic Ocean. Environ. Sci. Technol. 51, 3809–3815. https://doi.org/10.1021/acs.est.7b00755.

Meeker, J.D., Stapleton, H.M., 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. Environ. Health Perspect. 118, 318–323. https://doi.org/10.1289/ehp.0901332.

Moller, A., Xie, Z., Caba, A., Sturm, R., Ebinghaus, R., 2011. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. Environ. Pollut. 159, 3660–3665. https://doi.org/10.1016/j.envpol.2011.07.022.

Okeme, J.O., Yang, C., Abdollahi, A., Dhal, S., Harris, S.A., Jantunen, L.M., Tsirlin, D., Diamond, M.L., 2018. Passive air sampling of flame retardants and plasticizers in Canadian homes using PDMS, XAD-coated PDMS and PUF samplers. Environ. Pollut. 239, 109–117. https://doi.org/10.1016/j.envpol.2018.03.103.

Okonski, K., Degrendele, C., Melymuk, L., Landlova, L., Kukucka, P., Vojta, S., Kohoutek, J., Cupr, P., Klanova, J., 2014. Particle size distribution of halogenated flame retardants and implications for atmospheric deposition and transport. Environ. Sci. Technol. 48, 14426–14434. https://doi.org/10.1021/es5044547.

Ou, Y.X., Lang, L.C., 2010. Analysis and prediction of global flame retardants market. Plast. Addit. 1–4.

Peng, N., Li, Y., Liu, Z., Liu, T., Gai, C., 2016. Emission, distribution and toxicity of polycyclic aromatic hydrocarbons (PAHs) during municipal solid waste (MSW) and coal co-combustion. Sci. Total Environ. 565, 1201–1207. https://doi.org/10.1016/j.scitotenv.2016.05.188.

Ren, G., Chen, Z., Feng, J., Ji, W., Zhang, J., Zheng, K., Yu, Z., Zeng, X., 2016. Organophosphate esters in total suspended particulates of an urban city in East China. Chemosphere 164, 75–83. https://doi.org/10.1016/j.chemosphere.2016.08.090.

Salamova, A., Hermanson, M.H., Hites, R.A., 2014. Organophosphate and halogenated flame retardants in atmospheric particles from a European Arctic site. Environ. Sci. Technol. 48, 6133–6140. https://doi.org/10.1021/es500911d.

Salamova, A., Ma, Y., Venier, M., Hites, R.A., 2013. High levels of organophosphate flame retardants in the Great lakes atmosphere. Environ. Sci. Technol. Lett. 1, 8–14. https://doi.org/10.1021/ez400034n.

Salamova, A., Peverly, A.A., Venier, M., Hites, R.A., 2016. Spatial and temporal trends of particle phase organophosphate ester concentrations in the atmosphere of the Great Lakes. Environ. Sci. Technol. 50, 13249–13255. https://doi.org/10.1021/acs.est.6b04789.

Shanahan, C.E., Spak, S.N., Martinez, A., Hornbuckle, K.C., 2015. Inventory of PCBs in Chicago and opportunities for reduction in airborne emissions and human exposure. Environ. Sci. Technol. 49, 13878–13888. https://doi.org/10.1021/acs.est.5b00906.

Shoeib, M., Schuster, J., Rauert, C., Su, K., Smyth, S.A., Harner, T., 2016. Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants. Environ. Pollut. 218, 595–604. https://doi.org/10.1016/j.envpol.2016.07.043.

Singh, D.P., Gadi, R., Mandal, T.K., Saud, T., Saxena, M., Sharma, S.K., 2013. Emissions estimates of PAH from biomass fuels used in rural sector of Indo-Gangetic Plains of India. Atmos. Environ. 68, 120–126. https://doi.org/10.1016/j.atmosenv.2012.11.042.

Su, G., Letcher, R.J., Yu, H., 2016. Organophosphate flame retardants and plasticizers in aqueous solution: pH-dependent hydrolysis, kinetics, and pathways. Environ. Sci. Technol. 50, 8103–8111. https://doi.org/10.1021/acs.est.6b02187.

Suhring, R., Diamond, M.L., Scheringer, M., Wong, F., Pucko, M., Stern, G., Burt, A., Hung, H., Fellin, P., Li, H., Jantunen, L.M., 2016. Organophosphate esters in Canadian Arctic air: occurrence, levels and trends. Environ. Sci. Technol. 50, 7409–7415. https://doi.org/10.1021/acs.est.6b00365.

Van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A., 2011. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. Environ. Int. 37, 454–461. https://doi.org/10.1016/j.envint.2010.11.010.

Van der Veen, I., De Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153. https://doi.org/10.1016/j.chemosphere.2012.03.067.

Vojta, S., Melymuk, L., Klanova, J., 2017. Changes in flame retardant and legacy contaminant concentrations in indoor air during building construction, furnishing, and use. Environ. Sci. Technol. 51, 11891–11899. https://doi.org/10.1021/acs.est.7b03245.

Vykoukalova, M., Venier, M., Vojta, S., Melymuk, L., Becanova, J., Romanak, K., Prokes, R., Okeme, J.O., Saini, A., Diamond, M.L., Klanova, J., 2017. Organophosphate esters flame retardants in the indoor environment. Environ. Int. 106, 97–104. https://doi.org/10.1016/j.envint.2017.05.020.

Wang, C., Cai, J., Chen, R., Shi, J., Yang, C., Li, H., Lin, Z., Meng, X., Liu, C., Niu, Y., Xia, Y., Zhao, Z., Li, W., Kan, H., 2017. Personal exposure to fine particulate matter, lung function and serum club cell secretory protein (Clara). Environ. Pollut. 225, 450–455. https://doi.org/10.1016/j.envpol.2017.02.068.

Wei, G.L., Li, D.Q., Zhuo, M.N., Liao, Y.S., Xie, Z.Y., Guo, T.L., Li, J.J., Zhang, S.Y., Liang, Z.Q., 2015. Organophosphorus flame retardants and plasticizers: sources, occurrence, toxicity and human exposure. Environ. Pollut. 196, 29–46. https://doi.org/10.1016/j.envpol.2014.09.012.

Wolschke, H., Sühring, R., Mi, W., Möller, A., Xie, Z., Ebinghaus, R., 2016. Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast. Atmos. Environ. 137, 1–5. https://doi.org/10.1016/j.atmosenv.2016.04.028.

Yadav, I.C., Devi, N.L., Li, J., Zhang, G., Covaci, A., 2018. Concentration and spatial distribution of organophosphate esters in the soil-sediment profile of Kathmandu Valley, Nepal: implication for risk assessment. Sci. Total Environ. 613–614, 502–512. https://doi.org/10.1016/j.scitotenv.2017.09.039.

Yadav, I.C., Devi, N.L., Zhong, G., Li, J., Zhang, G., Covaci, A., 2017. Occurrence and fate of organophosphate ester flame retardants and plasticizers in indoor air and dust of Nepal: implication for human exposure. Environ. Pollut. 229, 668–678. https://doi.org/10.1016/j.envpol.2017.06.089.

Zhang, Y.L., Kawamura, K., Agrios, K., Lee, M., Salazar, G., Szidat, S., 2016. Fossil and nonfossil sources of organic and elemental carbon aerosols in the outflow from Northeast China. Environ. Sci. Technol. 50, 6284–6292. https://doi.org/10.1021/acs.est.6b00351.

Zhao, F., Wan, Y., Zhao, H., Hu, W., Mu, D., Webster, T.F., Hu, J., 2016. Levels of blood organophosphorus flame retardants and association with changes in human sphingolipid homeostasis. Environ. Sci. Technol. 50, 8896–8903. https://doi.org/10.1021/acs.est.6b02474.

Zhou, S., Davy, P.K., Huang, M., Duan, J., Wang, X., Fan, Q., Chang, M., Liu, Y., Chen, W., Xie, S., Ancelet, T., Trompetter, W.J., 2018. High-resolution sampling and analysis of ambient particulate matter in the Pearl River Delta region of southern China: source apportionment and health risk implications. Atmos. Chem. Phys. 18, 2049–2064. https://doi.org/10.5194/acp-18-2049-2018.