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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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A R T I C L E I N F O

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A B S T R A C T

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 $125.4 \pm 23.7\%$ for TPP-d_{21}, $80.8 \pm 10.4\%$ for TNBP-d_{27}, and $98.0 \pm 9.4\%$ 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 =