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Organophosphate esters in total suspended particulates of an urban city in East China

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HIGHLIGHTS

- OPEs were measured in TSP over 1 year at two sampling sites in Shanghai.
- ΣOPEs at the sub-urban site were amongst the highest concentrations yet reported.
- Composition profile for ΣOPEs concentrations was different between the two sites.
- Human exposures to the OPEs via inhalation were estimated in Shanghai.

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ABSTRACT

Organophosphate esters (OPEs) are ubiquitous contaminants in the environment, but little is known on the occurrence and distribution of OPEs in the background atmosphere of urban environments. In this study, air samples were collected from two sites in the city of Shanghai, a typical fast developing metropolitan of East China, for investigating the concentration levels, composition profiles, potential sources and human health risk to OPEs. The annual average (median) values of total suspended particulates ΣOPEs concentrations were 19.4 (16.6) and 6.6 (4.4) ng/m^3 for the sub-urban (BS) and urban (XJH) sampling sites, respectively. The ΣOPEs concentrations at BS were significantly higher than those at XJH ($P < 0.01$), suggesting that more local sources of these compounds in the sub-urban area. The composition profile for ΣOPEs concentrations was different between the two sites, possibly because they originated from different sources. At BS, the dominated OPEs profile was TPhP followed by TCPP and TCEP > TDCPP > TBP > TCP, accounting for 37.0%, 19.6%, 15.8%, 11.8%, 11.0% and 4.2% of the ΣOPEs, respectively. Comparatively, chlorinated OPEs (TCEP, TCPP, and TDCPP) were major contributors to ΣOPEs concentrations at XJH, with the sum of all three chlorinated OPEs concentrations comprising 69.0% of the ΣOPEs. Based on the measured data in the present study human daily intake of each OPEs through particulate inhalation were estimated using a Monte Carlo simulation and the preliminary exposure assessments suggested a low risk of OPEs via inhalation in Shanghai.

1. Introduction

Flame retardants (FRs) are widely used around the world to prevent combustion and to delay the spread of fire after ignition. However, researches have shown that some halogenated FRs are potentially toxic, bio-accumulative, ubiquitous and persistent in the environment (Fromme et al., 2016). As a result, stricter policies had been placed on some brominated flame retardants (BFRs), especially for polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), which were recently included in the Stockholm Convention on Persistent Organic Pollutants (Koch et al., 2015; Fromme et al., 2016). They might be replaced directly by some unregulated FRs, these are the cases of Organophosphate esters (OPEs). OPEs are derivates of phosphoric acid with different

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substitutes including alkyl chains, aromatic functions, as well as partly halogenated alkyl chains phosphate. Generally, halogenated OPEs are mainly used as flame retardants, whereas non-halogenated OPEs are predominantly used as plasticizers and for other applications (van der Veen and de Boer, 2012). OPEs have been used in electronic equipments, plastics products, rubbers, textiles and building materials for several decades (Reemtsma et al., 2008). Similar to PBDEs and HBCDs, OPEs are used additively in the material, which means that they are not fixed in the polymer product through chemical binding and could easily leak into the environment via volatilization, abrasion, and dissolution. Once in the environment, OPEs would undergo long-range atmospheric transport to even remote regions of the world (Möller et al., 2012; Salamova et al., 2014a). As a result of its historic and continued use and tendency for long-range atmospheric transport, nowadays, OPEs have been detected in almost every environmental compartment, including surface water and sediment (Cao et al., 2014a; Regnery and Puettmann, 2010), wastewater and sludge (Pang et al., 2016; Zeng et al., 2014), air and dust (Ali et al., 2012; Cao et al., 2014b), fish and biota (Sundkvist et al., 2010; Kim et al., 2011; Chen et al., 2012), and human samples (Shah et al., 2006; Sundkvist et al., 2010; Ding et al., 2016). Their metabolites were also found in human urine (Cooper et al., 2011; Carignan et al., 2013). Risk assessments have recognized the carcinogenicity, high toxicity and environmental persistence of some OPEs, such as tris (chloroethyl) phosphate (TCEP) and tris (2,3-dichloropropyl) phosphate (TDCPP), and also neurotoxic effects were found for tri-*n*-butyl phosphate (TBP) and triphenyl phosphate (TPhP) (Reemtsma et al., 2008). These results indicated that OPEs had widely influenced the environment, and were potential toxicity to human.

China is an important area of production of OPEs, where OPEs have been produced by more than 10 enterprises (www http://china.guidechem.com/). The accurate determination of OPEs production in China is difficult and the only available data is the production capacity of some big manufacturers. This data shows that in China the total OPEs annual production volume had reached more than 10,000 t in 2011. In addition, the production of OPEs are expected to gradually increase in connection with their excellent flame retardant performance and the forbidden of PBDEs and HBCD. Moreover, China is a rapidly developing country. With the fast growth of the manufacturing industry, the market demand for OPEs has increased markedly, and the production and consumption of large amounts of OPEs would lead to increasing release and high levels in environmental compartments. Several studies on OPEs in marine atmospheric environment have illustrated that China is an important source for the marine environment (Möller et al., 2012; Lai et al., 2015). Recently, scientific research as well as public interest on OPEs has been increased in China. OPEs have recently been reported in various environmental media in China including indoor air/dust (Cao et al., 2014b; He et al., 2015), drinking water (Li et al., 2014; Ding et al., 2015), surface water (Shi et al.; Hu et al., 2014), wastewater (Zeng et al., 2014), sediments (Cao et al., 2014a), sewage sludge and soil (Gao et al., 2016; Lu et al., 2014). In addition to production and usage of OPEs, China has received a large fraction of electronic waste (E-waste) from developed countries, treatment of E-waste, which has shown to be an important source of PBDEs in the Asian atmosphere, might be another important source of OPs in the outdoor environment, too. High levels of OPEs have been observed in indoor dust from the E-waste area in China (Bi et al., 2010).

Studies on OPEs in marine atmospheric environment from North-Sea proved that OPEs would undergo long-range atmospheric transport to even remote regions of the world (Möller et al., 2011). However, the long-range transport route of OPEs via the atmosphere still remains unclear. Globally, study on OPEs in the ambient atmosphere is not prominent and the limited data are primarily come from remote or un-urbanized area. Air concentrations of OPEs have been measured at background locations in the North Sea of German (Möller et al., 2011), the European Arctic (Salamova et al., 2014a), the Mediterranean Sea and Black Sea (Castro-Jimenez et al., 2014), and South China Sea (Lai et al., 2015), as well as in occupational settings such as electronic recycling and dismantling plants and domestic and workplace environments (Bi et al., 2010). By contrast, only a handful studies on the atmospheric distribution of OPEs in urban locations were conducted in the Great Lake region (Salamova et al., 2014b), Finland (Marklund et al., 2005), Japan (Ohura et al., 2006) and China (Yin et al., 2015; Liu et al., 2016). These investigations concluded that urban centers were a significant source of OPEs. Given that OPEs are used in commercial products that are used by people, monitoring of these compounds in urban air is important to better understand their sources and fate. In this study, we investigated the atmospheric OPEs through intensive sampling in an economically fast growing city, Shanghai, China. Shanghai is an important commercial and industrial base and a typical metropolitan city in East China. Sampling was carried out over one year (January 2008 to November 2008). The aims of the study were to: i) report the concentrations and compositional profiles of OPEs in urban air; ii) investigate the relationships and correlations among these compounds; iii) illustrate the potential sources of these compounds; and iv) determine human inhalation exposure for OPEs.

2. Experimental procedure

2.1. Sampling site and techniques

Two sampling sites (Fig. S1), including one typical sub-urban site and one urban site, were selected for collecting air using integrated high-volume air samplers in 2008. The sub-urban site is located in the Baoshan District (BS; latitude 31°19′N, longitude 121°23′E), which represent an old industrial and traffic center. This sampling site is surrounded by small cement and chemical industrial plants as well as by residential areas. The urban site is located in Xujiahui District (XJH; latitude 31°10′N, longitude 121°25′E), which represent a prosperous commercial and traveling center. Surrounding the sampling site are mainly residential and office/commercial buildings. Samplers were deployed on top of high buildings with heights of 15, and 20 m at XJH and BS, respectively. Twenty-four-hour air samples were collected every 5–10 days (without rain or snow) during January to December, 2008. Over each sampling period, approximately 1400 m^3 of air was pumped through quartz fiber filters ([QFFs], 20.3 cm × 25.4 cm, pore size: 0.46 μm) to trap the suspended particulate matters and subsequently through 6.5 cm in diameter × 7.5 cm in thickness polyurethane foam (PUF) to trap the gaseous matters. A total of 55 and 61 samples were obtained for BS and XJH, respectively. After sampling, the QFFs and PUF were packaged with aluminum foil and stored at −20 °C until analyzed.

2.2. Chemicals and materials

Seven organophosphate ester standards were purchased from Sigma-Aldrich (St. Louis, MO, USA), including tri-*n*-butyl phosphate (TBP, 99%), tris (2-butoxyethyl) phosphate (TBEP, 94%), tris (chloroethyl) phosphate (TCEP, 97%), tris (2-chloroisopropyl) phosphate (TCPP, 99.5%), tris (2,3-dichloropropyl) phosphate (TDCPP, 97%), triphenyl phosphate (TPhP, 99%) and tricresyl phosphate (TCP, 90%). Surrogate standard tri-*n*-butyl-d_{27} phosphate (d_{27}-TBP, 98%) was purchased from C/D/N Isotopes Inc. (Quebec, Canada). All solvents and other chemicals used for the analysis were *n*-hexane (Hex),