



# Occurrence of organophosphorus flame retardants in indoor dust in multiple microenvironments of southern China and implications for human exposure



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## HIGHLIGHTS

- OPFRs were measured in indoor dust from four microenvironments in southern China.
- The OPFR concentrations in indoor dust from the e-waste area were highest.
- The OPFR compositions reflected three types of OPFR sources to the indoor dust.
- Concerns should be paid to the exposure of toddlers in the e-waste area to OPFRs.

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## ABSTRACT

Organophosphorus flame retardants (OPFRs) are important alternatives to brominated flame retardants (BFRs), but information on their contamination of the environment in China is rare. We examined the occurrence of 12 OPFRs in indoor dust in four microenvironments of southern China, including a rural electronic waste (e-waste) recycling area, a rural non-e-waste area, urban homes, and urban college dormitory rooms. The OPFR concentrations (with a median of 25.0  $\mu\text{g g}^{-1}$ ) were highest in the e-waste area, and the concentrations in other three areas were lower and comparable (7.48–11.0  $\mu\text{g g}^{-1}$ ). The levels of OPFRs in the present study were generally relatively lower than the levels of OPFRs found in Europe, Canada, and Japan because BFRs are still widely used as the major FRs in China. The composition profile of OPFRs in the e-waste area was dominated by tricresyl phosphate (TCP) (accounting for 40.7%, on average), while tris(2-chloroethyl) phosphate (TCEP) was the most abundant OPFR (64.4%) in the urban areas (homes and college dormitories). These two distribution patterns represent two OPFR sources (i.e., emissions from past e-waste and from current household products and building materials). The difference in the OPFR profiles in the rural area relative to the OPFR profiles in the urban and e-waste areas suggests that the occurrence of OPFRs is due mainly to emissions from characteristic household products in rural homes. Although human exposures to all the OPFRs were under the reference doses, the health risk for residents in the e-waste area is a concern, considering the poor sanitary conditions in this area and exposure from other sources.

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## 1. Introduction

Flame retardants are an important class of additives for a wide range of commercial products to meet rigorous flammability

standards. With the phase-out or restriction of brominated flame retardants (BFRs), the consumption of BFRs is declining, while the market demand for alternative flame retardants is growing (Van der Veen and de Boer, 2012). Organophosphorus flame retardants (OPFRs), often used in furniture, building material, and electronic equipment (Stapleton et al., 2014; Takigami et al., 2009), are proposed as alternatives for polybrominated diphenyl ethers (PBDEs). For example, tris(2-chloroethyl) phosphate (TCEP),

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tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3-dichloroisopropyl)phosphate (TDCP) are used as replacements for penta-BDE (Dodson et al., 2012), and triphenyl phosphate (TPhP) is a potential deca-BDE alternative (USEPA, 2007). Some OPFRs are also used as plasticizers and additives in hydraulic fluids (Ali et al., 2012). The global market for OPFRs was estimated to be 150 000 metric tons in 2010 (Ou, 2011).

The physicochemical properties such as octanol-water partition coefficient ( $K_{ow}$ ), water solubility, and vapor pressure of OPFRs differ greatly (Reemtsma et al., 2008; Van der Veen and de Boer, 2012), and these chemicals are usually mixed into (not chemically bonded to) the polymer. Consequently, the OPFRs may be released into the environment through volatilization, abrasion, or leaching during production, use, and disposal of treated products (Marklund et al., 2005; Van den Eede et al., 2011). There is growing evidence of the extensive occurrence of OPFRs in various environmental media as well as human urine and milk (Cristale and Lacorte, 2013; Hoffman et al., 2014; Marklund et al., 2005; Sundkvist et al., 2010; Van den Eede et al., 2013).

Because of their wide application in consumer products and building materials, OPFRs in the indoor environment have received significant attention. A number of studies concerning the occurrence of OPFRs in dust or air in homes, offices, and cars have found that OPFRs show significantly higher levels than BFRs in many countries (Ali et al., 2012; Brommer et al., 2012; Fromme et al., 2014). Indoor dust is a crucial daily exposure source of OPFRs for humans, especially for children. Significant correlations between the metabolite levels in children's urine and the dust or air concentrations in daycare centers have been observed for some OPFRs by Fromme et al. (2014). OPFRs are reported to be easily absorbed after ingestion and inhalation (EU, 2008, 2009; HSDB, 2013). While evidence of the toxicological effects of OPFRs on human health is rare, animal experiments revealed that TCEP, TPhP and tricresyl phosphate (TCP) are neurotoxic and carcinogenic in animals, and TDCP and tris(2-butoxyethyl) phosphate (TBEP) have adverse effects on the liver and kidneys (ATSDR, 2012; EU, 2008, 2009; UKEA, 2009). These results raise concerns about the health risk of exposure to OPFRs.

OPFRs have been used in diverse products for decades, including electrical and electronic equipment (Van der Veen and de Boer, 2012). Therefore, electrical and electronic waste (e-waste) may be a significant potential source of OPFRs. Much of the e-waste generated in developed countries ends up in developing countries, where e-waste is dismantled in a primitive way (Tian et al., 2011). Numerous studies have revealed the serious environmental contamination resulting from BFRs and heavy metals released from dismantling e-waste in developing regions (Chen et al., 2014; Luo et al., 2009; Wu et al., 2008; Zheng et al., 2010). At an e-waste site in China, Bi et al. (2010) found that TPhP was one of the major components of the organic matter found in particles emitted during printed circuit board recycling. To our knowledge, however, little is known about the environmental occurrence of OPFRs associated with e-waste recycling. Moreover, China is a large FR consumer because of its rapid economic development, and the demands for OPFRs are expected to increase approximately 15% annually (Ou, 2011). Nevertheless, limited data on the environmental contamination levels of OPFRs have been reported.

In the present study, we measured the concentrations of a number of OPFRs in indoor dust in the rural region (including e-waste and non-e-waste areas) and in the urban region (including homes and college dormitory rooms) in southern China. We compared the distribution patterns of OPFRs in the four microenvironments and explored their sources in indoor dust. Moreover, human exposure to these chemicals through dust ingestion was estimated to understand the health risk to the residents posed by OPFRs.

## 2. Materials and methods

### 2.1. Sample collection

Indoor dust samples were collected from four microenvironments in two regions: homes and college dormitories in Guangzhou City (urban region) and e-waste recycling workshops and homes in Qingyuan (rural region) in southern China. Guangzhou is a metropolis located in the Pearl River Delta region, an important city cluster of China, and has a population of 13 million. Qingyuan, located north of Guangzhou, is a much less developed region where one of the largest e-waste recycling sites in China is located (Fig. S1). The indoor dust samples (mainly from furniture and floors of the bedroom and living room) were collected between September, 2013, and March, 2014, using a vacuum cleaner. The urban house dust samples ( $n = 11$ ) were collected from different districts, and dormitory samples ( $n = 15$ ) were all collected from Sun Yat-sen University. Seventeen dust samples were obtained from the family-run workshops in several villages in Qingyuan, where e-waste recycling has existed for some decades. As a comparison, dust samples ( $n = 25$ ) were also collected from villages near the e-waste recycling villages (with distance of 2–3 km).

### 2.2. Sample preparation and analysis

The dust samples were sieved through a stainless steel sieve (100- $\mu\text{m}$  mesh) to remove larger debris. Samples of approximately 0.2 g were spiked with surrogate standard (tri-*n*-butyl phosphate (TnBP- $d_{27}$ )) and Soxhlet-extracted with a mixture of acetone and hexane (1:1 v:v) for 48 h. Extracts were concentrated to 1 mL using a rotary evaporator and then further purified and fractionated by solid-phase extraction on a Florisil cartridge (Supelclean ENVI-Florisil, 3 mL 500 mg $^{-1}$ ) from Supelco (Bellefonte, USA). The cartridge was pre-cleaned with 8 mL ethyl acetate and 6 mL hexane separately, and then concentrated extracts were eluted with 10 mL hexane and 8 mL ethyl acetate, respectively. The effluents of ethyl acetate containing OPFRs were then evaporated to near dryness by a gentle nitrogen stream and re-dissolved in 300  $\mu\text{L}$  isooctane. Prior to injection, a quantitative standard (TPhP- $d_{15}$ ) was added to each sample.

### 2.3. Instrumental analysis

The analysis of OPFRs was performed with a Shimadzu 2010 gas chromatograph coupled to a mass spectrometer (GC/MS) with an electron impact ion source. A DB-5MS (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) capillary column was used, and injection of 1  $\mu\text{L}$  sample was performed with an automatic sampler using the splitless injection mode. The injection temperature was set at 70  $^{\circ}\text{C}$  and ramped to 300  $^{\circ}\text{C}$  with a sampling time of 1 min. Helium was the carrier gas with a flow rate of 1.0 mL min $^{-1}$ . Dwell times ranged from 20 to 30 ms. The ion source and interface temperatures were set at 200  $^{\circ}\text{C}$  and 290  $^{\circ}\text{C}$ , respectively. In total, 12 OPFRs were determined including triethyl phosphate (TEP), tri-isopropyl phosphate (TiPrP), TPhP, tri-*n*-butyl phosphate (TnBP), TCEP, TCPP, TDCP, TBEP, tri-*n*-propyl phosphate (TnPP), ethylhexyl diphenyl phosphate (EHDPP), tri-(2-ethylhexyl) phosphate (TEHP), and TCP.

### 2.4. Quality control

A procedural blank (pre-extracted filter) was analyzed with each batch of samples, and only TCEP was found in the five blanks (with a maximum concentration of 4.3 ng, less than 15% of the concentrations in the dust extracts). The concentrations in the sample

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