



## Distribution of organophosphorus flame retardants in sediments from the Pearl River Delta in South China



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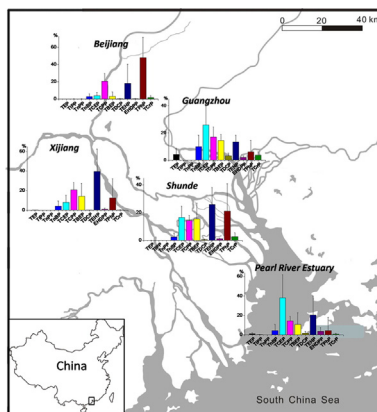
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### HIGHLIGHTS

- Levels of  $\sum$  12PFRs in sediments from the PRD ranged from 8.3–470 ng/g dw.
- High levels of PFRs were in the urbanized area and e-waste area.
- The dominant PFRs were TPhP, TCPP, TEHP, TCEP and TBEP in the PRD.
- Composition varied across different regions reflecting various sources of PFRs.
- Halogen and non-halogen PFRs exhibited different vertical profile in sediment core.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Twelve organophosphorus flame retardants (PFRs) were identified in the sediments and the sediment core collected from the rivers and the estuary in the Pearl River Delta, with the aim of investigating their spatial and vertical distributions. The concentrations of PFRs ranged from 8.3 to 470 ng/g dry weight with high levels of PFRs in the urban area and the e-waste recycling region. Generally, TPhP, TCPP, TEHP, TCEP, and TBEP were the dominant compounds of the PFRs, the composition of which varied across the different regions, reflecting the different sources of PFRs. In the estuary, the PFRs mainly derived from the Xijiang River and the Shunde sections. Increased concentrations of halogen-containing PFRs have been observed in the upper layers of the sediment core. Conversely, relatively high concentrations of halogen-free PFRs were observed in the lower layers of the sediment core, indicating different usage patterns or environmental behaviors between the halogen and the non-halogen PFRs in the study area.

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### 1. Introduction

Organophosphorus flame retardants (PFRs) are utilized as flame retardants, plasticizers, antifoaming agents, lubricants, and hydraulic

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fluids by diverse industries, including textiles, building materials, electronics, and chemicals (Marklund et al., 2005). Along with the gradual phasing out of brominated flame retardants, the consumption of alternative PFRs has increased dramatically (Harino et al., 2014). The global consumption of PFRs increased from 186,000 t in 2001 to 300,000 t in 2004, and the usage of PFRs in China was estimated at approximately 70,000 t in 2007, with an annual growth of 15% (Wei et al., 2015). As most PFRs are added to and mixed with, rather than chemically bound to the materials (van der Veen and de Boer, 2012), leaching could occur throughout the lifetime (Marklund et al., 2003) of these products. Reports have indicated that PFRs were ubiquitous in various environmental media, such as water (Chung and Ding, 2009; Bacaloni et al., 2008), air (Carlsson et al., 1997; Saito et al., 2007), dust (He et al., 2015; Stapleton et al., 2009), sediment (Cristale et al., 2013; Ricking et al., 2003), soil (Mihajlovic et al., 2011), and biota samples (Kim et al., 2011; Sundkvist et al., 2010). Furthermore, some of the harmful effects of PFRs on human health cannot be ignored. Chlorinated organophosphates, such as tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-isopropyl) phosphate (TCPP), and tris(2-chloro, 1-chloromethyl-ethyl) phosphate (TDCP) are suspected carcinogens (World Health Organization, 1998). Additionally, TCEP has been linked with incidents of acute death of dogs (Lehner et al., 2010), while TDCP was shown to be more neurotoxic than TCEP and TCPP (Dishaw et al., 2011). Tricresyl phosphate (TCrP), triphenyl phosphate (TPhP), and TDCP are considered as possibly toxic for reproduction (van der Veen and de Boer, 2012; Meeker and Stapleton, 2010). Kanazawa et al. (2010) reported that Sick House Syndrome was associated with tri-*n*-butyl phosphate (TnBP) and tris(2-butoxyethyl) phosphate (TBEP).

Most available data on PFRs contamination relate to the environmental matrices of dust, air, and water, but information on the contamination in sediments is limited and is mainly related to Western Europe and the US. To our knowledge (Kawagoshi et al., 1999; Chung and Ding, 2009; Cao et al., 2012), a limited number of reports have been published on PFRs in the sediments in the Asian Pacific region, pertaining to Japan, Taiwan, and Lake Taihu in China. The Pearl River Delta (PRD) is one of the most developed and urbanized regions in southern China, and, because of the extensive manufacturing industry in the region, there is widespread use of large amounts of chemicals. Reports have indicated that compared with global figures, high concentrations of halogenated flame retardants, such as polybrominated diphenyl ethers and decabromodiphenyl ethane, have been found in this region (Mai et al., 2005; Zhang et al., 2009). It is speculated that along with the phasing out of polybrominated diphenyl ethers in this region, the use of alternative flame retardants such as PFRs has increased sharply in recent years (He et al., 2015). However, scant information is available on PFRs pollution in the PRD.

PFRs were recently detected in the dust (Zheng et al., 2015) deriving from the e-waste recycling region, and in the sludge (Zeng et al., 2014) from the municipal wastewater treatment plants in the PRD. Sediment is one of the main reservoirs for pollutants deriving from domestic and industrial wastewater and can reflect the local spatial and vertical distributions of pollution in the region. Consequently, surface sediments as well as one sediment core were collected in the major rivers and the estuary in the PRD, which covers a large area of the PRD representing different levels of urbanization and industrialization. The aim of the present study is to investigate comprehensively the spatial and vertical distributions of 12 targeted PFRs (triethyl phosphate (TEP), tri-isopropyl phosphate (TiPP), tri-*n*-propyl phosphate (TnPP), TCEP, TCPP, TDCP, TnBP, TBEP, tris(2-ethylhexyl) phosphate (TEHP), 2-ethylhexyldiphenyl phosphate (EHDPP), TPhP and TCrP) in the sediments. In addition, the environmental behaviors, potential sources, and the fate of PFRs were also evaluated in the study.

## 2. Materials and methods

### 2.1. Sample collection

A total of 52 surface sediment samples and a sediment core were collected in the PRD region in April 2010 (Fig. 1). We collected 10 surface sediment samples from the main stream of the Xijiang (XJ) River, 7 from the Beijiang (BJ) River, 13 from the tributaries of the XJ and BJ rivers running through the Shunde (SD) industrial area, 12 from the Guangzhou (GZ) section of the Zhujiang River, and 10 samples and a sediment core from the Pearl River Estuary (PRE). This estuary is a reservoir of all the rivers and tributaries in the PRD. The XJ River mainly flows through rural zones, while the BJ River runs through rural areas in the upstream and urban areas in the lower reaches.

The sediment samples, taken from the top 5-cm layer, were collected with a Van Veen stainless steel grab sampler. A sediment core (N22°18'04", E113°41'17") of 44-cm depth was collected with a Plexiglas gravity corer. All the samples were transported immediately on ice to the laboratory and were stored at  $-20\text{ }^{\circ}\text{C}$ , prior to chemical analysis.

### 2.2. Sample preparation and analysis

The method was modified from a method published previously (Cao et al., 2012). Briefly, sediment samples were freeze-dried, ground, and homogenized by sieving through a stainless steel 80-mesh (0.2 mm) sieve. A dry sample (approximately 4 g) was spiked with the surrogate standard (150 ng of TnBP-d27), and Soxhlet extraction was performed with 200 mL dichloromethane for 24 h. Activated copper granules were added to the flasks during the extraction to remove elemental sulfur. The extract was concentrated and the solvent was changed to 10 mL methanol, and was diluted with 500 mL ultrapure water. The mixture was subsequently purified further and was fractionated by solid-phase extraction on an Oasis HLB cartridge (200 mg, 6 mL, Waters™, Milford, Massachusetts, USA), which was pre-rinsed separately with 4 mL ethyl acetate, 4 mL methanol, and 4 mL ultrapure water. After loading the mixture on the cartridge, the cartridge was dried for about 20 min under a gentle nitrogen stream and was eluted with  $2 \times 4\text{ mL}$  of ethyl acetate. Subsequently, anhydrous sodium sulfate was used to remove the remaining water from the effluent. After evaporation to near dryness, the effluent was redissolved in 300  $\mu\text{L}$  iso-octane. Afterwards, 150 ng of TPhP-d15 was added as a recovery standard, prior to instrumental analysis.

### 2.3. Instrumental analysis

The analysis of the PFRs was performed with 7890 Agilent (Santa Clara, California, USA) gas chromatography (GC), coupled with a 5975 mass spectrometer (MS), with an electron impact (EI) ion source, and separated by a HT-8 capillary column (25 m  $\times$  0.22 mm  $\times$  0.25  $\mu\text{m}$ ; SGE Analytical Science). The MS was operated in the selective ion monitoring (SIM) mode, with two characteristic ions acquired for each compound (Van den Eede et al., 2011). The GC temperature program was set as follows: 70  $^{\circ}\text{C}$  for 2 min, ramped with 15  $^{\circ}\text{C}/\text{min}$  to 300  $^{\circ}\text{C}$ , and held for 10 min. Injection of 1  $\mu\text{L}$  sample was done using the splitless mode and the injector temperature was 290  $^{\circ}\text{C}$ . The carrier gas was helium, at a flow rate of 1 ml/min. The temperatures of the interface, ion source, and quadrupole were 290, 230, and 150  $^{\circ}\text{C}$ , respectively.

After removal of the carbonates with 1 mol/L HCl, the total organic carbon (TOC) of the sediments was assessed by using an elemental analyzer (Vario EL III from Elementar, Germany).

### 2.4. QA/QC

Quality assurance (QA) and quality control (QC) were performed by analyzing the procedural blanks, spiked blanks, spiked matrixes, and the sample duplicates. The procedural blanks were processed for each batch

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