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

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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
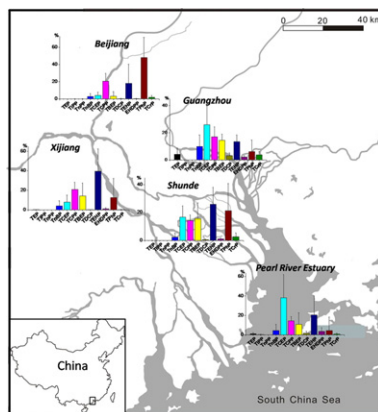
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ABSTRACT

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.

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-iso-propyl phosphate (TiPP), tri-n-propyl phosphate (TnPP), TCEP, TCPP, TDCP, TnBP, TBEP, tris(2-ethyhexyl) 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 °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 × 4 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 μL 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 × 0.22 mm × 0.25 μm; 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 °C for 2 min, ramped with 15 °C/min to 300 °C, and held for 10 min. Injection of 1 μL sample was done using the splitless mode and the injector temperature was 290 °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 °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
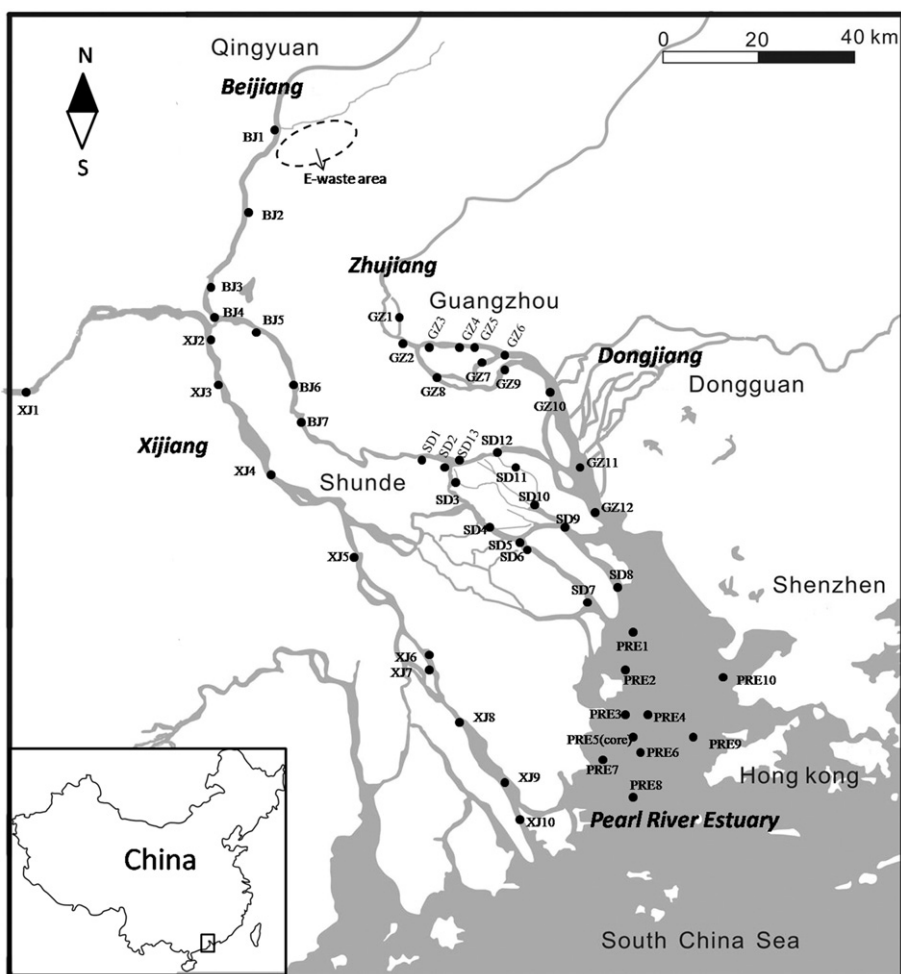
Fig. 1. Map of sampling sites in the Pearl River Delta (PRD) (modified from Chen et al., 2013). PRE, Pearl River Estuary; GZ, Guangzhou section; SD, Shunde section; XJ, Xijiang river; BJ, Beijiang river.

of 12 samples. Although TEP, TiPP, and TnPP were not detected in the procedural blanks, other PFRs were identified, ranging from 0.03 to 2.9 ng/g apart from TEHP (10 ng/g). The concentrations of these PFRs in sediment were background-subtracted. Except for TEP, TiPP, and TnPP, the recoveries of the PFRs ranged from 90 to 120% in the spiked blanks and from 86 to 117% in the spiked matrixes, with relative standard deviations of less than 8 and 11%, respectively. However, the recoveries of TEP (11%) and TiPP (13%) was extremely low in the spiked matrixes. The limits of quantification (LOQ) were set as the mean values of the target compounds detected in the procedural blanks, plus three times the standard deviation. The LOQ for the undetectable compound was set as a signal to noise ratio of 10. The LOQ of PFRs ranged from 0.09 to 3.2 ng/g dry weight, except for 10 ng/g for TEHP. The recoveries of surrogate standards in sediment samples (n = 74) ranged from 76 to 119%.

2.5. Data analysis

Statistical analysis was performed with the SPSS 19 for Windows7 software (SPSS Inc., Chicago, Illinois, USA). Before one-way analysis of variance (ANOVA) accompanied by Tukey's test was conducted, the non-normally distributed data (determined by the Shapiro–Wilk test) were log-transformed to display a normal distribution. The correlation between the TOC and the levels of PFRs was examined by using the Pearson correlation analysis. Statistical significance was accepted at $p < 0.05$ throughout the present study. The principal components analysis (PCA) was employed to assess the input source of the PFRs. The first

two principle components (PCs) with eigenvalues > 1 were retained and considered the most significant factors.

3. Results and discussion

3.1. PFRs levels and spatial distribution

The concentrations of the total and the individual PFRs in the surface sediment samples from the PRD are listed in Table 1 and in detail in Table S1 in the Supplementary data. All the compounds except TnPP were detected. The concentrations of the PFRs varied from 8.3 to 470 ng/g dry weight (dw), with a median of 48 ng/g dw (n = 52). The occurrence of other flame retardants, such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs), tetrabromobisphenol A (TBBPA), decabromodiphenyl ethane (DBDPE), dechlorane plus (DP), and chlorinated paraffins (CPs) in the sediment has been reported in our previous studies (Chen et al., 2011; Chen et al., 2013; Feng et al., 2012). The levels of the PFRs were comparable with those of the PBDEs (3.7–910 ng/g dw) and DBDPE (ND–1180 ng/g dw), but were one to two orders of magnitude higher than were those of TBBPA (0.06–127 ng/g dw), HBCD (ND–9.4 ng/g dw), and DPs (ND–45 ng/g dw), while they were one order of magnitude lower than those of CPs (370–3700 ng/g dw) (Table 1). This result suggested that CPs were the main flame retardants used in the PRD regions, followed by PFRs, PBDEs, and DBDPE, and the other halogenated flame retardants. Considering the lower octanol–water partition coefficient

Table 1
Concentrations (median and range, ng/g) of PFRs in sediments from the Pearl River Delta.

	PRE (n = 10)	GZ (n = 12)	SD (n = 13)	XJ (n = 10)	BJ (n = 7)
TEP	0.40 (ND–0.91)	4.9 (ND–9.5)	(ND–0.08)	(ND–0.14)	(ND–0.14)
TiPP	0.04 (ND–0.29)	(ND–0.12)	ND	ND	(ND–2.3)
TnPP	ND[a]	ND	ND	ND	ND
TnBP	0.60 (ND–13)	9.4 (0.83–37)	0.48 (ND–7.8)	0.58 (ND–3.5)	2.9 (ND–11)
TCEP	13 (1.5–33)	30 (10–58)	6.3 (1.2–17)	1.6 (ND–9)	4.6 (ND–8.5)
TCPP	4.3 (1.5–11)	24 (3.5–58)	5.4 (2.9–16)	5.7 (0.91–13)	19 (7.3–185)
TBEP	3.5 (ND–10)	16 (5.8–46)	9.2 (ND–13)	1.9 (ND–13)	1.2 (ND–11)
TDCP	0.34 (ND–1.8)	4.1 (0.33–10)	0.23 (ND–0.98)	(ND–0.17)	0.39 (ND–1.0)
TEHP	4.2 (0.86–12)	14 (6.2–44)	9.6 (3.0–56)	10 (3.1–21)	12 (4.0–31)
EHDPP	0.62 (0.32–4.8)	2.5 (0.47–5.1)	0.49 (ND–1.6)	0.16 (ND–1.5)	0.29 (0.16–1.5)
TPhP	(ND–16)	4.2 (ND–44)	11 (ND–78)	1.1 (ND–26)	71 (5.6–253)
TCrP	0.30 (0.02–1.2)	3.8 (1.0–11)	0.79 (0.05–7.6)	0.06 (ND–0.21)	1.7 (0.19–4.3)
$\sum$ PFRs	34 (12–66)	132 (62–222)	45 (23–169)	32 (8.3–48)	112 (48–470)
$\sum$ PBDEs[b]	16 (3.7–46)	233 (11–910)	68 (5.8–240)	32 (4.1–65)	35 (10–183)
HBCDs[c]	0.33 (ND–1.1)	2.0 (ND–9.4)	1.4 (0.21–5.2)	0.35 (ND–1.0)	0.50 (0.09–1.9)
TBBPA[c]	0.47 (0.06–1.4)	13 (0.10–127)	1.4 (0.26–27)	0.42 (ND–1.3)	2.7 (0.54–6.2)
DBDPE[b]	7.8 (ND–31)	200 (12–1180)	80 (2.9–320)	24 (2.9–80)	70 (ND–260)
DPs[b]	0.22 (ND–2.1)	2.3 (0.41–45)	0.88 (0.09–3.4)	0.29 (ND–0.95)	1.3 (0.57–3.5)
SCCPs[d]	1650(1200–2500)	810 (590–2500)	900 (510–3700)	580 (370–730)	680 (540–820)

[a] ND: not detectable or below the LOQs.
[b] Reference: Chen et al. (2013).
[c] Reference: Feng et al. (2012).
[d] Reference: Chen et al. (2011).

(K_{ow}) of PFRs compared with PBDE, the PFR pollution in the PRD could be underestimated using the data relevant to the sediment.

Only limited data have been reported on the occurrence of PFRs in sediments. The concentrations of $\sum$ 10PFRs in 21 sediment samples from the Navarra, Asturias, and the Catalonia rivers in Spain were between 3.8 and 824 ng/g (Cristale et al., 2013), which were comparable with those in the present study. Cao et al. (2012) found that the levels of $\sum$ 7PFRs ranged from 3.4 to 14 ng/g in sediments from Taihu Lake in China. Sediment samples from the southwestern coast of Taiwan (Chung and Ding, 2009) showed concentrations of $\sum$ 5PFRs, ranging from 1.0 to 13 ng/g. These concentrations were all lower than were those found by the present study. However, Martínez-Carballo et al. (2007) have reported concentrations of $\sum$ 9PFRs up to 1900 ng/g in the sediment of the Schwechat River in Austria. The levels of $\sum$ 9PFRs in the sediments from the waste-disposal site and the surrounding sea of Osaka North Port in Japan were up to 10,900 ng/g and 1800 ng/g, respectively (Kawagoshi et al., 1999), which were markedly higher than were those found in the PRD.

The spatial distribution order of PFRs in the PRD was as follows: GZ and BJ sections > SD and XJ sections, and the PRE. The concentrations of PFRs in the sediment collected from the GZ section were significantly higher than were those from SD and XJ sections and the PRE ($p < 0.05$). This is not surprising, as Guangzhou city is the capital of the highly urbanized and industrialized Guangdong Province, which has a vast population. Consequently, a large amount of domestic and industrial sewage, containing PFRs from household applications, including furniture, textiles, polyurethane foams, wallpaper, baby products, and electronics (García-López et al., 2009a; Zeng et al., 2014), is discharged into the rivers. The concentrations of PFRs in the BJ River were comparable with those in the Guangzhou section of the Pearl River, while the highest level of PFRs (470 ng/g dw) was found in site BJ1, located at the outlet of the Dayan River, which runs through one of the largest e-waste recycling areas in the PRD. E-waste has been indicated as an important source of PFRs in the environment (Green et al., 2008; Marklund et al., 2003; Araki et al., 2014). Recently, Zheng et al. (2015) have reported substantially high PFRs concentrations in the dust from the e-waste recycling region. Therefore, emission from the e-waste

recycling activities could be the reason for the highest concentration of PFRs being found in the BJ1 site.

The concentrations of PFRs in the sediments from the XJ River were significantly lower than were those from the other sections of the Pearl River. There are at least two reasons for this finding. Firstly, the XJ River is the main stream of the Pearl River and the average annual total runoff of this river is estimated at 8.84×10^{10} m^3/year, which is larger than is that of the other streams (Mai et al., 2002). The mass flow could therefore dilute the PFRs pollution. Additionally, some PFRs with lower K_{ow} values partition into the freshwater and migrate downstream. Secondly, the drainage of the XJ River was lower in the level of urbanization and industrialization than the GZ, SD, and BJ sections. The PRE collects PFRs from the rivers in the PRD. The concentrations of PFRs in the PRE were comparable with those in the XJ River and the SD section, but were lower than were those in the GZ section.

In a previous study, we found relatively high correlations (r = 0.74, $p < 0.001$) between the concentration of $\sum$ 4PFRs and TOC in the sediments from the Dongjiang River (Ruan et al., 2014). In the present study, moderate correlations (r = 0.60, $p < 0.05$) (Table S3) between $\sum$ 11PFRs and TOC were found in sediment samples from the GZ section. However, no significant correlations were found between TOC and PFRs in the other areas. This result indicated that TOC was not the single influencing factor for the distribution of PFRs in the study area, although it did play an important role in some instances. Other factors such as the emission intensity and degradation could also affect the distribution of PFRs.

3.2. Patterns and compositional analysis

TnPP was not detectable in any of the field samples. The detected frequencies of TEP and TiPP were less than 50%, while high detection frequencies (67–100%) were found for the other PFRs. The compositions of the PFRs in the surface sediments from the five areas in the PRD are shown in Fig. 2. It was found that the most abundant chemical varied subject to the different sampling area. Among the 12 selected targets in the PRD, TPhP, TCPP, TEHP, TCEP, and TBEP were generally the dominant PFRs, collectively accounting for up to 89% of the total PFRs. This
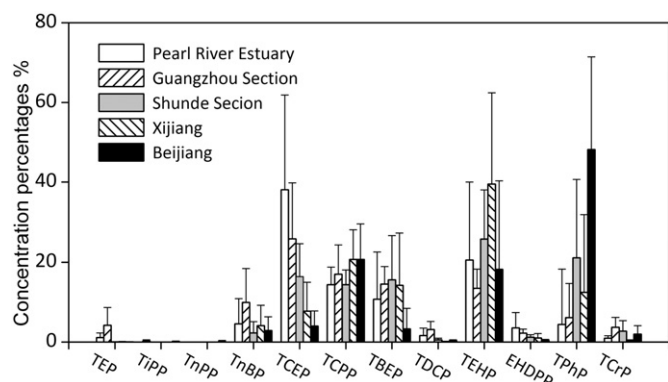
Fig. 2. Composition of PFRs in surface sediments from the Pearl River Delta (PRD). Error bars represent standard deviation.

pattern was consistent with that observed previously in sediments from Austria, Norway, and Taiwan (Martínez-Carballo et al., 2007; Green et al., 2008; Chung and Ding, 2009).

TCPP exhibited approximately equal abundance and was the main PFR component in all five sampling areas, indicating that TCPP was widely used in the PRD (Fig. 2). Reports have indicated that TCPP was the most abundant PFR in sediments from Germany, Austria, the US, Spain, Norway, and Taiwan (Stachel et al., 2005; Martínez-Carballo et al., 2007; García-López et al., 2009b; Cristale et al., 2013; Cristale and Lacorte, 2013; Green et al., 2008; Chung and Ding, 2009), as well as in sediments from Dongjiang in the PRD (Ruan et al., 2014). This finding is mainly attributed to the large consumption of TCPP accounting for 80% consumption of halogen-PFRs in Europe (van der Veen and de Boer, 2012). TEHP is highly abundant in the PRD, probably because of its high soil adsorption coefficient (log K_{oc} = 6.87) and moderate water solubility (0.6 mg/L at 25 °C) (van der Veen and de Boer, 2012). TBEP is a component of floor polishes (World Health Organization, 2000), of which the consumption in urban and industrial areas is high. This is why this chemical exhibited the highest abundance in GZ section. Brandsma et al. (2015) found the highest concentrations of TBEP and TiBP in the sediments collected from the Western Scheldt estuary, an important shipping lane and industrialized area in the southern region of The Netherlands. TBEP was also found to have the highest concentration in the water of Maizuru Bay in Japan (Harino et al., 2014). TCEP and TCPP were widely used in industrial activities. So, it was not surprised that these two chemicals showed high abundance in GZ section. TPhP was indicated as the most abundant chemical in the BJ River. Zheng et al. (2015) recently reported PFRs in the dust from the e-waste recycling workshops, scattered over four e-waste recycling regions in the PRD. TPhP and TCPP were indicted as the most abundant chemicals

in these dust samples, a finding that is consistent with the findings of the present study concerning the samples from the BJ River. These findings confirm the influence of the e-waste recycling activities on the BJ River. TPhP is used on a large scale in developed countries as a plasticizer and flame retardant in a variety of electronic equipment (Carlsson et al., 2000). As TPhP is added to but not bonded with the materials, it is readily released from the e-waste products to the environment. Although its flame retardant effect is superior, the concentration of TDCP was the lowest of the halogen-PFRs detected, probably because it is expensive (van der Veen and de Boer, 2012).

Fig. 2 shows that the compositions of the PFRs differ significantly across the five sampling areas. A PCA was conducted to gain an insight into the source contributions to the PFRs in the different areas. Data for TEP, TiPP, and TnPP were excluded from the present analysis, as these compounds were not detected in most of the sediments. Sixty-seven percent of the variance in PFRs was explained by the first two PCs (PC1: 47%, PC2: 20%) (Fig. 3a). Factor 1 was heavily weighted by TDCP, EHDPP, TBEP, TCrP, TnBP, and TCEP. Factor 2 had a significant positive loading in TPhP and TCPP. As mentioned above, TPhP and TCPP were found to be the major components of PFRs in the dust from the e-waste recycling region. Thus, factor 2 can be contributed to the e-waste source of PFRs. TEHP had low loadings in both factors, indicating that it had different sources, or environmental behaviors different from the other PFRs. The factor score plot (Fig. 3b) showed that the GZ section and the BJ were located separately from the other sites. The samples from the GZ section had high scores in factor 1, while the samples from the BJ had high scores in factor 2, indicating different sources of PFR for these two areas. Factor 1 exhibited high loading on most of PFRs, suggesting industrial sources of PFRs. Thus, the source of PFRs in the Guangzhou section is the industrial activities in the location. The source of PFRs in the XJ and SD section was also believed to be the industrial activities. However, more evidences are needed to support it since the transport process might alter the PFRs profiles. The samples of XJ overlapped with the samples of the SD section, indicating that they shared a similar source of PFRs. The data points of PRE in the score plot were between the data point of GZ and the data point of XJ and SD, indicating that the GZ section, SD section, and XJ all contributed to the PFRs in the PRE. The contribution of the XJ and SD sections was higher than was that of the GZ section, since the data point in PRE was closer to the XJ and SD sections than to GZ. This is also in line with the geography location of sites where sample were collected. The BJ seemed to have little influence on the PFR pollution in the PRE.

Zeng et al. (2014) reported PFRs in the sludge from the wastewater treatment plants located in the same region as the present study. Since sewage is one of major sources of PFRs in rivers, a comparison between sludge and sediments could provide useful information on the environmental behavior of PFRs. The concentrations of PFRs in the sludge
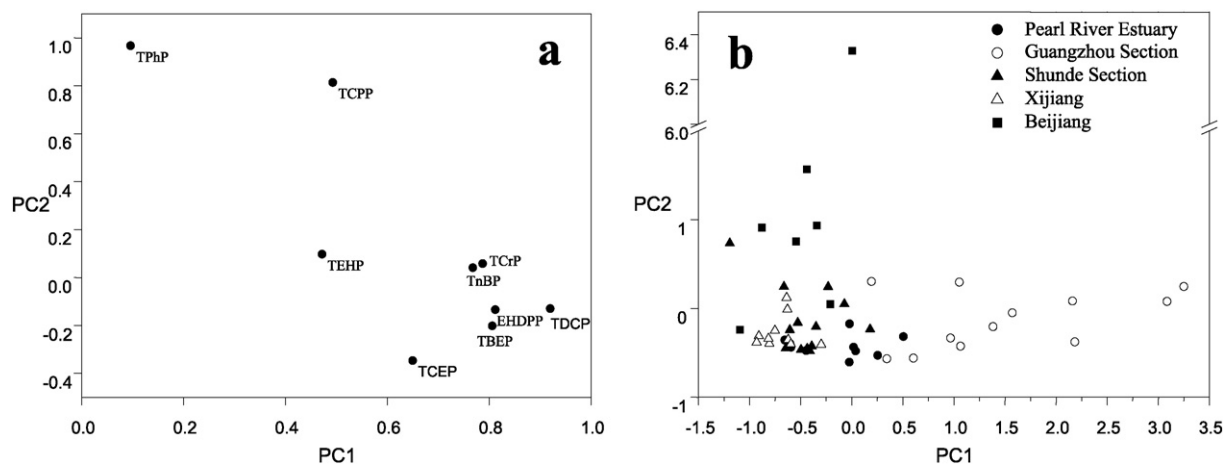

Fig. 3. Principal component analysis results of PFRs (PC1, 47% variance; PC2, 20% variance). The figure legends represent the factor loadings (a) and factor scores (b).

ranged from 97 ng/g to 1313 ng/g, which was an order of magnitude higher than were those in the sediment. TBEP and TPhP were the dominant contaminants in the sludge, an observation similar to those of the present study regarding the sediments. This could be regarded as evidence that wastewater was one of the major sources of PFRs in the PRD. The median concentrations of TCPP, TCEP, TBEP, and TnBP in the sludge were 15.9, 11.4, 102, and 17.4 ng/g, respectively. Compared with the results of the present study, the concentrations of TCEP and TCPP in the sludge were the same order of magnitude as were those in the sediment, while TBEP and TnBP were 1–2 orders magnitude higher than were those in the sediment. This finding provided the most conclusive evidence of the persistence of halogenated PFRs in the environment. And it coincides with the result of Regnery and Püttmann (2010) that TBEP and TnBP would degrade rapidly, while the chlorinated PFRs, TCPP, and TCEP seemed resistant to degradation. TCEP was phased out by TCPP due to toxicity issues (World Health Organization, 1998). Thus, the contribution of this chemical in source (Pearl River) decreased sharply. Besides, difference in degradation rate among different chemicals may be an alternative reason for the high abundance of this chemical in the PRE.

3.3. Vertical distribution

The vertical distributions of individual PFRs in the sediment core collected in the PRE are shown in Fig. 4 (TEP, TnPP, TiPP, and TnBP were under the limits of determination in the sediment core). The PFRs concentrations ranged from 4.0–96 ng/g dw. The highest concentration was indicated in a section of 10–12 cm, where an outlier for TPhP (81 ng/g dw) was found. If this outlier was removed, the concentrations would range from 4.0–27 ng/g dw. Eight of the twelve PFRs targeted were detectable in the sediment core; however, TEP, TiPP, TnPP, and TnBP were not detected. The probable reason for their non-detection is their lower resistance to degradation in the environment and higher solubility in water. TPhP, TEHP, TCPP, and TCEP were the main PFR components, on average accounting for 28%, 22%, 19%, and 13% of the total PFRs, similar to the surface sediments.

The concentrations of three halogen-containing PFRs (TCEP, TCPP, and TDCP) in the upper segments (above 24 cm) were significantly higher than were those in the lower segments of the sediment core. This finding shows the obvious gradually increasing trend with decreasing depth in the upper segments, indicating an increased usage of these halogen-containing PFRs in the study area. However, the concentration of TCEP sharply decreased in the top three segments (from 0 to 6 cm), and the concentration of TCPP was especially low at 0–2 cm. This decreasing trend could be attributed to the good water solubility of these components (TCEP: 7.0 g/L; TCPP: 1.6 g/L, ATSDR, 2009), or to a decline in usage in recent years.

The vertical distributions of non-halogen PFRs exhibited profiles different from those of the halogen-containing PFRs. TEHP showed a declining trend with decreasing depth, in complete contrast with those of the three halogen-containing PFRs. TBEP was only detected in the lower segments (below 16 cm), different from TDCP, which could only be detected in the upper segments (above 28 cm). As regards EHDPP, high concentrations were found mainly in the middle of the segments
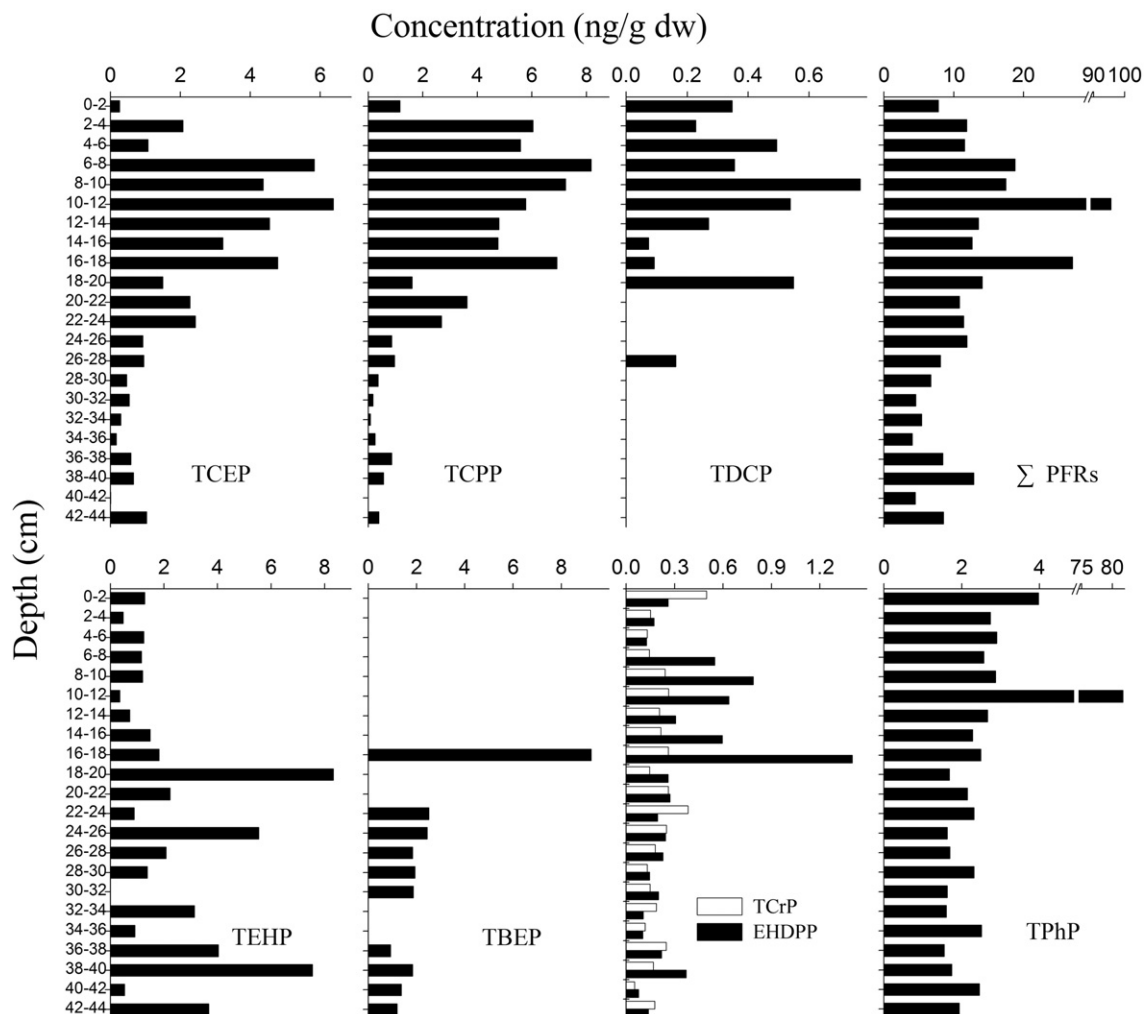

Fig. 4. Vertical distribution of $\sum$ PFRs and individual PFRs in the sediment core collected from Pearl River Estuary.

(6–18 cm). A slight gradually increasing trend in the concentration of TPhP was observed, which could suggest an increased usage of TPhP in recent years. In addition to the usage of PFRs in the study area, other factors could also affect the vertical distribution of non-halogen PFRs in the sediment core. Most of the non-halogen PFRs that are not considered as persistent, such as rapid photodegradation for TBEP and biodegradation for TPhP and TCrP (van der Veen and de Boer, 2012; Regnery and Püttmann, 2010), while the halogen PFRs are difficult to degrade (Kawagoshi et al., 2002). Taking this factor into consideration, a more accurate vertical distribution of non-halogen PFRs could not be presented readily.

4. Conclusions

In the present study, the spatial and vertical distribution of PFRs was assessed by determining PFRs in sediments from the PRD and a sediment core from the PRE. The levels of PFRs in the PRD were comparable with those of other regions worldwide. Relatively high PFR concentrations were found in the highly urbanized and industrialized area (GZ section) and the e-waste area (BJ section). The PFR compositions differed across the different regions, reflecting the various sources of PFRs in the study area. The halogen-containing PFRs in the sediments exhibited levels similar to those in sludge, but the levels of the non-halogen PFRs were remarkably lower than were those in the sludge samples. This finding indicates the different environmental behaviors of the halogen and the non-halogen PFRs. Three halogen-containing PFRs exhibited a rapid increase in levels in recent years. However, the vertical distributions of non-halogen PFRs exhibited profiles different from those of the halogen-containing PFRs, indicating different usage patterns for the halogen and the non-halogen PFRs. Further studies are needed on the effects of the degradation of non-halogen PFRs on the vertical distribution.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.11.089.

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