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RESEARCH ARTICLE

Phthalate esters in water and surface sediments of the Pearl River Estuary: distribution, ecological, and human health risks

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Abstract The Pearl River Estuary (PRE) is vulnerable due to the increasingly serious environmental pollution, such as phthalate esters (PAEs) contaminants, from the Pearl River Delta (PRD). The concentrations of six US Environmental Protection Agency (USEPA) priority PAEs in water and surface sediments collected from the PRD's six main estuaries in spring, summer, and winter 2013 were measured by GC-MS. Total PAEs ($\sum_6$PAEs) concentrations were from 0.5 to 28.1 μg/L and from 0.88 to 13.6 μg/g (dry weight (DW)) in water and surface sediments, respectively. The highest concentration was detected in summer. Higher concentrations of PAEs were found in Yamen (YM) and Humen (HM) areas than the other areas. Bis(2-ethylhexyl)phthalate (DEHP) and dibutyl phthalate (DBP) were the dominant PAEs in the investigated areas, contributing between 61 and 95 % of the PAEs in water and from 85 to 98 % in surface sediments. Based on risk quotients (RQs), DEHP posed greater ecological risks to the studied aquatic environments than other measured compounds. Little human health risk from the target PAEs was identified.

Keywords Phthalate esters · Pearl River Estuary · Seasonal variation · Spatial distribution · Ecological risk assessment · Health risk assessment

Introduction

The Pearl River is the third largest river in China. Where it meets the sea, the river forms the complex, branched Pearl River Delta (PRD) which is subtropical monsoon climate whose feature is the largest amount of rainfall in summer while the least in winter. The PRD region covers an area of ~54,000 km^2, within which a population of more than 42 million people lives. As one of the most rapidly developing and densely populated area in southern China, there is concern about trace organic chemical contamination by polybrominated diphenyl ethers (PBDEs), endocrine-disrupting chemicals (ECDs), polycyclic aromatic hydrocarbons (PAHs), etc. (Chen et al. 2013; Feng et al. 2012; Zhang et al. 2011). Phthalate esters (PAEs) are widely used in plastic products, building materials, pesticides, automobile parts, cosmetics, and food packaging (Gómez-Hens and Aguilar-Caballos 2003; Hu et al. 2003). In China, the amount of the production and consumption of PAEs is about 1.3 million t/year (He et al. 2013), or at least 20 % of worldwide consumption (more than 6 million t/year; Arbeitsgemeinschaft and Umwelt 2006; Zhiyong et al. 2007). PAEs are easily leached into the environment (Dargnat et al. 2009) and have been found in the atmosphere, sediments, water, soil, and biota,

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including humans worldwide (Cai et al. 2008; Hongjun et al. 2013; Liu et al. 2014; Sun et al. 2013; Wang et al. 2012).

Aquatic environments may be polluted by PAEs through various ways including discharge wastewater, surface run-off (Adeniyi et al. 2011; Fan et al. 2008; Fromme et al. 2002; He et al. 2013; Liu et al. 2014; Sun et al. 2013; Yuan et al. 2002; Zeng et al. 2008), and because they bio-accumulate and recalcitrance in aquatic organisms, PAEs pose great threats to aquatic ecosystems (Adeniyi et al. 2011; Liu et al. 2014; Sun et al. 2013). Xu et al. (2013a) showed that some PAEs, such as DBP and diethyl phthalate (DEP), have potential neurotoxicity to embryos of zebra fish by inhibiting the activity of acetyl cholinesterase. Other studies have shown that most of PAEs produce endocrine-disrupting effects, for example, developmental and reproductive toxicities in mammals (Chen et al. 2011; Gray et al. 2000; Harris et al. 1997; Horn et al. 2004; Matsumoto et al. 2008). Consequently, there is concern that humans may be exposed to PAEs not only by consuming contaminated surface water but also by feeding on aquatic organisms.

The USEPA has classified DEP, DBP, BBP, DEHP, dimethyl phthalate (DMP), and di-*n*-octyl phthalate (DnOP) as top-priority contaminations (Keith and Telliard 1979). Li et al. (2015) suggested that the six priority PAEs pose different levels of ecological risk to aquatic ecosystems and that the different sensitivities of different aquatic species are neglected when assessing risk. Indeed, the human health risk of the six priority PAEs from the PRE is still unknown.

In this context, the major objectives of the paper were (a) to investigate the seasonal variation and spacial distribution of top-priority PAEs in the water and surface sediments in the estuaries of PRD, (b) to assess the risk of the dissolved PAEs to aquatic environment in the sampling sites for three different kinds of aquatic organism, and (c) to evaluate noncarcinogenic and carcinogenic risks of studied PAEs in water for female and male residents via bathing and drinking water routes.

Material and methods

Chemicals and reagents

Analytical standard mixture including dimethyl phthalate (DMP), diethyl phthalate (DEP), di(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DnOP), butylbenzyl phthalate (BBP), di-*n*-butyl phthalate (DBP) in isooctane at 1 g/L each, and surrogate standards, consisting of diisophenyl phthalate, di-*n*-phenyl phthalate, di-*n*-benzyl phthalate, and an internal standard (benzyl benzoate) in acetone at 0.5 mg/L each were purchased from Dr Ehrenstorfer GmbH (Germany). HPLC grade *n*-hexane was obtained from Secco romeo Corporation (Tianjin, China). Neutral silica gel (100–200 mesh) was activated at 500 °C for 8 h and then deactivated by adding 5 % distilled water. Anhydrous sodium sulfate was baked at 420 °C for 12 h and stored in sealed glass jars. All the glassware used for organic compounds analyses was burned at 450 °C for 6 h prior to use.

Sample collection and pretreatment

There are six major estuaries in the PRD, namely the Humen (HM), Jiaomen (JM), Hongqimen (HQ), Modaomen (MD), Jitimen (JT), and Yamen (YM).

Sampling campaigns of surface sediments and water samples at the six major estuaries (seven riverine outlets), as shown in Fig. 1, of the PRD were carried out in spring (2–4 April 2013), summer (on 25–27 June 2013), and winter (on

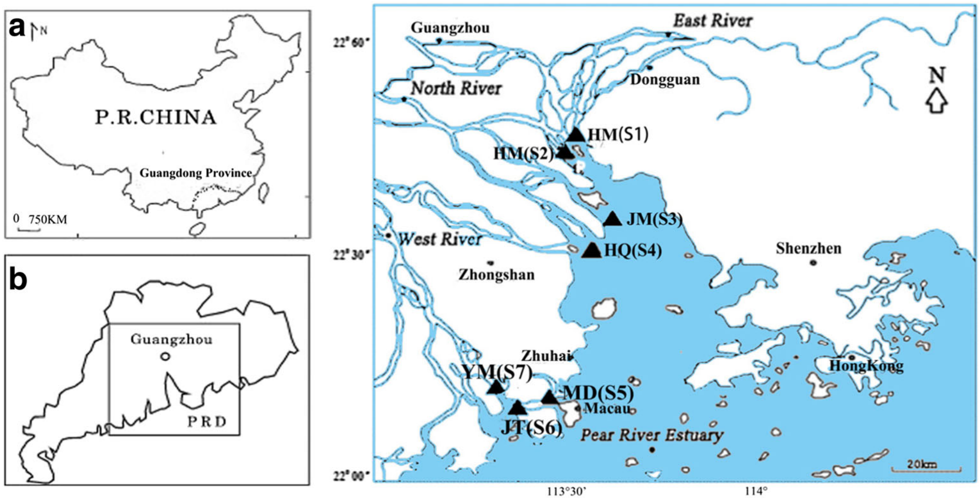

Fig. 1 Schematic showing the geographical locality of **a** the Guangdong Province in China, **b** the Pearl River Delta (PRD) region, and **c** the sampling sites within six major estuaries in the PRD are labeled with HM (Humen), JM (Jiaomen), HQ (Honqimen), MD(Modaomen), JT (Jitimen), and YM (Yamen)

Table 1 The toxicity data of PAEs to the most sensitive aquatic organisms

	Species group	Species scientific name	Toxicity data (μg/L)	Assessment factor	$PNEC_{water(\mu g/L)}$	References
DMP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} = 142000	1000	142	Adams et al. 1995
	Crustaceans	*Daphnia magna*	EC_{50} = 33000	1000	33	Adams et al. 1995
	Fish	*Lepomis macrochirus*	EC_{50} = 50000	1000	50	Adams et al. 1995
DEP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} = 16000	1000	16	Adams et al. 1995)
	Crustaceans	*Daphnia magna*	EC_{50} = 86000	1000	86	Adams et al. 1995
	Fish	*Lepomis macrochirus*	NOEC = 1650	100	16.5	Adams et al. 1995
DBP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} = 400	1000	0.4	Adams et al. 1995
	Crustaceans	*Daphnia magna*	EC_{50} = 3000	1000	3	Adams et al. 1995
	Fish	*Danio rerio(Zebra Danio)*	NOEC = 100	100	1	Ortiz-Zarragoitia et al. 2006
BBP	Algae	*Pseudokirchneriella subcapitata*	NOEC = 30	100	0.3	Rhodes et al. 1995
	Crustaceans	*Daphnia magna*	EC_{50} = 3700	1000	3.7	Gledhill et al. 1980
	Fish	*Lepomis macrochirus*	EC_{50} = 1700	1000	1.7	Adams et al. 1995
DEHP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} = 100	1000	0.1	Adams et al. 1995
	Crustaceans	*Daphnia magna*	EC_{50} = 77	1000	0.77	Rhodes et al. 1995
	Fish	*Lepomis macrochirus*	EC_{50} = 200	1000	0.2	Adams et al. 1995
DnOP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} = 100	1000	0.1	Adams et al. 1995
	Crustaceans	*Molluscs Haliotis diversicolor*	NOEC = 17.9	100	0.179	Liu et al. 2009
	Fish	*Channel Catfish*	EC_{50} = 700	1000	0.7	He et al. 2013

Table 2 Parameters used in exposure cancer and noncancer risk assessments

Parameter		Value	References
RfD	DMP DEP	10.0 0.8	US EPA 2013
	DnBP	0.1	
	BBP	0.2	
	DEHP	0.02	
	DnOP	0.02	
CC	Adults	0.1	Shi et al. 2012
RM	Adults	0.1	Shi et al. 2012
IR_w	Adults	1.5	US EPA 2013
EF	Adults	365	US EPA 2013
ED	Adults	30	US EPA 2013
BW	Female Male	50 57	He et al. 2013
H	Female Male	156 169	He et al. 2013
AT	Noncancer risk Cancer risk	365 × ED 365 × 70	US EPA 2013
TE	Adults	0.546	Wan et al. 2009
FE	Adults	0.3	Wan et al. 2009
f	Adults	1	Wan et al. 2009
k	Adults	0.001	Wan et al. 2009
τ_I	Adults	1	Wan et al. 2009
SF	DEHP BBP	0.014 0.019	US EPA 2013

10–15 January 2013). A clean brown glass bottles (1 L) were used to collect water samples 500 mm below the surface; these were closed with Teflon lids. Samples of surface sediments (0–5 cm) were collected with a gravity sampler and then stored in clean aluminum foil envelopes. To avoid tidal influences, three samples were collected during the falling tide at each investigated areas. Water samples were filtered through glass fiber filters (Whatman GF/F, 0.45-μm pore sizes), the pH adjusted to 2, then kept at 4 °C freezer prior to further treatment, usually within 3 days. The sediment samples were stored at −20 °C until further analyses.

The pretreatment methods for water and sediment samples were similar to those of Liu et al. (2010) and Zeng et al. (2008), with only minor modification. Briefly, the filtered water was spiked with 20 μL of a surrogate standards stock solution and then extracted with 90 mL (3 × 30 mL) dichloromethane (DCM). The extracts were dried with anhydrous sodium sulfate and evaporated to approximately 2.0 mL using a rotary evaporator. The sediment samples were freeze-dried, ground, homogenized, and then spiked with 20 μL of 0.1 mg/L surrogate standards into 20 g of sediment samples. Activated copper granules were added to the samples to remove elemental sulfur prior to extraction using acetone/*n*-hexane (1:1, *v*:*v*). Extracting was repeated three times. The supernatants were merged, concentrated until nearly dry, and then inverted into 10 mL *n*-hexane. The hexane solution was then further reduced to 2.0 mL using a rotary evaporator.

Table 3 Summary of concentrations of six PAE target pollutants in the water (μg/L) and surface sediments (μg/g dw) in the investigated areas, respectively, in summer, spring, and winter

PAEs	Spring[a]						Summer						Winter[a]					
	Surface water			Sediment			Surface water			Sediment			Surface water			Sediment		
	Range	Mean	DF	Range	Mean	DF	Range	Mean	DF	Range	Mean	DF	Range	Mean	DF	Range	Mean	DF
DMP	0.044–0.14	0.07	100	n.d.–0.22	0.03	25.9	n.d.–12.1	2.38	85.7	0.12–0.49	0.28	100	n.d.–3.39	0.57	57.1	0.09–1.75	0.78	60.9
DEP	n.d.–0.95	0.15	85.7	n.d.–0.18	0.05	55.6	0.010–0.15	0.046	100	n.d.–0.018	n.d.	14.3	n.d.–0.49	0.22	85.7	0.02–0.17	0.06	65.2
DBP	0.06–2.04	0.55	100	0.15–2.50	0.53	100	0.48–14.8	8.49	100	0.056–4.66	1.02	100	0.042–1.01	0.41	100	0.28–1.16	0.65	100
BBP	0.79–5.32	2.16	100	n.d.–0.12	0.01	77.8	n.d.	n.d.	0	n.d.–0.14	0.071	42.8	n.d.–0.80	0.19	71.4	0.01–0.16	0.04	78.3
DEHP	1.08–8.84	3.61	100	0.47–2.72	1.15	100	0.49–12.1	5.62	100	1.22–8.53	3.97	100	0.15–1.36	0.57	100	0.81–2.11	1.3	100
DnOP	0.079–4.30	1.07	100	0.01–0.31	0.05	100	n.d.	n.d.	0	n.d.–0.046	0.036	28.6	n.d.–0.13	0.028	71.4	0.04–0.23	0.13	100
$_6$PAE	2.78–20.7	7.61	100	0.88–5.69	1.82	100	1.27–28.1	16.5	100	1.56–13.6	5.31	100	0.50–5.03	1.99	100	1.60–4.62	2.97	100

Reported concentrations were corrected by subtracting the mean blank values

n.d. concentration was lower than the method detection limit, *DF* detected frequency (%)

[a] The data cited from our previous study (Li et al. 2015)

Both water and sediment concentrates were further purified on a prepared silica gel glass column filled (from bottom to top) with 1.5 g anhydrous sodium sulfate, 10-g neutral silica gel, and 1.5 g anhydrous sodium sulfate. The column was washed by 40 mL *n*-hexane and PAEs eluted by 80 mL of diethyl ether/*n*-hexane (3:7, *v*/*v*). The eluent was evaporated to 1 mL by a rotary evaporator and then further reduced to almost dryness under a stream of pure N_2. Redissolve the extracts in 1 mL of HPLC grade *n*-hexane for analysis. Two replicate samples were performed.

Instrumental analysis

A Thermo Trace DSQ GC-MS with a TG-1MS capillary column (30 m × 0.25 mm, 0.25-μm film thickness) in electron impact and selective ion monitoring (SIM) mode were used to determine PAEs in water and surface sediments extracts. The transfer line temperature was kept at 280 °C, and the ion source was maintained at 250 °C. Initial oven temperature was set at 40 °C for 2.0 min, then increased to 110 °C at 35 °C/min, ramped to 130 °C at 15 °C/min, then at 10 °C/min up to 270 °C (1.0 min held), and finally increased at 20 °C/min to 280 °C (10.0 min held) finally. The sample extracts (1.0 μL) were injected into GC-MS at an injector temperature of 250 °C in splitless mode. Helium gas with a speed of 1 mL/min was used as a carrier. The solvent delay was 4.0 min. The benzyl benzoate as internal calibration method was used to quantity individual PAEs based on a five-point calibration curve. Concentrations of PAEs in surface sediments were normalized to dry weight (DW).

Quality control and quality assurance

The QA/QC procedures that included analysis of spiked blanks, procedural blanks, matrix spiked, solvent blanks, and sample duplicates were conducted. Only low concentrations of DBP (0.022 μg/L) and DEHP (0.042 μg/L) were detected in the procedural blanks. The blank values were used to correct the results. The relative standard deviations (RSD) of all samples were below 10 % and the recoveries of six PAEs were within acceptable limits ranging from 76 to 106 %. Instrumental detection limits (IDL) were based on three times the signal-to-noise ratio. The calculated IDL (mean) values for DEP, DMP, DnOP, DEHP, DBP, and BBP were 0.078, 0.041, 0.063, 0.12, 0.020, and 0.054 ng, respectively. The method detection limits (MDLs) for the six PAEs were ranged from 0.38 to 3.68 ng/L in water and 0.11 to 4.31 ng/g (dw).

Risk assessment

Risk quotients (RQs) calculation of individual PAEs on the basis of the European technical guidance document about risk

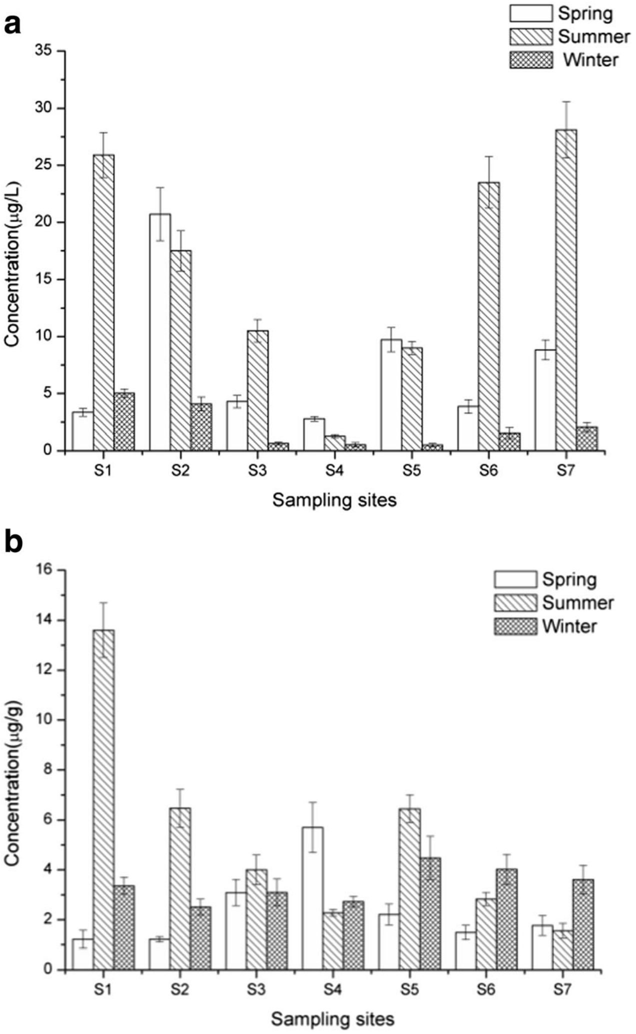

Fig. 2 Distribution of Σ_6PAE in the water (**a**) and surface sediments (**b**) in the investigated areas of the PRE, respectively, in summer, spring, and winter. Each point is the mean of three replicates ± standard deviation (SD)

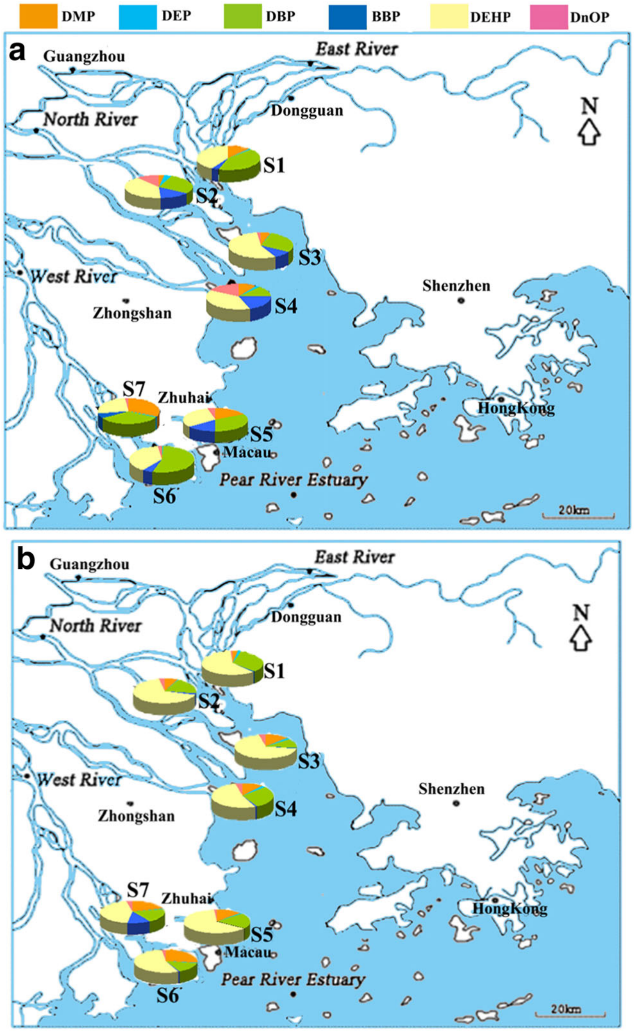

Fig. 3 Proportion of PAE congeners to the Σ_6PAE concentration in the water (**a**) and surface sediments (**b**)

evaluation were used to estimate the ecological risk for the three sensitive aquatic species (EC, 2003). The assessment was based on the measured environmental concentration (MEC) in water samples compared to the predicted no-observed-effect concentrations (PNEC). PNEC was calculated based on no observed effect concentration (NOEC) or median effective concentrations (EC_{50}), which were divided by an assessment factor (AF) (Gros et al. 2010). The average concentration of PAEs and three types of aquatic organisms (fish, crustaceans, algae) were used to assess the risk. The toxicity data and AF of the selection for six PAEs were collected from literatures and the database of US EPA (http://cfpub.epa.gov/ecotox/; Table 1) The estimated environment risk could be considered negligible if $RQ < 0.1$, low within the 0.1–1, moderate from 1 to 10, and high if $RQ > 10$ (Cristale et al. 2013).

Human health risk assessment

Human health risk assessment was performed assuming that residents may be exposed to phthalate esters in several ways with oral ingestion from drinking water considered to be the most important route (Das et al. 2014). The carcinogenic risk of DEHP and BBP, and the noncarcinogenic risks of individual PAEs were estimated based on the methods proposed by US EPA (2013) and Hamidin et al. (2008). The equation of hazard index (HI) of noncarcinogenic compounds risk is as follows:

$$HI = E/RfD \tag{1}$$

where RfD is defined as the maximum acceptable concentration of pollutants everyday (mg/kg/day) and *E* is the average daily doses of contaminants (mg/kg/day) via drinking water or

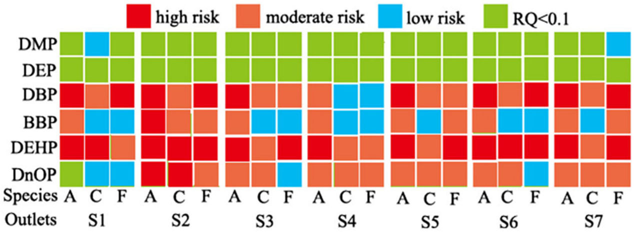

Fig. 4 Figure based on the calculated risk quotients (*RQs*) to the most sensitive aquatic organisms for the six target PAE detected in the water in each site (*A*, *C*, and *F* represents algae, crustaceans, and fish, respectively)

bathing. The value is calculated applying two approaches as follows:

$$E_1 = \mathrm{CC} \cdot \mathrm{RM} \cdot (C \cdot \mathrm{IR_w} \cdot \mathrm{EF} \cdot \mathrm{ED})/\mathrm{BW}/\mathrm{AT} \tag{2}$$

$$E_2 = \mathrm{CC} \cdot \mathrm{RM} \cdot (6\tau \cdot \mathrm{TE}/\pi)^{0.5} \cdot (C \cdot k \cdot A_{\mathrm{sb}} \cdot \mathrm{EF} \cdot \mathrm{FE} \cdot \mathrm{ED})/500/\mathrm{BW}/\mathrm{AT}/f \tag{3}$$

$$A_{\mathrm{sb}} = 10000 \cdot (\mathrm{BW} \cdot 0.0124 + 0.0061 \cdot H - 0.0099) \tag{4}$$

where E_1 is the exposure to water via the oral ingestion and E_2 is for bathing, CC is the conversion coefficient, RM is the residual ratio factor of individual PAEs after waterworks, C is the highest detected concentration of PAEs in the water (mg/L), and $\mathrm{IR_w}$ is the daily intake rate. EF, ED, BW, and H represent the exposure frequency, the exposure duration, body weight (kg), and body height (cm), respectively. AT is the average length of life (days), A_{sb} is the body surface area (cm^2), TE is the time of bathing (h), FE is the frequency of bathing (/day), f is the intestinal absorption coefficient, k is the skin absorption parameters (cm/h), and τ is the detention time for individual PAEs in the body (1 h).

The carcinogenic risk (R) of DEHP and BBP was calculated using following equation:

$$\begin{array}{ll} \mathrm{R} = \mathrm{SF{\cdot}E} & \mathrm{R} < 0.01 \\ \mathrm{R} = 1 - \exp(-\mathrm{SF{\cdot}E}) & \mathrm{R} \geq 0.01 \end{array} \tag{5}$$

where SF is the slope factor ($[\mathrm{mg/kg/day}]^{-1}$). The values of each parameter for the model are listed in Table 2. The acceptable level of carcinogenic risk (R) of chemical contaminates was less than 1×10^{-6}. For the noncarcinogenic hazard index (HI), the limit was 1.0. The standards were suggested by USEPA.

Statistical analysis

All data were indicated as means ± standard error of replicates. The statistical analyses were conducted with Origin 8.0 for Windows.

Results and discussion

Seasonal variation and spatial distribution of $\sum_6$PAEs concentrations both in water and surface sediments

The $\sum_6$PAEs concentrations in the water were 7.6, 16.5, and 2.0 μg/L (range from 2.78 to 20.7, 1.27 to 28.1, and 0.50 to 5.03 μg/L) in spring, summer, and winter, respectively (Table 3). That the highest concentrations of total PAEs were found in summer and the lowest levels were in winter is in accordance with data on other pollutants in this region, with urban stormwater runoff contributing PAEs during summer into the estuary and atmospheric deposition (Feng et al. 2009; Gevao et al. 2008; Seung-Kyu and Kurunthachalam 2007; Xu et al. 2013b).

The highest concentration of $\sum_6$PAEs was found at site S7 (2.05–28.1 μg/L; Fig. 2a), particular in summer, mainly due to that its location was in the downstream of emerging industrial cities such as Zhongshan and Jiangmen. For similar reasons, S6 also had relatively high contamination by PAEs (1.53–23.5 μg/L) in summer. However, after S7, site S2 had the highest concentrations of $\sum_6$PAEs (3.35–25.9 μg/L) perhaps because of the influence of Guangzhou and Dongguan, which are densely populated, heavy industrial, and commercial cities discharging a great amount of PAEs (Pei et al. 2013; Peng et al. 2008). Relatively low levels of total PAEs were found in S4 (0.53–7.59 μg/L) and S5 (0.50–9.72 μg/L), since their location was in Nansha scenic region where there are fewer emission sources.

Table 4 Calculated carcinogenic risk (R) values for DEHP and BBP in investigated areas

Sampling position	Gender	Carcinogenic risk (R) values for PAEs		Gender	Carcinogenic risk (R) values for PAEs	
		DEHP	BBP		DEHP	BBP
S1	Female	5.11×10^{-8}	7.11×10^{-10}	Male	4.14×10^{-8}	5.77×10^{-10}
S2		3.74×10^{-8}	3.05×10^{-9}		3.03×10^{-8}	2.47×10^{-9}
S3		2.48×10^{-8}	7.34×10^{-10}		2.01×10^{-8}	5.95×10^{-10}
S4		4.56×10^{-9}	4.53×10^{-10}		3.70×10^{-9}	3.67×10^{-10}
S5		1.75×10^{-8}	1.58×10^{-9}		1.42×10^{-8}	1.28×10^{-9}
S6		3.68×10^{-8}	7.28×10^{-10}		2.98×10^{-8}	5.90×10^{-10}
S7		2.31×10^{-8}	1.41×10^{-9}		1.87×10^{-8}	1.14×10^{-9}

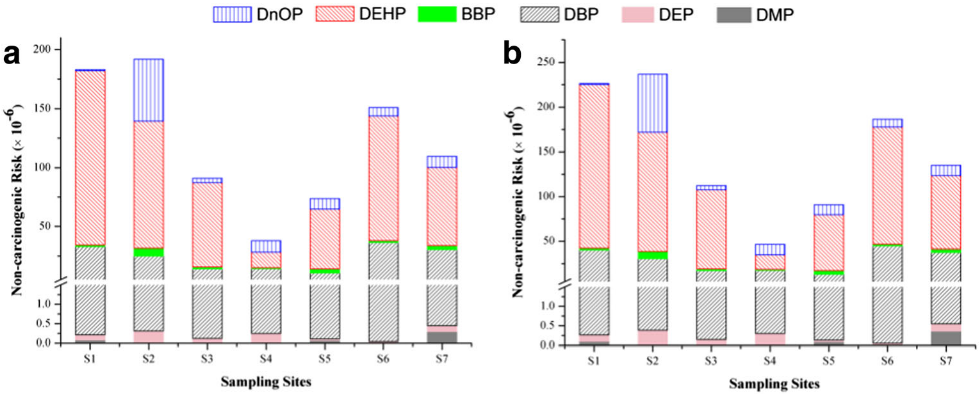

Fig. 5 Noncarcinogenic hazard risks of each PAE through drinking water intake for male (**a**) and female (**b**) citizens in the PRD region

In sediments, the average concentration of $\sum_6$PAEs was 1.82 μg/g (dw), 5.31 μg/g (dw), and 2.97 μg/g (dw) in spring, summer, and winter, respectively (Table 3). Sediments exhibit different seasonal trends in $\sum_6$PAEs compared to water samples, with the highest levels in summer and the lowest levels in spring. The distribution of PAEs was similar to that observed in rivers elsewhere (Adeniyi et al. 2011; Mackintosh et al. 2006; Sha et al. 2007). This might be because water temperature in spring was higher than that in winter and the biodegradation of PAEs was accelerated during spring (Liu et al. 2010).

Generally, the concentration of $\sum_6$PAEs in sediments was higher in western outlets than eastern ones, except for site S1 (Fig. 2b), because the rate of deposition of sediments in the west of the PRD is faster than the east and may absorb more PAEs (Gan et al. 2002). An interesting phenomenon was observed in S4 where the total concentration of PAEs was highest in sediments and lowest in water in spring. That can be explained by the attenuation/exchange process of the daily tides from the SCS. The relationship maybe as a result of the PAEs' balanced/unbalanced distribution activity among water, particles phase, and sediments (Doong and Lin 2004; Shi et al. 2005).

PAEs congeners distribution in water and surface sediments

Of the six PAEs studied, DBP (0.06–14.8 μg/L) and DEHP (0.81–12.5 μg/L) were ubiquitously in the water samples (Table 3; Fig. 3). Other main congeners found in water were DEP (n.d.–0.95 μg/L) and DMP (n.d.–12.1 μg/L). The order of average content of six PAEs was DEHP > DBP > DMP > BBP > DnOP > DEP in total three seasons; a similar distribution was found by Feng et al. (2009). The concentrations of DEHP in spring and summer at S2 and the contents of DBP in summer at the same site exceeded the acceptable values for these chemicals in surface water in China (8 μg/L for DEHP and 3 μg/L for DBP, respectively; Ministry of Environmental Protection of the People's Republic of China and General Administration of Quality Supervision, 2002).

In the sediments, DEHP (0.47–8.53 μg/g (dw)), DBP (0.05–4.66 μg/g (dw)), and DMP (n.d.–3.39 μg/g (dw)) were the dominant species (Table 3; Fig. 3). In this context, the concentration of both DEHP and DBP in the surface sediments in the investigated areas was similar to those in topsoil of Bincheng District of Yellow River Delta, lower than those in the rivers in Taiwan, Yellow River, and Yangtze River, but higher than Jianghan Plain (Fan et al. 2008; Hongjun et al. 2013; Liu et al. 2010; Sha et al. 2007; Yuan et al. 2002). Correlation analysis of target compounds in water and surface sediments was conducted. Pearson correlation coefficient values of DBP and DEHP ($p < 0.05$, $r \geq 0.779$), and DnOP and DEP ($p < 0.05$, $r \geq 0.814$) indicated the significant correlations in between. Furthermore, individual PAE congener in water and surface sediments was highly correlated to the$\sum_6$PAEs concentration. The value between DBP and the $\sum_6$PAEs concentration in water was 0.897, and between DEHP and the $\sum_6$PAEs concentration in surface sediments was 0.953 ($p < 0.01$). It was indicated that DEHP and DBP were predominant in surface sediments and water of the PRE, respectively (Fig. 3).

Ecological risk assessment of PAEs in water

The average concentrations of individual PAEs in water were used to assess the aquatic toxicity by risk quotient (RQ) calculation. Overall, DMP and DEP posed no or very low risk to aquatic environment based on fish, invertebrates, and algae RQ values that were almost all lower than 0.1 (Fig. 4). This is consistent with Selvaraj et al. (2015) and Zhang et al. (2015). Of the remaining four PAEs, DEHP may pose the most significant potential adverse effects on aquatic organisms with 71 and 29 % of samples in the high and medium risk categories, respectively. Accordingly, the ecological risks of PAE congeners were DEHP > DBP > DnOP > BBP > DMP > DEP. This ranking may be contrary to an evaluation of PAEs in surface water of the Lake Chaohu (He et al. 2013), because the pollution is different in the different areas.

Noncarcinogenic and carcinogenic risk assessment of PAEs in seven investigated areas

Both noncarcinogenic risks and carcinogenic risks via the bathing routes were far less than the risks through the oral ingestion (Table S1; Table S2). In addition, females are more susceptible to PAEs. DEHP and BBP are classified as a possible human carcinogen defined by the USEPA, so the carcinogenic risks posed by DEHP and BBP via oral intake were calculated (Table 4). The carcinogenic risks for DEHP (3.70×10^{-9}–5.11×10^{-8}) were higher than BBP (3.67×10^{-10}–3.05×10^{-9}). Fortunately, their carcinogenic risk was much lower than 10^{-6}, suggesting that the carcinogenic risk from these chemicals is very low.

The noncarcinogenic hazard risk of the PAEs for female and male via the oral intake was generally below 1 (Fig. 5), indicating that PAEs would cause little noncarcinogenic risk.

The samples with the highest health risks were found in sites S1 and S2, respectively.

Conclusion

All six selected PAEs were detected in water and surface sediments samples from the seven investigated areas of the PRE. DEHP, the most abundant compound, was found at the highest levels in S1 with the relative contribution of total PAEs that was 55 % in the water and 69 % in surface sediments. The seasonal distribution of Σ_6PAEs suggested that the highest levels were observed in summer both in water and sediments, which might be mainly attributed to urban stormwater runoff. DEHP and DBP posed much greater potential adverse effects on aquatic ecosystem than the other studied PAE congeners as indicated by risk quotients (RQs). There is little health risk posed by the PAE congeners to the residents in the PRD at the concentrations observed in water samples.

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