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ORIGINAL PAPER

The evolution of pollution profile and health risk assessment for three groups SVOCs pollutants along with Beijiang River, China

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Abstract Three important groups of semi-volatile organic compounds (SVOCs), polycyclic aromatic hydrocarbons (PAHs), organic chlorinated pesticides (OCPs) and phthalate esters (PAEs), were produced by various human activities and entered the water body. In this study, the pollution profiles of three species including 16 PAHs, 20 OCPs and 15 PAEs in water along the Beijiang River, China were investigated. The concentrations of Σ_{16}PAHs in the dissolved and particulate phases were obtained as 69–1.5 × 10^2 ng L^{-1} and 2.3 × 10^3–8.6 × 10^4 ng g^{-1}, respectively. The levels of Σ_{20}OCPs were 23–66 ng L^{-1} (dissolved phase) and 19–1.7 × 10^3 ng g^{-1} (particulate phase). Nevertheless, higher levels of PAEs were found both in the dissolved and particulate phases due to abuse use of plastic products. Furthermore, non-cancer and cancer risks caused by these SVOCs through the ingestion absorption and dermal absorption were also assessed. There was no non-cancer risk existed through two kinds of exposure of them at current levels, whereas certain cancer risk existed through dermal absorption of PAHs in the particulate phase in some sampling sites. The results will show scientific insights into the evaluation of the status of combined pollution in river basins, and the determination of strategies for incident control and pollutant remediation.

Keywords Beijiang River · PAHs · OCPs · PAEs · Risk assessments

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Introduction

During the past several decades, ever increased population growth and rapid industrialization have imposed enormous pressure on traditional freshwater sources (Rabodonirina et al. 2015). Various organics ubiquitously are present in the global aquatic environment by different discharges.

Semi-volatile organic compounds (SVOCs) were a class of organics mostly with high toxicity, lipophilicity and bioaccumulation properties (Li et al. 2013). Polycyclic aromatic hydrocarbons (PAHs) are a large group of SVOCs mainly originated from the incomplete burning of biomass, fossil fuel, organic matter and lipophilic chemicals that are widely distributed in various environments, including water (Rabodonirina et al. 2015), soil (Qu et al. 2015; Ruby et al. 2016), dust (Iwegbue and Obi 2016), air (Li et al. 2013) and even in biota (Gauthier et al. 2015), especially in the industrial areas (An et al. 2011). Among them, 16 PAHs were listed as the priority pollutants by US Environmental Protection Agency (USEPA) and European Union, and seven of them (benzo[*a*]anthracene (B*a*A), chrysene (Chry), benzo[*b*]fluoranthene (B*b*F), benzo[*k*]fluoranthene (B*k*F), benzo[*a*]pyrene (B*a*P), dibenz[*a,h*]anthracene (D*i*B), indeno[1, 2, 3-*cd*]pyrene (In*cd*P)) were identified carcinogens in the experimental animal (Tavakoly Sany et al. 2014). Therefore, excessive attentions were paid to PAHs for their impact on the human health and the environment (Gauthier et al. 2015), owning to their bioaccumulation and toxicity properties (Tavakoly Sany et al. 2014; Ruby et al. 2016).

OCPs are an important group of anthropogenic environmental organic contaminants (Qiao et al. 2010). Nine of OCPs were regarded as persistent organic pollutants (POPs) by the Stockholm convention because of their recalcitrant degradation, bioaccumulation and high toxicity in nature environment (Li et al. 2016b), as well as ubiquitously distributed in various environmental matrices (Zhang et al. 2013b; Sun et al. 2014). Furthermore, like high lipophilicity of halogenated tetrabromobisphenol A (Li et al. 2016a), residues of DDTs and HCHs were detected even in human breast milks (Wang et al. 2016a), presenting an harm for not only environment, but also human beings.

Phthalate esters (PAEs) are another class of important SVOCs widely used as plasticizers (accounted for 10–60% of the total plastic) in polyvinyl chloride, polyvinyl acetates, cellulosic and polyurethanes (Zeng et al. 2008). As a result of excessive use of plasticizers, they also widely occurred in different environmental matrices (Sun et al. 2014; Net et al. 2015). Furthermore, their toxicity and biological effect were drawn attention of public (Feng et al. 2009). For example, some PAEs, including di(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DnBP) and their metabolites, could disturb the tryptophan–niacin metabolism in the experimental rats (Fukuwatari et al. 2002). Diisobutyl phthalate (DiBP) could impair reproductive development of male rat (Saillenfait et al. 2008). Therefore, six PAEs, including DnBP, diethyl phthalate (DEP), dimethyl phthalate (DMP), butyl benzyl phthalate (BBP), DEHP and dioctyl phthalate (DnOP), were listed as priority pollutants by USEPA.

Beijiang River, the second largest of the three tributaries to the Pearl River and located in the north-central region of Guangdong Province China, is one of the main of drinking water sources in Pearl River Delta. However, various anthropogenic activities might constitute a potential threat to the water usage of the local and downstream people due to large amount of people lived along with Beijiang River. For instance, different wastewaters were frequently discharged from the mines, factories, and urban and rural sewage systems into the Beijiang River. Previously, the pollution profile of the three kinds of SVOCs had been studied in Dongjiang River, Pearl River and Xijiang River in Pearl River Delta (Zeng et al. 2008; Zhang et al. 2013b; Liu et al. 2014b); however, there were few studies on PAHs, OCPs and PAEs conducted simultaneously in Beijiang River so far, as well as their sources apportionment, mutual correlations and integrated risk. Only one paper about the assessment of PAHs in surface sediments in the Beijiang River was published (Song et al. 2014). As such, basic and systematic environmental data for PAHs, OCPs and PAEs were urgently needed.

Given this background, the pollution level and distribution of 16 PAHs, 20 OCPs and 15 PAEs in Beijiang River mainly from different areas with the cities, towns, dams, factories and e-waste dismantling workshops were investigated. In addition, to acquire more exact information explaining possible pollution distributions, the composition and possible sources of target organics were discussed in detail. Finally, human health assessment through water consumption (ingestion and dermal absorption) of target pollutants was evaluated by using exposure risk mode and health risk parameter by the USEPA.

Materials and methods

Materials

Standard solutions for the quantification analysis and quality control experiments were achieved as our early published references (Li et al. 2013; Sun et al. 2014). The detailed information was provided in supplementary information.

Study area and sampling sites

Water samples were collected from twenty sampling sites from Sanshui City to Shaoguan City in Beijiang River during April, 2014 as showed in Fig. S1. During the sampling, pH, water temperature and dissolved O_2 (data listed in Table S1) were also measured in situ to understand the real status of water. Approximately 10 L water was collected using an amber glass bottle (precleaned with detergent and high purity water), and then 0.5 g sodium azide was spiked in the water to prevent microbial degradation. Subsequently, water samples were carried back to laboratory as soon as possible and stored at 4 °C refrigerator.

Sample pretreatment, analysis and quality control

Sample extraction and purifying were performed as our previous study (Sun et al. 2014). The detailed pretreatment steps were provided in supplementary information (SI). All the samples were quantified using a 7890A gas chromatography (GC) coupled with a 5975C mass spectrometer detector (Agilent Technologies, USA) equipped with a HP-5MS silica-fused capillary column (30 m × 250 μm × 0.25 μm). The detailed analysis procedures were also provided in the SI.

The quantification of the target compounds were based on the ratio of target peak area and the internal standard peak corresponding to the six-point calibration curves with $R^2 \geq 0.99$. Blank experiment and spiked blank experiment were performed to determine the values of blank and the recoveries of target compounds. Ten samples are inserted into a blank experiment and a spiked blank experiment. The recoveries of the target organics were defined as the ratio of target spiked concentration values—blank concentration values/target spiked concentrations. The recoveries of PAHs in the dissolved and particulate phases were 68–114% and 69–172%, respectively. The recoveries of OCPs were 44–134% and 51–129% in the dissolved and particulate phases, respectively. The recoveries of PAEs were 41–242% and 46–245% in the dissolved and particulate phases, respectively. All samples were spiked with known amount of surrogate standards before the extraction, and these values are listed in Table S2. The method detection limit (MDL) was obtained through our pervious study (Sun et al. 2014). The MDL of PAHs, OCPs and PAEs was 0.03–0.14, 0.05–0.18 and 0.08–0.23 ng L^{-1} in the dissolved phase, respectively, and 5.3–23, 8.9–20 and 13–39 ng g^{-1} in the particulate phase, respectively.

Risk exposure assessment

Health risk assessment is based on the available risk exposure model of compounds (USEPA 1989, 2014). Residential exposure pathways to pollutants in water are mainly including direct ingestion though drink water, dermal contact through bath and incidental ingestion while swimming (Liu et al. 2014a). In this study, first and second pathways were taken into account for risk assessment, since there is uncertainty amount for incidental ingestion while swimming (Tavakoly Sany et al. 2014).

Exposure dose by direct ingestion through drink water The exposure doses (Di, mg/kg·day) of ingestion were calculated using Eq. 1, which are obtained from the USEPA (USEPA 1989).

$$\mathrm{Di} = \frac{\mathrm{CW} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{1}$$

where CW is chemical concentration in water (mg L^{-1}); IR is ingestion rate (L d^{-1}); EF is exposure frequency (d y^{-1}); ED is exposure duration (y); BW is body weight (kg); AT is pathway-specific period of exposure for non-cancer effects (i.e., ED × 365 d y^{-1}), and 70-year lifetime for carcinogenic effects was employed (i.e., 70 y × 365 d y^{-1}).

Exposure dose by dermal absorption with chemistry through bath. The exposure doses (Dd, mg/kg·day) of dermal contact were calculated using Eq. 2 (USEPA 1989).

$$\mathrm{Dd} = \frac{\mathrm{CW} \times \mathrm{SA} \times \mathrm{Kp} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{CF}}{\mathrm{BW} \times \mathrm{AT}} \tag{2}$$

where SA is skin surface area available for contact (cm^2); ET is exposure time (h d^{-1}); CF is volumetric conversion factor for water (1 L per 1000 cm^3); Kp is dermal permeability coefficient of compound in water (cm h^{-1}), which was obtained from Eq. 3 (USEPA 2014).

$$\text{Log Kp} = -2.8 + 0.66 \text{ Log Kow} - 0.55\text{MW} \quad (3)$$

where Kow is octanol/water partition coefficient of non-ionized species (dimensionless), which acquired from software program ECOSAR v.1.11 (Ecological Structure Activity Relationships). MW is molecular weight (g mol^{-1}).

Health risk assessment The health risk (non-cancer and cancer risks) caused by pollutants through the direct ingestion and dermal contact was assessed, respectively.

1. The hazard quotient (HQ) for non-cancer risk was calculated according to Eq. 4:

$$\text{HQ} = D/\text{RfD} \quad (4)$$

where D is obtained though the Eqs. 1 (Di) and 2 (Dd). RfD is reference dose oral of a special compound for non-cancer risk (mg/kg·day), which gained from USEPA IRIS and listed in Table S3. Simultaneously, the dermal absorbed dose was derivation of oral RfD using Eq. 5 (USEPA 2014):

$$\text{RfD}_{\text{ABS}} = \text{RfD} \times \text{ABS}_{\text{GI}} \quad (5)$$

where RfD_{ABS} is the dermal absorbed dose (mg/kg·day); ABS_{GI} is gastrointestinal absorption efficiencies (dimensionless).

2. Lifetime cancer risk (LCR) was also calculated by Eq. 6 (USEPA 2014):

$$\text{LCR} = D \times \text{SF} \quad (6)$$

where SF (per mg/kg day) is the oral carcinogenic slope factor of each compound obtained from USEPA IRIS, Environmental Criteria and Assessment Office and PPRTX (USEPA 2016), which are listed in Table S3. The dermal carcinogenic slope factor is deduced using Eq. 7 (USEPA 2014) through oral carcinogenic slope factor.

$$\text{SF}_{\text{ABS}} = \text{SF}/\text{ABS}_{\text{GI}} \quad (7)$$

Additionally, related parameters for risk assessment are listed in Table S4.

Result and discussion

PAHs pollution profile

The pollution profile of PAHs in the dissolved and particulate phases was investigated along with Beijiang River. As shown in Fig. 1, S2 and Table S5, the concentrations of 16 PAHs in the dissolved and particulate phases of 20 sampling sites were 69–1.5×10^2 ng L^{-1} and 2.3×10^3–8.6×10^4 ng g^{-1}, respectively. In the dissolved phase, the most abundant PAHs present was phenanthrene (Phe, accounted for 15–27% of total PAHs), followed by naphthalene (Nap, 13–23%), fluoranthene (Flua, 7.7–12%) and pyrene (Pyr, 6.0–8.8%); the minor ingredients were B*b*F (2.1–5.8%), B*k*F (1.7–4.8%), acenaphthylene (Ace, 1.8–2.6%) and benzo[*g,h,i*]perylene (B*ghi*P, 0–4.9%). In contrast, the distribution profile of those PAHs in the dissolved and particulate phases was different dramatically; that is, the less abundance congeners in the dissolved phase were the dominate congeners in the particulate phase. The reason for this is mainly due to low solubility and high partition coefficient of high-weight PAHs (Feng et al. 2007). Further analysis found that the concentrations of $\sum_{16}$PAHs in the dissolved phase at S9 and S20 sampling site were much higher than those at other sites. Higher concentration at S9 site may be due to that a huge dam was situated at S9 site which might stop the flow of river and further enriched the target compounds in the water. Higher concentration at S20 site was because lots of industrial mining areas near there may lead to a series of large-scale mechanical operation, heavy-duty vehicle transport, and these industrial activities are also sources of PAHs (Yun et al. 2016). However, similar results did not appear in the particulate phase, and $\sum_{16}$PAHs concentration at site S14 (8.6×10^4 ng g^{-1}) was the highest, followed by sites S8, S4 and S7 (4.6×10^4, 3.7×10^4 and 3.4×10^4 ng g^{-1}, respectively), but the lowest levels were obtained at sites S1 and S17 (2.5×10^3 and 2.3×10^3 ng g^{-1}, respectively). This might be different sources contributing to PAHs.

The distribution of PAHs with different rings in the dissolved and particulate phases was also analyzed. As Fig. 2a shows, in the dissolved phase, PAHs with 2- and 3-rings were the most abundant and their compositions reached to 22–50% and 26–42% of total PAHs, respectively, followed by 4-rings PAHs (17–29%),

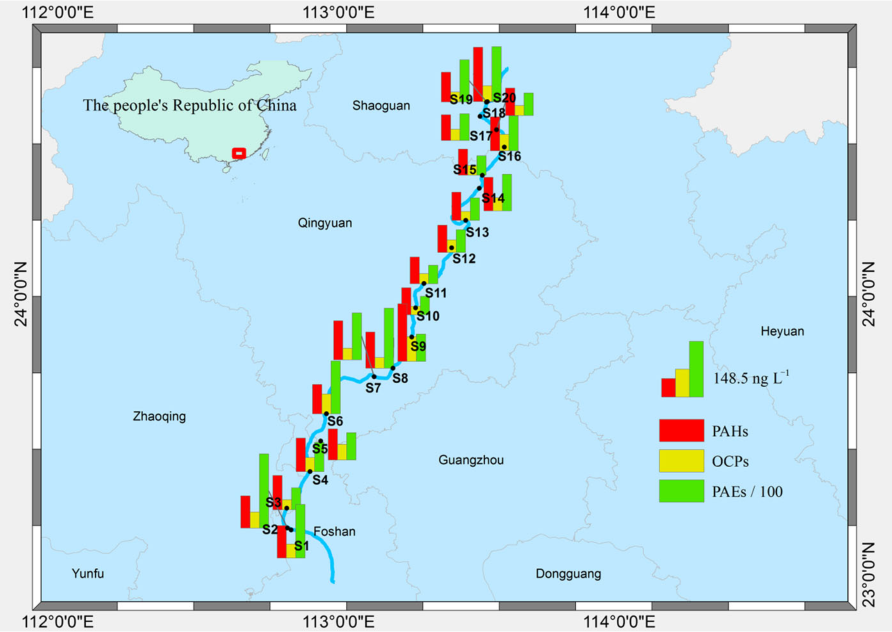

Fig. 1 PAHs, OCPs and PAEs concentrations in the dissolved phase in Beijiang River

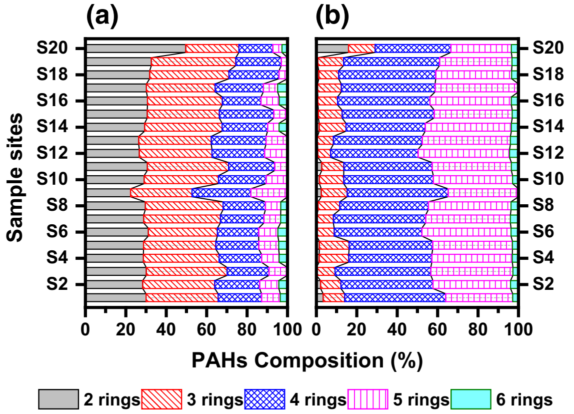

Fig. 2 Compositions of PAHs in dissolved phase (**a**) and particulate phase (**b**) in Beijiang River

with low specific weight of 5 (3–18%)- and 6-rings (0–5%). In contrast, in the particulate phase (Fig. 2b), the most abundant PAHs were 4-rings (38–50% of the total PAHs) and 5-rings PAHs (30–45%), whereas 3 (6.3–15%)-, 6 (0–4.1%)- and 2-rings (0–16%) PAHs were less abundant. This is because low-ring PAHs were more water soluble and high-ring PAHs were more likely to attach to particulate because of their high log K_{OW} (Sun et al. 2009).

Compared with other surveyed rivers around the China (Table S6), in the dissolved phase, the highest level of PAHs was found in Hun River (1.6 × 10^3–5.3 × 10^3 ng L^{-1}) during the flood period (Zhang et al. 2013a), followed by Yangtze River (3.2 × 10^{-1}–6.2 μg L^{-1}) (Feng et al. 2007). Comparatively, the concentrations of $\sum_{16}$PAHs in this study were much lower than those from most other Chinese rivers, including Weihe River (3.5 × 10^2–4.4 × 10^3 ng L^{-1}) (Chen et al. 2015), Humen River (8.5 × 10^2–1.4 × 10^3 ng L^{-1} during the flood tides and 6.3 × 10^2–2.0 × 10^3 ng L^{-1} during the ebb tides) (Liu et al. 2014b), Daliao River (71–4.3 × 10^3 ng L^{-1}) (Zheng et al. 2016), Liaohe River (1.1 × 10^2–2.9 × 10^3 ng L^{-1} in the dry period and 95–2.8 × 10^3 ng L^{-1} in the level period) (Lv et al. 2014), Songhua River (1.6 × 10^2–2.7 × 10^3 ng L^{-1}) (Zhao et al. 2014), East Lake (10-5.3 × 10^2 ng L^{-1}) (Yun et al. 2016) and Jialing River (4.7 × 10^2–9.9 × 10^2 ng L^{-1}) (Cai et al. 2012), nearly as same as those of Taihu Lake (38–1.8 × 10^2 ng L^{-1}) (Qiao et al. 2007), but slightly higher than Xijiang River (22–1.4 × 10^2 ng L^{-1}) (Deng et al. 2009). Compared with other surveyed rivers around the world (Table S6), in the dissolved phase, the concentrations of PAHs in this study were slightly higher than Moscow River in Russia (Eremina et al. 2016) and Riverine waters of Ulsan Coast in Korea (You et al. 2012), but much lower than Ikpa River in Nigeria (Inam et al. 2016). Furthermore, the levels of PAHs in the particulate phase were compared in rivers around the world

(Table S6) and found less PAHs pollution in the particulate phase. The PAHs concentrations in this study were markedly higher than those in Taihu Lake (Qiao et al. 2007) and Xijiang River (Deng et al. 2009). The results indicated, compared with other studies, the PAHs levels as well as pollution profiles in the dissolved and particulate phases in this study are different, which might be due to different contaminant sources.

Source apportionment of target compounds is important for further environmental remediation precisely and effectively. By calculating of the special ratios of PAHs (Sun et al. 2014), the sources of PAHs in the dissolved and particulate phases were probed (Figs. S3 and S4). The ratios of Ant/(Ant + Phe) and Flua/(Flua + Pry) were 0.08–0.16 and 0.54–0.60 in the dissolved phase, as well as 0–0.31 and 0.45–0.88 in the particulate phase, respectively. These indicated the combustions of biomass and coal as the major sources for PAHs in the dissolved phase, while the petroleum and the combustions of biomass and coal were the main sources for PAHs in the particulate phase (Sun et al. 2014). Furthermore, the calculated ratios of IncdP/(IncdP + Bghip) and BaA/(BaA + Chr) ranged from 0 to 1.0 and from 0.34 to 0.48 in the dissolved phase; 0.67–1.0 and 0.32–0.62 in the particulate phase, respectively. These illustrated the combustions of petroleum products, biomass and coal were the main sources for PAHs in the dissolved phase (Liu et al. 2014b); besides, the combustions of biomass and coal were the main PAHs sources, a small part was originated from mixed of sources of petroleum and combustion in the particulate phase (Sun et al. 2014).

OCPs pollution profile

The concentrations of $\sum_{20}$OCPs in the dissolved phase were not as variable as in the particulate phase at different sampling sites (Figs. 1 and S2). In the dissolved phase, the $\sum_{20}$OCPs concentrations ranged from 23 to 66 ng L^{-1}, and above 50 ng L^{-1} were obtained at sites S9 and S6, which were much higher than those at other sites, followed by sites S16, S2 and S20 with concentrations of 44, 43 and 42 ng L^{-1}, respectively. Low levels of OCPs were detected at sites S10, S13 and S15. High levels of OCPs present in those regions were mainly due to that they are located in cities, upstream of dam, confluence of rivers and industrial area, where OCPs could be transported into aquatic environment through runoff from nonpoint sources, atmospheric deposition, industrial discharge and other means (Feng et al. 2011). As shown in Table S7, among these OCPs, the detectable rates of most individual OCPs were up to 100%, except α-HCH (45%), α-chlordane (95%), aldrin (70%), endrin (0%), β-chlordane (0%) and heptachlor epoxide (0%). p,p′-DDD and endosulfan sulfate were most frequently detected with a high concentrations ranging from 8.9×10^{-1} to 17 ng L^{-1} and from 3.0 to 11 ng L^{-1}, respectively. Both of them were the most dominant OCPs in the dissolved phase occupied 3.3–32% and 8.1–34% of total OCPs, respectively. Endosulfan was used during 1994–2004 as technical or formulated products in Guangdong Province (Sun et al. 2014), while endosulfan sulfate is the main component in the environment derived from photolysis and biodegradation of endosulfan (Wang et al. 2016b). Besides, δ-HCH (1.9–6.4 ng L^{-1}) and α-endosulfan (4.0×10^{-1}–14 ng L^{-1}) were also frequently present, accounting for 6.6–23% and 1.5–21%, respectively. However, some OCPs including heptachlor epoxide, β-chlordane and endrin are not present in all the samples investigated. The results showed that OCPs were frequently detected in Beijiang River, indicating somewhat polluted, owning to continual use for agricultural, domestic or industrial origin (Geyikçi and Büyükgüngör 2011).

Compared with in the dissolved phase, the OCPs concentrations were more fluctuant at different sampling sites in the particulate phase. The concentrations of $\sum_{20}$OCPs ranged from 19 to 1.7×10^3 ng g^{-1} with the highest level at site S19, and the sites S18, S9 and S11 were also heavily polluted with $\sum_{20}$OCPs concentrations of 1.4×10^3, 1.3×10^3 and 1.4×10^3 ng g^{-1}, respectively, which were almost 6 to 100 times higher than those at sites S17 (19 ng g^{-1}), S16 (1.7×10^2 ng g^{-1}), S1 (1.8×10^2 ng g^{-1}) and S4 (1.8×10^2 ng g^{-1}). The huge gap among sampling sites indicated that anthropogenic activities might bring different amount of OCPs to different areas. Additionally, α-endosulfan (4.2–2.3×10^2 ng g^{-1}, accounting for 7.8–37% of the total OCPs) and aldrin (2.8–77 ng g^{-1}, accounting for 1.3–15%) were detectable at all sampling sites. The probable reason is that endosulfan is still in use globally, and technical endosulfan contains 70% α-endosulfan (Wang et al. 2016b), while aldrin is used as alternative to DDT and widely used during 1950s to 1970s (Zhang et al.

2012a). Although γ-HCH (detectable rate, 90%) was not present at all sites, the highest concentration was detected for γ-HCH (from not detected (nd) to 5.6×10^{2} ng g^{-1}, accounting for 0–35% of $\sum_{20}$-OCPs). Similarly to their homologues, δ-HCH (nd-2.6×10^{2} ng g^{-1}), β-HCH (nd-2.6×10^{2} ng g^{-1}) and α-HCH (nd-1.1×10^{2} ng g^{-1}) were also the predominant compounds in the particulate phase, accounting for 0–20%, 0–20% and 0–12% of $\sum_{20}$-OCPs, respectively. In contrast, both low levels and detectable rates were found for p′p-DDE, γ-chlordane and heptachlor epoxide. This is due to that p′p-DDE is metabolic product of DDTs under aerobic conditions and only account for 5% of technical DDTs (Yang et al. 2014). Besides, chlordane production began in 1948 and was utilized globally over the next 50 years. And, technical chlordane involves α-chlordane (11%), γ-chlordane (13%) and heptachlor (5%) (Bidleman et al. 2002), and γ-chlordane is easier to be degraded than α-chlordane, which is potential reason for low levels γ-chlordane (Nomeir and Hajjar 1987). The reason for low levels and detectable rate of heptachlor epoxide is due to that it is a metabolite of heptachlor (Alam et al. 2014). Similar to the dissolved phase, endrin was also not present in all samples. Nevertheless, α-chlordane and endosulfan sulfate were not present in the particulate phase.

The compositions of OCPs in the dissolved and particulate phases were also investigated. Twenty of OCPs was divided into six groups including HCHs, DDTs, chlordane, heptachlor, endosulfan and others as grouped in Table S7. As shown in Fig. S5, in the dissolved phase, the most abundant groups were HCHs, DDTs and endosulfan, which accounted for 13–39%, 12–36% and 14–49% of the total OCPs, respectively, followed by 'others' (12–25%). Heptachlor and chlordane were the minor groups with proportion of 2.8–7.2% and 0–9.5%, respectively. Comparatively, in the particulate phase, HCHs and endosulfan were still the main groups with proportion of 0–70% and 7.8–37%, respectively, at most sampling sites. The difference is that the proportion of endosulfan was nearly same in both phases, but the proportions of HCHs in the particulate phase were much higher than those in the dissolved phase. The proportion of the 'others' group was also high (5.5–45%) in the particulate phase, which was almost the same as those in the dissolved phase, whereas DDTs accounted for 0–60% of total OCPs in the particulate phase, which was onefold lower than those in the dissolved phase (mean value). Similar to the dissolved phase, the proportions of heptachlor and chlordane were very low in the particulate phase at most sites except heptachlor at S16 in the particulate phase. The result is consistent with our previous study (Sun et al. 2014).

To further understand the status of OCPs in the Beijiang River, the OCPs levels in this study were compared with other studies around the world. As shown in Table S8, in the dissolved phase, the highest levels of Σ_{23}OCPs were found in Karun River in Iran (22–89 μg L^{-1}) (Behfar et al. 2013) and Nanshan underground River in China (61–9.4×10^{2} ng L^{-1}) (Alam et al 2014). The Σ_{20}OCPs was 19–1.1×10^{2} ng L^{-1} in Poyang Lake (Zhi et al. 2015), which was slightly higher than those in the current study. The pollution levels of OCPs in Yangchaihu Lake, East Lake, Riverine runoff of the Pearl River Delta, Hangzhou Bay and Huaihe River in China (Guan et al. 2009; Feng et al. 2011; Yang et al. 2014; Li et al. 2016b) were comparable to the present study. As compared with the rivers outside of China, the OCPs levels in Chenab River in Pakistan and Sarno River in Italy (Mahmood et al. 2014; Montuori et al. 2014) were lower than those in the current study. As for OCPs in the particulate phase (Table S8), owning to the concentration unit or the number of congeners is different, further comparison in levels of OCPs in the particulate will not be performed with this study. Nevertheless, the HCHs and DDTs levels with others studies were compared. As shown in Table S8, HCHs and DDTs in the dissolved phase in this study are in middle level, but present relatively high contaminated levels in the particulate phase.

Furthermore, the ratios of α-HCH/γ-HCH were also used to infer the possible sources of HCHs in the river basin (Sun et al. 2014). As shown in Fig. 3, in the dissolved phase, the ratios were in the range of 0–3.0, implying that HCHs mainly originated from lindane and the mixed of lindane and technical HCHs (Sun et al. 2014). In the particulate phase, the ratios were obtained as 0–4.8, indicating lindane was the major source for HCHs (Yang et al. 2014). Similarly, the ratio of (DDD + DDE)/DDTs is used to determine the possible sources of p′p-DDTs (Mahmood et al. 2014). As shown in Fig. S6, the (DDD + DDE)/DDTs ratios in the dissolved and particulate phases were 0.29–0.88 and 0.22–1.0, respectively, indicating that historical

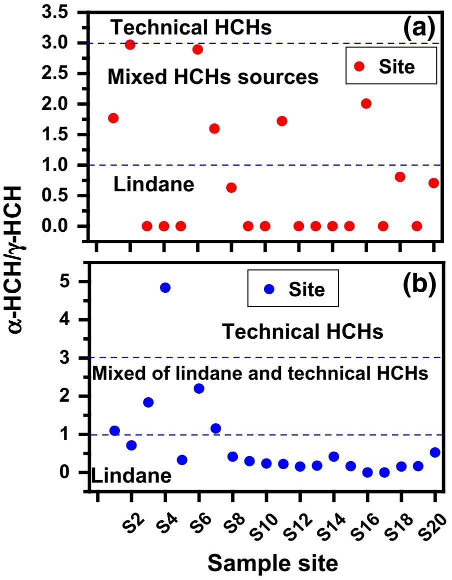

Fig. 3 Sources determining of HCHs in dissolved phase (**a**) and particulate phase (**b**) in Beijiang River

residue of p′p-DDT was the main source of DDTs in the dissolved phase, while there was a new input of p′p-DDT in the particulate phase (Wang et al. 2013).

PAEs pollution profile

Fifteen PAEs in the dissolved and particulate phases were also determined. As shown in Figs. 1 and S2, the concentrations of $\sum_{15}$PAEs ranged from 4.9×10^3–2.0×10^4 ng L^{-1} to 3.0×10^3–2.2×10^4 ng g^{-1} in the dissolved and particulate phases, respectively. In the dissolved phase, the highest $\sum_{15}$PAEs concentration was observed at site S2, followed by at sites S8, S20, S1 and S6, with all concentrations over 1.4×10^4 ng L^{-1}, whereas the lowest $\sum_{15}$PAEs concentrations were at sites S10 and S11, less than 5×10^3 ng L^{-1}. It is obviously observed that highly contaminated sites were mainly located near the cities, industrial regions and confluence of rivers, which were probable sources for PAEs. In the particulate phase, the highest concentrations of $\sum_{15}$PAEs were found at sites S8 and S9, upstream of dam, both reaching to 2.1×10^4 ng g^{-1}. The next high level of $\sum_{15}$PAEs is present at sites S7, S19, S18, S15 and S11, where are near the e-waste dismantling and mining area. Therefore, the PAEs concentrations in residual sites (except for above 7 sites) were almost in the same order of magnitude.

As for the distribution of individual PAEs (Table S9), in the dissolved phase, the most dominant PAEs were DiBP and DnBP, accounting for 42–70% and 24–55% of the total PAEs, respectively. Followed by DMP and DEP, which present a proportion of 0.52–6.5% and 1.0–5.2%, respectively, consequently, those high levels of low-molecular-weight PAEs are ubiquitously found, mainly due to widely applied to cosmetics and personal care products (Zheng et al. 2014). DEHP is also a very prevalent organics for plasticizer, but the proportion of DEHP was very low, only accounting for 0.02–2.5% of total PAEs in the dissolved phase. Except for above-mentioned five main PAEs, the concentrations of other PAEs were considerably low, less than 0.5% of the total PAEs. Compared with those in the dissolved phase, the pollution profiles of individual PAEs in the particulate phase were slightly different. DnBP was the most predominant PAEs with substantially high levels (2.3×10^3–1.8×10^4 ng g^{-1}) and proportion (accounting for 60-87% of the total PAEs). Besides, the relative high levels of DEHP were found (1.9×10^2–3.5×10^3 ng g^{-1}, accounting for 6.3–24% of the total PAEs). Nevertheless, unlike in the dissolved phase, the proportion of DiBP in the particulate phase was obviously lower than that in the dissolved phase, that is, probable due to DiBP with short chains with more water soluble, always consistent with previous study (Sun et al. 2014; Zheng et al. 2014).

The compositions of PAEs in the dissolved and particulate phases were also investigated. Fifteen PAEs were divided into six groups, including DMP, DEP, DiBP, DnBP, DEHP and ‘others’ (Table S9). As shown in Fig. 4, DiBP (accounting for 42–70% of the total PAEs) and DnBP (24–55%) were the most predominant PAEs groups, whereas other four groups only made up 2.1–13% of total PAEs in the dissolved phase. In contrast, DnBP (60–87%) was the only predominate PAEs groups in the particulate phase, followed by DEHP (6.3–24%) and ‘other’ (0.11–17%), with least groups of DMP (0–1.1%) and DEP (0.01–0.14%). Results indicated that PAEs with shorter side chain, such as DnBP and DiBP, were more water soluble, while more lipophilic longer side chain PAEs were more inclined to assemble to the particulate (Sun et al. 2014).

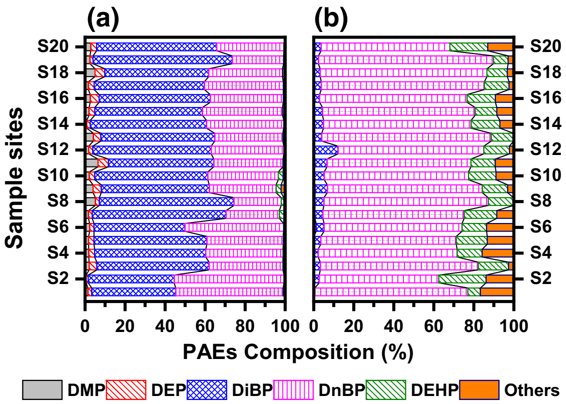

Fig. 4 Compositions of PAEs in the dissolved phase (**a**) and particulate phase (**b**) in Beijiang River

Furthermore, six priority PAEs, including DnBP, DEP, DMP, BBP, DEHP and DnOP, were taken out for comparison with other studies around the world (Table S10). In this study, total concentrations of them in the dissolved and particulate phases were obtained as 2.1×10^3–1.1×10^4 ng L^{-1} and 2.6×10^3–2.1×10^4 ng g^{-1}, respectively, accounting for 30–57% and 85–98% of total PAEs. Compared with other studies, considerably higher Σ_6PAEs levels were detected in Hun River (Li et al. 2015), Yellow River (Sha et al. 2007) and Yangtze River (Du et al. 2013) than those in the current study, while the Σ_6 PAEs levels in Yangtze River (Zhang et al. 2012b) and lakes of Beijing (Zheng et al. 2014) were slightly lower than this study. Even though PAEs pollution was heavy in China, PAEs concentrations in foreign showed exceedingly low values, such as Moscow River in Russia, Selangor River in Malaysia and Kaveri River in India according to the reports (Santhi and Mustafa 2013; Selvaraj et al. 2015; Eremina et al. 2016). As for PAEs in the particulate phase, related literatures were quite limited. Only two papers reported that PAEs concentrations in lakes of Beijing (Zheng et al. 2014) and Yellow River (Sha et al. 2007), were higher than those in the current study.

Correlation of PAHs, OCPs and PAEs

As shown in Figs. 1 and S2, the concentrations of PAEs were highest in the dissolved phase. The probable reason is that PAEs is widely applied to construction material, clothing, furnishings, polyvinyl chloride plastic, varnishes and personal care products (Zheng et al. 2014). Followed by PAHs, they are also abundant, due to their widely sources and not easily degraded in the environment. Although banned use of OCPs, it could be detected with relatively low levels. Simultaneously, Pearson's correlation coefficients with three contaminants were analyzed to measure the relative closeness of the two variables. As showed in Table S11, the concentrations of PAHs were positively correlative with OCPs in the dissolved phase, while PAEs was not relative to PAHs and OCPs. However, in the particulate phase, the highest levels were loaded in PAHs, which are slightly higher than PAEs levels, far exceeded the OCPs levels. Further analysis found that high level of PAHs is mainly originated from vehicular emissions, a mix of oil and coal emissions, and coal combustion (Sofowote et al. 2008), owning to larger proportion of high-ring PAHs than low-ring PAHs. However, high levels of PAHs were not relative to OCPs and PAEs, while OCPs showed a positive correlation with PAEs. The probable reason is that as mentioned above, high levels in the particulate phase mainly originated from vehicular emissions which is not related to OCPs and PAEs.

Human health risk assessment

Non-cancer and cancer risks of three groups of SVOCs in the dissolved and particulate phases were calculated. As shown in Fig. 5a, the HQ values for non-cancer risk of PAHs through two pathways in both

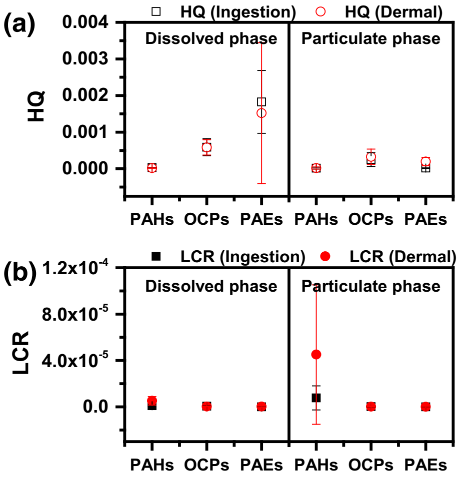

Fig. 5 Non-cancer (**a**) and lifetime cancer risks (**b**) of PAHs, OCPs and PAEs in the dissolved and particulate phases

phases were almost at the same level around 10^{-5}, which was far lower than 1, indicating completely no non-cancer risk (Liu et al. 2014a; Sun et al. 2014) posed by PAHs through two pathways in Beijiang River. Although the HQ values of OCPs were slightly higher than those of PAHs, with 3.5×10^{-4}–1.4×10^{-3} (dissolved phase) and 3.4×10^{-5}–7.4×10^{-4} (particulate phase) through the ingestion absorption, as well as 4.0×10^{-4}–1.4×10^{-3} (dissolved phase) and 7.1×10^{-5}–8.6×10^{-4} (particulate phase) through the dermal absorption, they still posing no non-cancer risk. It is interesting that high levels of PAEs posed low HQ values (the ingestion absorption: 8.6×10^{-4}–3.9×10^{-3} and 6.5×10^{-6}–4.6×10^{-5} in the dissolved and particulate phases; the dermal absorption: 3.0×10^{-4}–7.0×10^{-3} and 4.4×10^{-5}–4.6×10^{-4} in the dissolved and particulate phases, respectively). This may be due to that PAEs has higher RfD values.

As for the cancer risk, as shown in Fig. 5b, the LCR values of PAHs through the ingestion absorption in the dissolved and particulate phases were 4.4×10^{-7}–3.3×10^{-6} and 9.1×10^{-7}–4.8×10^{-5}, respectively, which is lower than the cancer risk through the dermal absorption with the values of 1.8×10^{-6}–1.9×10^{-5} and 5.2×10^{-6}–2.8×10^{-4} in the dissolved and particulate phases, respectively. According to the reference (Bandowe and Nkansah 2016), there is also negligible or acceptable cancer risk posed by PAHs, except for through the dermal absorption in the particulate phase at sites S14 and S20 (LCR values exceeded 10^{-4}), which are adjacent to intensively industrial regions. The cancer risk posed by OCPs was negligible, because their LCR values were all below 10^{-6} except site S9 (1.1×10^{-6}) through the direct ingestion. Though high levels of PAEs were detected in both phases, the LCR values were also much lower than those of PAHs and OCPs, indicating there is negligible or acceptable risk posed by PAEs. In addition, the HQ and LCR of the individual compound at each sampling site are provided in Figs. S7–S18. Generally speaking, the high risks were mainly located at S20 and S9 in the dissolved phase, and S20 and S14 in the particulate phase, which is consistent with the concentrations mentioned above. As same as the PAHs, S20 and S9 were still the high risk of OCPs in the particulate phase, while only S9 is highest in the dissolved phase. For PAEs in the dissolved phase, high risks were present at S6, S7, S8, S9 and S10, except for HQ through the ingestion absorption at sites of S2, S8 and S20, while in the particulate phase, the risks at S2, S9 and S20 were obviously higher than the other sites. It is inconsistent with the concentrations present above, mainly due to DEHP which is dominated contributor of total risk.

Conclusions

Total of 41 SVOCs, including 16 PAHs, 20 OCPs and 15 PAEs, were determined both in the dissolved and particulate phases along with Beijiang River. Low concentrations of PAHs and OCPs were found in the dissolved phase, while higher levels of PAEs in the dissolved phase were obtained due to strong contribution of DiBP and DnBP. Similarly, high levels of PAEs were also found in the particulate phase, with the dominated compounds of DnBP and DEHP. These indicated the use of plastics led to a tremendous pollution of PAEs in water system. Composition analyses found that PAHs with 2- and 3-rings (more water soluble) were mainly present in the dissolved phase, while PAHs with high rings like 4- and 5-rings were in more proportion in the particulate phase. For OCPs, endosulfan and HCHs were the main components both in the dissolved and particulate phases, while DDTs were only abundant in the dissolved phase. Source apportionment indicated that the combusted biomass and coal, as well as petroleum, were the main sources for PAHs in both phases. Lindane was the main source for HCHs in both phases, while DDTs were mainly originated from history residual of p′p-DDT in dissolved phase, and new input of p′p-DDT was main sources in the particulate phase. Furthermore, human health risk assessment found that little or no potential cancer and non-cancer risks are posed by three groups of contaminants through the ingestion or the dermal absorption. These results indicated that although the water in Beijiang River was slightly polluted by various human activities, the cancer and non-cancer risks are very low via daily water consumption. However, the combined effects of all the pollutants were not taken into consideration in this study. As such, the hazard risk caused by all the pollutants should not be overlooked and will be seriously considered later.

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References

Alam, M. J., Daoxian, Y., Jiang, Y. J., Yuchuan, S., Yong, L., & Xin, X. (2014). Sources and transports of organochlorine pesticides in the Nanshan underground river, China. *Environmental Earth Sciences, 71,* 1977–1987.

An, T. C., Sun, L., Li, G. Y., Gao, Y. P., & Ying, G. G. (2011). Photocatalytic degradation and detoxification of o-chloroaniline in the gas phase: Mechanistic consideration and mutagenicity assessment of its decomposed gaseous intermediate mixture. *Applied Catalysis, B: Environmental, 102,* 140–146.

Bandowe, B. A. M., & Nkansah, M. A. (2016). Occurrence, distribution and health risk from polycyclic aromatic compounds (PAHs, oxygenated-PAHs and azaarenes) in street dust from a major West African Metropolis. *Science of the Total Environment, 553,* 439–449.

Behfar, A., Nazari, Z., Rabiee, M. H., Raeesi, G., Oveisi, M. R., Sadeghi, N., et al. (2013). The organochlorine pesticides residue levels in Karun river water. *Jundishapur Journal of Natural Pharmaceutical Products, 8,* 41–46.

Bidleman, T. F., Jantunen, L. M., Helm, P. A., Brorström-Lundén, E., & Juntto, S. (2002). Chlordane enantiomers and temporal trends of chlordane isomers in arctic air. *Environmental Science and Technology, 36,* 539–544.

Cai, W. L., Luo, G. Y., Xu, X. Y., & Du, X. (2012). Contamination characteristics of polycyclic aromatic hydrocarbons (PAHs) in surface water from Jialing River in Chongqing. *Environmental Science, 33,* 2341–2346.

Chen, Y., Jia, R., & Yang, S. (2015). Distribution and Source of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Dissolved Phase, Suspended Particulate Matter and Sediment from Weihe River in Northwest China. *International Journal of Environmental Research and Public Health, 12,* 14148–14163.

Deng, H. M., Chen, Y. H., & Chang, X. Y. (2009). Distribution and partition of polycyclic aromatic hydrocarbons (PAHs) in the Gaoyao section of Xijiang River. *Environmental Science, 30,* 3276–3282.

Du, X., Li, X., Luo, T., Matsuur, N., Kadokami, K., & Chen, J. (2013). Occurrence and Aquatic Ecological Risk Assessment of Typical Organic Pollutants in Water of Yangtze River Estuary. *Procedia Environmental Sciences, 18,* 882–889.

Eremina, N., Paschke, A., Mazlova, E. A., & Schuurmann, G. (2016). Distribution of polychlorinated biphenyls, phthalic acid esters, polycyclic aromatic hydrocarbons and organochlorine substances in the Moscow River, Russia. *Environmental Pollution, 210,* 409–418.

Feng, Z., Cui, K., Xie, Z., Wu, L., Luo, D., Chen, L., et al. (2009). Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. *Journal of Hazardous Materials, 164,* 1171–1178.

Feng, C., Xia, X., Shen, Z., & Zhou, Z. (2007). Distribution and sources of polycyclic aromatic hydrocarbons in Wuhan section of the Yangtze River, China. *Environmental Monitoring and Assessment, 133,* 447–458.

Feng, J. L., Zhai, M. X., Liu, Q., Sun, J. H., & Guo, J. J. (2011). Residues of organochlorine pesticides (OCPs) in upper reach of the Huaihe River, East China. *Ecotoxicology and Environmental Safety, 74,* 2252–2259.

Fukuwatari, T., Suzuki, Y., Sugimoto, E., & Shibata, K. (2002). Elucidation of the toxic mechanism of the plasticizers, phthalic acid esters, putative endocrine disrupters: effects of dietary di(2-ethylhexyl)phthalate on the metabolism of tryptophan to niacin in rats. *Bioscience, Biotechnology, and Biochemistry, 66,* 705–710.

Gauthier, P. T., Norwood, W. P., Prepas, E. E., & Pyle, G. G. (2015). Metal–polycyclic aromatic hydrocarbon mixture toxicity in hyalella azteca. 1. response surfaces and isoboles to measure non-additive mixture toxicity and ecological risk. *Environmental Science and Technology, 49,* 11772–11779.

Geyikçi, F., & Büyükgüngör, H. (2011). Monitoring of organochlorine pesticides in the surface waters from Mid-Black Sea Region, Turkey. *Environmental Monitoring and Assessment, 173,* 127–137.

Guan, Y. F., Wang, J. Z., Ni, H. G., & Zeng, E. Y. (2009). Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: Assessment of mass loading, input source and environmental fate. *Environmental Pollution, 157,* 618–624.

Inam, E., Offiong, N. A., Essien, J., Kang, S., Kang, S. Y., & Antia, B. (2016). Polycyclic aromatic hydrocarbons loads and potential risks in freshwater ecosystem of the Ikpa River Basin Niger Delta-Nigeria. *Environmental Monitoring and Assessment, 188,* 49.

Iwegbue, C. M. A., & Obi, G. (2016). Distribution, sources, and health risk assessment of polycyclic aromatic hydrocarbons in dust from urban environment in the Niger Delta, Nigeria. *Human and Ecological Risk Assessment, 22,* 623–638.

Li, X., Hou, L., Li, Y., Liu, M., Lin, X., & Cheng, L. (2016a). Polycyclic aromatic hydrocarbons and black carbon in intertidal sediments of China coastal zones: Concentration, ecological risk, source and their relationship. *Science of the Total Environment, 566–567,* 1387–1397.

Li, B., Hu, X., Liu, R., Zeng, P., & Song, Y. (2015). Occurrence and distribution of phthalic acid esters and phenols in Hun River Watersheds. *Environmental Earth Sciences, 73,* 5095–5106.

Li, G. Y., Sun, H. W., Zhang, Z. Y., An, T. C., & Hu, J. F. (2013). Distribution profile, health risk and elimination of model atmospheric SVOCs associated with a typical municipal garbage compressing station in Guangzhou, South China. *Atmospheric Environment, 76,* 173–180.

Li, G. Y., Xiong, J. K., Wong, P. K., & An, T. C. (2016b). Enhancing tetrabromobisphenol a biodegradation in river sediment microcosms and understanding the corresponding microbial community. *Environmental Pollution, 208,* 796–802.

Liu, F., Liu, Y., Jiang, D., Zhang, R., Cui, Y., & Li, M. (2014a). Health risk assessment of semi-volatile organic pollutants in Lhasa River China. *Ecotoxicology, 23,* 567–576.

Liu, F., Yang, Q. S., Hu, Y. J., Du, H. H., & Yuan, F. (2014b). Distribution and transportation of polycyclic aromatic hydrocarbons (PAHs) at the Humen River Mouth in the Pearl River delta and their influencing factors. *Marine Pollution Bulletin, 84,* 401–410.

Lv, J., Xu, J., Guo, C., Zhang, Y., Bai, Y., & Meng, W. (2014). Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in surface water from Liaohe River Basin, northeast China. *Environmental Science and Pollution Research International, 21,* 7088–7096.

Mahmood, A., Malik, R. N., Li, J., & Zhang, G. (2014). Levels, distribution pattern and ecological risk assessment of organochlorines pesticides (OCPs) in water and sediments from two tributaries of the Chenab River, Pakistan. *Ecotoxicology, 23,* 1713–1721.

Montuori, P., Cirillo, T., Fasano, E., Nardone, A., Esposito, F., & Triassi, M. (2014). Spatial distribution and partitioning of polychlorinated biphenyl and organochlorine pesticide in water and sediment from Sarno River and Estuary, southern Italy. *Environmental Science and Pollution Research International, 21,* 5023–5035.

Net, S., Sempere, R., Delmont, A., Paluselli, A., & Ouddane, B. (2015). Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environmental Science and Technology, 49,* 4019–4035.

Nomeir, A. A., & Hajjar, N. P. (1987) Metabolism of chlordane in mammals. In G. W. Ware, (Ed.), *Reviews of environmental contamination and toxicology* (pp. 1–22). New York: Springer.

Qiao, M., An, T. C., Zeng, X. Y., Zhang, D. L., Li, G. Y., Sheng, G. Y., et al. (2010). Safety assessment of the source water within the Pearl River Delta on the aspect of organochlorine pesticides contamination. *Journal of Environmental Monitoring, 12,* 1666–1677.

Qiao, M., Huang, S., & Wang, Z. (2007). Partitioning characteristics of PAHs between sediment and water in a shallow lake. *Journal of Soils and Sediments, 8,* 69–73.

Qu, C. S., Li, B., Wu, H. S., Wang, S., & Giesy, J. P. (2015). Multi-pathway assessment of human health risk posed by polycyclic aromatic hydrocarbons. *Environmental Geochemistry and Health, 37,* 587–601.

Rabodonirina, S., Net, S., Ouddane, B., Merhaby, D., Dumoulin, D., Popescu, T., et al. (2015). Distribution of persistent organic pollutants (PAHs, Me-PAHs, PCBs) in dissolved, particulate and sedimentary phases in freshwater systems. *Environmental Pollution, 206,* 38–48.

Ruby, M. V., Lowney, Y. W., Bunge, A. L., Roberts, S. M., Gomez-Eyles, J. L., Ghosh, U., et al. (2016). Oral bioavailability, bioaccessibility, and dermal absorption of PAHs from soil-state of the science. *Environmental Science and Technology, 50,* 2151–2164.

Saillenfait, A. M., Sabaté, J. P., & Gallissot, F. (2008). Diisobutyl phthalate impairs the androgen-dependent reproductive development of the male rat. *Reproductive Toxicology, 26,* 107–115.

Santhi, V. A., & Mustafa, A. M. (2013). Assessment of organochlorine pesticides and plasticisers in the Selangor River basin and possible pollution sources. *Environmental Monitoring and Assessment, 185,* 1541–1554.

Selvaraj, K. K., Sundaramoorthy, G., Ravichandran, P. K., Girijan, G. K., Sampath, S., & Ramaswamy, B. R. (2015). Phthalate esters in water and sediments of the Kaveri River, India: Environmental levels and ecotoxicological evaluations. *Environmental Geochemistry and Health, 37,* 83–96.

Sha, Y., Xia, X., Yang, Z., & Huang, G. H. (2007). Distribution of PAEs in the middle and lower reaches of the Yellow River, China. *Environmental Monitoring and Assessment, 124,* 277–287.

Sofowote, U. M., McCarry, B. E., & Marvin, C. H. (2008). Source apportionment of PAH in Hamilton Harbour suspended sediments: Comparison of two factor analysis methods. *Environmental Science and Technology, 42,* 6007–6014.

Song, M. W., Gao, M., Wang, P. F., Xie, K. Z., & Zhang, H. (2014). Multivariate assessment of polycyclic aromatic hydrocarbons in surface sediments of the Beijiang, a tributary of the Pearl River in Southern China. *Environmental Monitoring and Assessment, 186,* 907–918.

Sun, H. W., An, T. C., Li, G. Y., Qiao, M., & Wei, D. B. (2014). Distribution, possible sources, and health risk assessment of SVOC pollution in small streams in Pearl River Delta, China. *Environmental Science and Pollution Research International, 21,* 10083–10095.

Sun, J. H., Wang, G. L., Chai, Y., Zhang, G., Li, J., & Feng, J. (2009). Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. *Ecotoxicology and Environmental Safety, 72,* 1614–1624.

Tavakoly Sany, S. B., Hashim, R., Rezayi, M., Salleh, A., Rahman, M. A., Safari, O., et al. (2014). Human health risk of polycyclic aromatic hydrocarbons from consumption of blood cockle and exposure to contaminated sediments and water along the Klang Strait, Malaysia. *Marine Pollution Bulletin, 84,* 268–279.

USEPA. (1989). *Risk Assessment Guidance for Superfund Volume I: Human health evaluation manual (Part A).* http://rais.ornl.gov/documents/HHEMA.pdf.

USEPA (2014). *Risk assessment guidance for superfund volume i: human health evaluation manual.* (Part E, Supplemental Guidance for Dermal Risk Assessment) http://rais.ornl.gov/documents/RAGS_E_EPA540R99005.pdf.

USEPA (2016). Regional removal management levels for chemicals (RMLs) - HQ3 PDFs. (May 2016) https://www.epa.gov/sites/production/files/2016-05/documents/summary_ table_hq3_may_2016.pdf .

Wang, Y., He, W., Qin, N., He, Q. S., Kong, X. Z., Tao, S., et al. (2013). Distributions, sources, and ecological risks of DDT-related contaminants in water, suspended particulate matter, and sediments from Haihe Plain, Northern China. *Environmental Monitoring and Assessment, 185,* 1777–1790.

Wang, W., Wang, Y., Zhang, R., Wang, S., Wei, C., Chaemfa, C., et al. (2016a). Seasonal characteristics and current sources of OCPs and PCBs and enantiomeric signatures of chiral OCPs in the atmosphere of Vietnam. *Science of the Total Environment, 542*(Part A), 777–786.

Wang, B., Wu, C., Liu, W., Teng, Y., Luo, Y., Christie, P., et al. (2016b). Levels and patterns of organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in Henan province, China. *Environmental Science and Pollution Research, 23,* 6680–6689.

Yang, Y., Yun, X., Liu, M., Jiang, Y., Li, Q. X., & Wang, J. (2014). Concentrations, distributions, sources, and risk assessment of organochlorine pesticides in surface water of the East Lake, China. *Environmental Science and Pollution Research International, 21,* 3041–3050.

You, Y. S., Lee, J. H., Park, J. C., Kim, D. M., & Cho, H. S. (2012). Distribution Characteristics of Polycyclic Aromatic Hydrocarbons(PAHs) in Riverine Waters of Ulsan Coast, Korea. *Journal of the Korean Society of Marine Environment and Safety, 18,* 398–405.

Yun, X. Y., Yang, Y. Y., Liu, M. X., Zhang, M. M., & Wang, J. (2016). Distribution, seasonal variations, and ecological risk assessment of polycyclic aromatic hydrocarbons in the East Lake, China. *Clean-Soil Air Water, 44,* 506–514.

Zeng, F., Cui, K., Xie, Z., Wu, L., Liu, M., Sun, G., et al. (2008). Phthalate esters (PAEs): Emerging organic contaminants in agricultural soils in peri-urban areas around Guangzhou, China. *Environmental Pollution, 156,* 425–434.

Zhang, L., Dong, L., Ren, L., Shi, S., Zhou, L., Zhang, T., et al. (2012a). Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, China. *Journal of Environmental Sciences, 24,* 335–342.

Zhang, J., Liu, F., Chen, R., Feng, T., Dong, S., & Shen, H. (2012b). Levels of polychlorinated biphenyls and organochlorine pesticides in edible shellfish from Xiamen (China) and estimation of human dietary intake. *Food and Chemical Toxicology, 50,* 4285–4291.

Zhang, H., Sun, L., Sun, T., Li, H., & Luo, Q. (2013a). Spatial distribution and seasonal variation of polycyclic aromatic hydrocarbons (PAHs) contaminations in surface water from the Hun River, Northeast China. *Environmental Monitoring and Assessment, 185,* 1451–1462.

Zhang, K., Wei, Y. L., & Zeng, E. Y. (2013b). A review of environmental and human exposure to persistent organic pollutants in the Pearl River Delta, South China. *Science of the Total Environment, 463,* 1093–1110.

Zhao, X., Ding, J., & You, H. (2014). Spatial distribution and temporal trends of polycyclic aromatic hydrocarbons (PAHs) in water and sediment from Songhua River, China. *Environmental Geochemistry and Health, 36,* 131–143.

Zheng, B. H., Wang, L. P., Lei, K., & Nan, B. X. (2016). Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area, China. *Chemosphere, 149,* 91–100.

Zheng, X., Zhang, B. T., & Teng, Y. (2014). Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities. *Science of the Total Environment, 476–477,* 107–113.

Zhi, H., Zhao, Z., & Zhang, L. (2015). The fate of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water from Poyang Lake, the largest freshwater lake in China. *Chemosphere, 119,* 1134–1140.