

Spatial distributions, source apportionment and ecological risk of SVOCs in water and sediment from Xijiang River, Pearl River Delta

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Abstract Xijiang River is an important drinking water source in Guangxi Province, China. Along the Xijiang River and surrounding tributary, the pollution profile of three important groups of semi-volatile organic compounds, including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and phthalate esters (PAEs), was analyzed. Relatively low levels of PAHs ($64\text{--}3.7 \times 10^2 \text{ ng L}^{-1}$) and OCPs ($16\text{--}70 \text{ ng L}^{-1}$), but high levels of PAEs ($7.9 \times 10^2\text{--}6.8 \times 10^3 \text{ ng L}^{-1}$) occurred in the water. Comparatively, low levels of OCPs ($39\text{--}1.8 \times 10^2 \text{ ng g}^{-1}$) and PAEs ($21\text{--}81 \text{ ng g}^{-1}$), but high levels of PAHs ($41\text{--}1.1 \times 10^3 \text{ ng g}^{-1}$) were found in sediment. Principal component analyses for source identification indicated petroleum-derived residues or coal and biomass combustion, and vehicular emission was

the main sources for PAHs. The OCPs sources of each category were almost independent, whereas the new input of HCHs and *p,p'*-DDTs probably existed in some areas. PAEs were mainly originated from personal care products of urban sewage, plastic and other industrial sources. Ecological risk through the risk quotient analysis indicated a small or significant potential adverse effect on fish, daphnia and green algae. Nevertheless, the integrated risk of all pollutants should be taken into account in future study.

Keywords Xijiang River · PAHs · OCPs · PAEs · Ecological risks

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), composed of two or more fused rings, are an important group of

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environmental semi-volatile organic compounds (SVOCs) (Goswami et al. 2016). PAHs in environment were mainly originated from nature and anthropogenic combustion process. Volcanic eruptions, forest as well as prairie fire are the main sources from nature (Zhang et al. 2004). Anthropogenic sources principally included fossil fuel combustion, waste incineration, petroleum refining, coke and biomass combustion, as well as other industrial activities (Yun et al. 2016). Owing to their mutagenicity and carcinogenicity, 16 unsubstituted PAHs were listed as priority pollutants by the United States Environmental Protection Agency (USEPA) (Manoli et al. 2000). What's more, seven PAHs including benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (D*h*B) and indeno[1,2,3-*cd*]pyrene (IncdP) were regarded as carcinogens (Wang et al. 2010). Meanwhile, they have bioaccumulation property because of their high lipophilicity. As a result, they might lead to both acute and chronic risks in aquatic plants, fish, waterfowls and other mammals that feed on aquatic organisms (Yun et al. 2016). Therefore, their extensive distribution, potential risks to the health of human and ecosystem have been the focus of much attention (Manoli and Samara 1999).

Organochlorine pesticides (OCPs), another important group of SVOCs, had been banned for decades, but they still frequently occurred in various matrix, such as sediment (Lin et al. 2016), lake (Hu et al. 2010), river (Zhang et al. 2012), air (Zheng et al. 2010). As known, OCPs can effectively control the pests and diseases in the agriculture plantations. For instance, dieldrin, heptachlor and lindane were used for controlling termites of wood, while dichlorodiphenyltrichloroethane (*p,p'*-DDT) and heptachlor were used for malaria fumigation (Santhi and Mustafa 2013). Meanwhile, as important persistent organic pollutants (POPs), OCPs had been paid a serious attention due to their toxicity, persistence and bioaccumulation (Kata et al. 2015). Furthermore, the chemical properties of OCPs such a slow polarity and high lipophilicity have the potential to accumulate in the food chain, posing a considerable harm to humans and ecosystem (Kamel et al. 2015).

Phthalate esters (PAEs) are another class of important SVOCs, which are widely used as industrial chemicals served as important additives aiming to

improve their softness and flexibility in polyvinylchloride resins (Stales et al. 1997; Santhi and Mustafa 2013). Short-side-chain PAEs are mainly used in cosmetics and personal care products, including perfumes and nail polishes, while most of the long- or middle-side-chain PAEs are widely applied to plasticizers (Zheng et al. 2014). Furthermore, several PAEs have been reported with environmental hormones, which can lead to the instability of internal secretions and procreation ability (Fan et al. 2008). Besides, release of PAEs into the environment during manufacture, use and disposal has caused increasing concerns, owing to be suspected as mutagens, hepatotoxic agents, carcinogens, especially endocrine disruptor chemicals (Yuan et al. 2010).

Currently, high levels of PAHs, OCPs and PAEs in the surface water and sediment of Jialing River (Cai et al. 2012), East Lake (Yun et al. 2016), Tiber River (Montuori et al. 2016) had been driven much attention. Nevertheless, relative studies are relatively very rare for Xijiang River, the main tributary of Pearl River in China. During the past several decades, with the rapid increase of population, economic, urbanization and industrialization, city sewages and industrial wastewater are always dumped into the rivers. Furthermore, constructions of factories and cities along the river are very common in China, which were further aggravated pollution of rivers. Thus, this work aims to investigate the pollution profile of PAHs, OCPs and PAEs caused by different anthropogenic activities. Furthermore, their spatial distributions, source apportionment and ecological risks were also investigated in this area.

Materials and methods

Materials

Standard solutions for the quantification analysis and quality control experiments were achieved as mentioned in our previous studies (Li et al. 2013; Sun et al. 2014). The detailed information is provided in supporting information.

Study area and sampling sites

Total of 12 pairs of water and sediment were collected from Xijiang River using amber glass bottles and stainless steel boxes, respectively (Fig. S1).

Approximately 10 L water and 500 g surface sediment (depth 0–5 cm) were sampled at each site. Meanwhile, 0.5 g sodium azide was spiked in the water and sediment to prevent microbial degradation. During the sampling, the pH value, temperature, conductivity and dissolved oxygen (DO) were measured in situ to reflect the status of water (Table S1). The water and sediment were carried back to laboratory as soon as possible and stored at 4 and -20 °C, respectively, until pretreatment.

Sample pretreatment

Sample pretreatment was performed as our previous studies (Sun et al. 2014). The water samples were filtered through prebaked glass microfiber filters (GF/Fs, 142 mm in diameter, Whatman, England) to remove suspended particulate. Three categories surrogate standards including five deuterated PAHs, 2,4,5,6-tetrachloro-*m*-xylene (TMX) and 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (PCB209), as well as diphenylphthalate (DphP), were added and then passed through the pretreated XAD-2 columns (Supelco, Bellefonte, USA) to enrich the target compounds. The enrichment of target compounds was gradually eluted by using 50 mL menthol, 40 mL methanol/dichloromethane (DCM) = 4:1 (twice) and 50 mL methanol/DCM = 1:1 (twice) and the remaining XAD-2 resins using 90 and 50 mL \times 2 methanol/DCM = 1:1 with ultrasonication for 15 min, respectively. The mixed solutions were further refined using liquid–liquid extraction with DCM, saturation salt water and deionized water according to their relatively low polarities. The DCM fractions including target compounds (PAHs, OCPs and PAEs) were collected and concentrated to approximately 5–10 mL using rotary evaporation. After exchanged with *n*-hexane, the samples were concentrated to approximately 1 mL for cleanup with a silica gel-alumina column (8 mm inner diameter) followed by 12 cm silica, 6 cm gel-alumina and 1 cm anhydrous sodium sulfate from the bottom to top. The PAHs and OCPs were eluted with 70 mL *n*-hexane/DCM = 7:3, and the PAEs were eluted using 60 mL of *n*-hexane/acetone = 8:2. The separated fractions were finally concentrated to 200 μ L under a gentle stream of high-purity nitrogen for further instrumental analysis. The sediment was freeze-dried, and 20 g sediment which spiked surrogate standards was Soxhlet-extracted with 200 mL

DCM for 72 h. Before extraction, activated copper was added for the removal of element sulfur during sediment pretreatment. The subsequent steps were identical as water sample pretreatment, except the last fractions were concentrated to 500 μ L. Finally, known amount of internal standard were spiked for instrumental analysis.

Instrument analysis

A 7890A gas chromatograph (GC) coupled with a 5975C mass spectrometer (MS) detector (Agilent Technologies, USA) and equipped with HP-5MS silica-fused capillary column (30 m \times 250 μ m \times 0.25 μ m) was used for quantifying analysis. The column temperature for PAHs was executed from initial 80 to 280 °C at a rate of 3 °C min⁻¹, then reached 300 °C at 10 °C min⁻¹ and held there for 10 min. For OCPs, the temperature was held at 80 °C for 1 min and programmed to 140 °C at a rate of 15 °C min⁻¹ and further to 280 °C at 4 °C min⁻¹, finally at 10 °C min⁻¹ to 300 °C for 10 min. For PAEs, the oven temperature program was as follows: initial 80 °C held for 1 min, increased to 180 °C at 10 °C min⁻¹ and held there for 1 min, and then reached 260 °C at 2 °C min⁻¹, finally to 300 °C at 10 °C min⁻¹ and held there for 10 min. The injector temperature for PAHs, OCPs and PAEs was 290, 250, 300 °C, respectively. The mass spectrometer was performed in selective ion monitoring (SIM) mode by using positive ion electron impact ionization (EI). An aliquot sample (1 μ L) was injected in the splitless mode, and high-purity helium was served as the carrier gas (1.0 mL min⁻¹). Total organic carbon (TOC) content in water was measured using a Shimadzu TOC-VCPH analyzer (Shimadzu Corp, Kyoto, Japan).

Quality control

Every ten samples inserted a blank experiment and spiked blank experiment, which were performed to determine the values of blank and the recoveries of target compounds. Blank experiment only added categories surrogate standards, while spiked blank experiment further added standard solutions. The followed treatments were consistent with those of sample treatment. The recoveries of the target compounds were defined as target spiked concentration values minus blank concentration values, and then

divided by target spiked concentrations. The recoveries of PAHs in water and sediment samples were 76–165 and 63–148%, respectively. The recoveries of OCPs were 53–140 and 42–143% in water and sediment samples, respectively. The recoveries of PAEs were 49–189 and 55–272% in water and sediment samples, respectively. Surrogate standards in samples are shown 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 water, respectively, and 0.04–0.17, 0.07–0.23 and 0.10–0.29 ng g⁻¹ in sediment, respectively.

Ecological risk assessment

Ecological risk assessment for target compounds in water and sediment was performed using the risk quotient (RQ) on nontarget organisms (Cristale et al. 2013a; Xiong et al. 2015). The RQ was calculated using a ratio of measured environmental concentration (MEC) to predicted no effects concentrations (PNECs) as shown in Eq. 1. The PNEC is the ratio of a toxicological relevant concentration (EC₅₀ or LC₅₀) with a security factor ($f = 1000$).

$$RQ = \frac{MEC}{PNEC} = \frac{MEC}{(EC_{50 \text{ or } LC_{50}})/f} \quad (1)$$

For sediment, MEC is based on pore water concentration, achieved using Eq. 2 (Cristale et al. 2013b; Xiong et al. 2015).

$$C_{pw} = \frac{C_s}{f_{oc}K_{oc}} \quad (2)$$

where C_{pw} is the pore water concentration (ng L⁻¹); C_s is the sediment concentrations (ng g⁻¹), f_{oc} (=0.1) is the fraction of organic carbon on sediments, and K_{oc} is the partition coefficient for sediment organic carbon, which is predicted using Advanced Chemistry Development software (ACD/Labs, Toronto, ON, Canada).

In this study, fish, daphnia and green algae were chosen for ecological risk assessment and their EC₅₀ or LC₅₀ values were achieved from ECOSAR v1.1 (Ecological Structure Activity Relationships) developed by USEPA's Office of Chemical Safety and Pollution Prevention.

Results and discussion

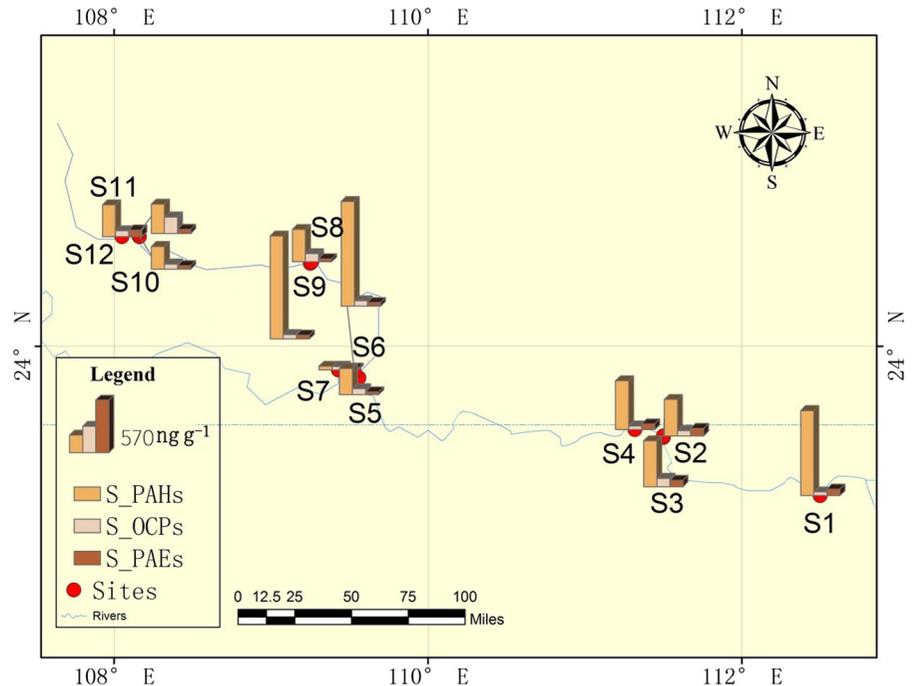
PAHs

Levels

Condensed industrial activities and river confluence make PAHs enriched in water and sediment. The total concentrations of 16 PAHs ($\sum_{16}PAHs$) in water and sediment in 12 samplings sites were 64– 3.7×10^2 ng L⁻¹ (mean value 1.9×10^2 ng L⁻¹) and 41– 1.1×10^3 ng g⁻¹ (mean value 5.1×10^2 ng g⁻¹), respectively (Figs. 1 and S2). In water, the highest levels of $\sum_{16}PAHs$ were at site 4 (3.7×10^2 ng L⁻¹), which sits in the confluence of Xijiang River and Guijiang River, located in industrially developed city of Wuzhou City. With rapid urbanization and industrial development of Wuzhou City, high level of PAHs is probably derived from urban runoff, sewage outfalls and wastewater discharges (Zhang et al. 2004). The second highest PAHs concentration was at site 8 (the confluence of Rongjiang River) and 6 (Shilong Town near the Liujiang River) both with relatively high concentrations (3.3×10^2 ng L⁻¹). It is possible that the pollutants from two rivers were accumulated at the confluence (site 8). In addition, site 12 near the Hechi City was also heavily polluted with PAHs (2.8×10^2 ng L⁻¹), which was probably from the Hechi Smelt. In contrast, low PAHs concentrations were found at site 9 (64 ng L⁻¹) and site 3 (65 ng L⁻¹), which was almost five times lower than those at site 4. In sediment, the highest PAHs levels were also at sites 8 and 6 (both 1.1×10^3 ng g⁻¹), indicating high PAHs pollution in both phases within these areas, while the lowest PAHs concentration (41 ng g⁻¹) was obtained at site 7, much lower than those at other sites.

Specifically, as Table S3 shows, the pollutions at different sampling sites of seven carcinogenic PAHs (\sum_7PAHs) in water and sediment ranged from 4.0 to 7.3 ng L⁻¹ and 27 to 7.2×10^2 ng g⁻¹, which accounted for 1.4–9.5 and 54–68% of total PAHs, respectively. More specifically, the distributions of individual PAHs in water and sediments were also investigated. In water, phenanthrene (Phe) ($29\text{--}1.4 \times 10^2$ ng L⁻¹), fluorine (Flu) ($4.5\text{--}1.4 \times 10^2$ ng L⁻¹) and naphthalene (Nap) (8.3–28 ng L⁻¹) were the main

Fig. 1 Concentrations of PAHs, OCPs and PAEs in sediment in Xijiang River



ingredients, accounting for 34–48, 6.0–38 and 3.5–18% of total PAHs, respectively. In sediment, however, benzo[*b*]fluoranthene (BbF) ($6.7\text{--}1.8 \times 10^2 \text{ ng g}^{-1}$), benzo[*a*]pyrene (BaP) ($5.6\text{--}1.7 \times 10^2 \text{ ng g}^{-1}$) and fluoranthene (Flua) ($4.3\text{--}1.4 \times 10^2 \text{ ng g}^{-1}$) were the main contributors, which accounted for 13–19, 11–16 and 10–14%, respectively. The results could be explained from relatively high vapor pressure and water solubility of these low-ring PAHs (Sun et al. 2009).

Composition

The distributions of different ring number PAHs in water and sediment at all sampling sites were further analyzed. As Fig. S3 shows, more water-soluble PAHs including three rings and two rings were the main PAHs in water, making up 49–63 and 20–47% of total PAHs, respectively. Low molecular weight PAHs dominated in water is due to their relatively high vapor pressure and water solubility (Sun et al. 2009). The rest of PAHs (4–6 rings) only accounted for 1.4–18% of total PAHs. However, PAHs in sediment were dominated by four rings (36–50%) and five rings (19–31%). Followed by three-ring PAHs, they occupied 15–26% of total PAHs in sediment. The lowest compositions of PAHs in sediment were two rings and

six rings, with a ratio of 1.8–8.4 and 0.61–8.0%, respectively. Results further demonstrated low-ring PAHs were more soluble, while high-ring PAHs were more likely absorbed onto sediment.

Comparison

Comparing with other studies (Table S6), the highest level of $\sum_{16}\text{PAHs}$ in water was found in Gomti River in India ($60\text{--}8.4 \times 10^4 \text{ ng L}^{-1}$) (Malik et al. 2011), which far exceeded this study. Furthermore, $\sum_{16}\text{PAHs}$ in water in this study were also lower than those in Songhua River (Zhao et al. 2014), Weihe River (Chen et al. 2015), Daliao River estuary (Zheng et al. 2016), Henan Reach of Yellow River (Sun et al. 2009) and Liaohe River (Lv et al. 2014), but much higher than those in Elbe and Weser rivers, Germany (Siemers et al. 2015). Furthermore, $\sum_{15}\text{PAHs}$ previously reported in water in Xijiang River in 2006 ($22\text{--}1.4 \times 10^2 \text{ ng L}^{-1}$) (Deng et al. 2006) was lower than those in the present study. This indicated more serious PAHs pollution in Xijiang River ever after. In sediment, PAHs concentration in this study was comparable to that in Henan Reach of Yellow River (Sun et al. 2009), was lower than that in Weihe River in China (Chen et al. 2015), Gomti River in India (Malik et al. 2011), especially in Daliao River estuary

(Zheng et al. 2016) and Baiyangdian Lake in China (Hu et al. 2010), but was higher than that in Tiber River in Italy (Montuori et al. 2016), Yangtze Estuary (Li et al. 2012) and Songhua River in China (Zhao et al. 2014). The results indicated the polluted levels of PAHs in this study are at moderate levels.

OCPs

Levels

Frequent agriculture productions contributed to enrichment of OCPs. $\sum_{20}\text{OCPs}$ in water and sediment ranged from 16 (site 9) to 70 ng L^{-1} (site 6) and 39 (site 7) to $1.8 \times 10^2 \text{ ng g}^{-1}$ (site 11), respectively (Figs. 1 and S2). In water, the highest $\sum_{20}\text{OCPs}$ was at site 6, which was the same $\sum_{16}\text{PAHs}$ level at same site, indicating heavy pollution with various pollutants in this region. Much lower and comparable $\sum_{20}\text{OCPs}$ were found at sites 4 (67 ng L^{-1}), 5 (66 ng L^{-1}), 8 (65 ng L^{-1}), 12 (64 ng L^{-1}) and 11 (52 ng L^{-1}), which obviously exceeded those at other sites (all below 30 ng L^{-1}). Low levels of $\sum_{20}\text{OCPs}$ were found at sites 7 and 10 (both with concentrations of 20 ng L^{-1}).

Unlikely, the spatial distributions of $\sum_{20}\text{OCPs}$ in sediment were more variable at sampling sites than those in water. $\sum_{20}\text{OCPs}$ at site 11 ($1.8 \times 10^2 \text{ ng g}^{-1}$) were significantly higher than the other sites, which was almost two times as high as the second highest level of site 2. In contrast, low levels in water but very high in sediment (88 ng g^{-1}) of $\sum_{20}\text{OCPs}$ were found at site 9. The reason for this may be the different sources, which lead to more sediment deposited there. Low levels of $\sum_{20}\text{OCPs}$ in sediment were obtained at sites 1, 4 and 7, with concentrations of 40, 40 and 39 ng g^{-1} , respectively. In addition, low $\sum_{20}\text{OCPs}$ in sediment at sites 1 and 7 were consistent with those in water. This may be these two areas far from agricultural regions.

Specifically, as Table S4 shows, $\sum\text{HCHs}$ (α -HCH, β -HCH, γ -HCH and δ -HCH) in water and sediment ranged from 3.0 to 53 ng L^{-1} and 4.0 to 14 ng g^{-1} , respectively. The composition of OCPs showed that HCHs were the main components in water, but were the minor components in sediment (Fig. S4). As Fig. 2 shows, among these HCHs, α -HCH was the most abundant HCHs in water, especially at sites 4 (31 ng L^{-1}), 6 (33 ng L^{-1}), 11 (26 ng L^{-1}) and 12

(32 ng L^{-1}), contributing up to 66, 65, 65 and 63% of total HCHs, respectively. Followed by β -HCH (1.3–6.8 ng L^{-1}) and γ -HCH (5.6×10^{-1} –13 ng L^{-1}), they accounted for 10–51 and 16–30% of total HCHs, respectively. Like those in water, highest portion of α -HCH (1.2–4.4 ng g^{-1} , contributing 31–38% of total HCHs) was still found in sediment. Differently, δ -HCH (1.8–3.4 ng g^{-1} , accounting for 17–44%) was the second main components of HCHs, followed by γ -HCH (5.0×10^{-2} –4.2 ng g^{-1} , 1.0–32%) and β -HCH (9.3×10^{-1} –2.6 ng g^{-1} , 8.0–24%).

In this study, the $\sum\text{DDTs}$ levels in water and sediment were 8.2×10^{-1} –2.7 ng L^{-1} and 7.1–43 ng g^{-1} , respectively (Table S5), indicating that total concentrations of p,p' -DDTs in water were not variable as those in sediment. Furthermore, p,p' -DDTs compositions were also investigated (Fig. S5), and p,p' -DDT was found more abundant than p,p' -DDD and p,p' -DDE in water, contributing 36–100% of total DDTs at different sampling sites. The concentrations of p,p' -DDD and p,p' -DDE in water were nd-1.3 and nd- $4.3 \times 10^{-1} \text{ ng L}^{-1}$, accounting for 0–56 and 0–29%, respectively. Possible reason for this is that the parent p,p' -DDT can be degraded to p,p' -DDE and p,p' -DDD metabolites, which were more difficult to be further degraded (Meijer et al. 2001). However, extremely high proportion of p,p' -DDT (6.3–42 ng g^{-1} , making up 83–97% of total DDTs) was detected in sediment. The reason was explained that light could not penetrate sediment to degrade p,p' -DDT effectively.

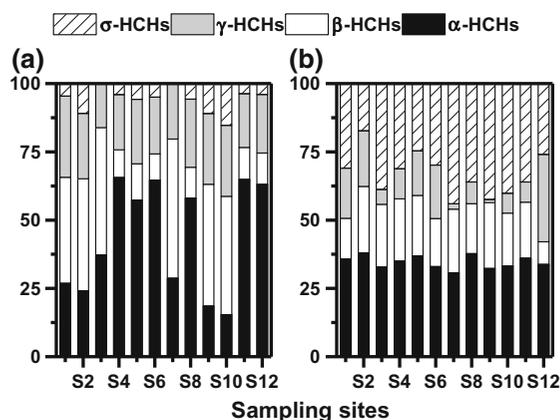


Fig. 2 Composition of HCHs in water (a) and sediment (b)

More specifically, the distributions of individual OCPs were also investigated (Table S5). The most abundant OCPs in water were α -HCHs (contributing 3.2–50% of total OCPs), followed by endosulfan sulfate (2.2–28%) and γ -HCHs (2.5–20%). Low levels of heptachlor (nd–1.2 ng L⁻¹; 0–1.9%) and endrin (nd–1.7 ng L⁻¹; 0–2.5%) were found. Comparatively, endosulfan sulfate (4.6–1.3 × 10² ng g⁻¹; 8.4–74%) and *p,p'*-DDT (6.3–42 ng g⁻¹; 16–56%) were the dominant OCPs in sediment. However, endrin aldehyde and endrin were not found in sediment at all sites.

Composition

Composition profiles of OCPs, dividing into six groups (HCHs, DDTs, heptachlors, chlordanes, endosulfans and others) were further analyzed (Fig. S4). In water, the most dominated OCPs were HCHs, contributing 15–82% of total OCPs. Endosulfans (4.2–46%) and others (9.6–39%) also accounted for a relatively large proportion of total OCPs. Lower compositions were heptachlors and chlordanes, which merely occupied 0–2.9 and 1.1–7.3% of total OCPs, respectively. In sediment, endosulfans also were one of the highest compositions, contributing 13–76% of total OCPs. Unlike in water, DDTs (17–59%) in sediment occupied a great proportion of total OCPs. The others accounted for 2.0–38% of total OCPs, while HCHs occupied small portion of total OCPs (with 2.9–20%). The heptachlors (1.1–7.5%) and chlordanes (0–2.0%) in sediment were consistent with those in water. According to this division, the results may also explain the distributions of homologues.

Comparison

Compared with other studies (Table S7), \sum_{20} OCPs in both water and sediment in this study were comparable to those in small streams in Pearl River Delta in China (Sun et al. 2014) and Chenab River in Pakistan (Mahmood et al. 2014). \sum_{20} OCPs levels in water in this study were slightly lower than those in Poyang Lake (Zhi et al. 2015), while those in sediment exceeded levels in Chaohu Lake (Li et al. 2015a). Further, \sum HCHs and \sum DDTs were also compared with other studies (Table S6). Except in Poyang Lake (4.4–60 ng L⁻¹) (Zhi et al. 2015), \sum HCHs in water in this study were higher than most of studies, namely Chenab River in Pakistan (Mahmood et al. 2014),

small streams in Pearl River Delta (Sun et al. 2014) and Yangtze River in China (Tang et al. 2013), whereas \sum HCHs in sediment in this study were almost comparable with Chaohu Lake (Li et al. 2015a), Yangtze River (Tang et al. 2013) and Chenab River in Pakistan (Mahmood et al. 2014), but below small streams in Pearl River Delta (Sun et al. 2014). In addition, \sum in water and sediment in this study were comparable to small streams in Pearl River Delta (Sun et al. 2014), Poyang DDTs Lake (Zhi et al. 2015) and Chaohu Lake (Li et al. 2015a). This result indicated water and sediment in Xijiang River were moderately polluted by OCPs.

PAEs

Levels

Urban sewage, plastic and other industrial sources resulted in high PAEs. \sum_{15} PAEs in water and sediment were obtained 7.9 × 10²–6.8 × 10³ ng L⁻¹ and 21–81 ng g⁻¹, respectively (Figs. 1 and S2). In water, the highest PAEs levels was found at site 1 (6.8 × 10³ ng L⁻¹), far exceeding the other sites. This is due to that site 1 is near to the Zhaoqing Paint Factory and a ferry. Sites 2 (3.4 × 10³ ng L⁻¹) and 7 (3.3 × 10³ ng L⁻¹) were also heavily polluted with PAEs. The reason for this is that a real estate company is around site 2 and Dawan ferry located at site 7, since the lacquers, coatings and varnishes were large sources of low molecular weight PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP) and dibutyl phthalate (DnBP) (Schettler 2006). Meanwhile, low levels of \sum_{15} PAEs in water were detected at sites 6, 8, 11 and 12, with concentrations of 9.7 × 10², 9.6 × 10², 7.9 × 10² and 9.0 × 10² ng L⁻¹, respectively. Comparatively, in sediment, the highest \sum_{15} PAEs level was found at site 3 (81 ng g⁻¹) located at Hejiang River estuary, where many fishing boats docked; boat paint might consequently cause PAEs pollutants. The second polluted site was at site 12 (72 ng g⁻¹). The reason for the different distributions in water and sediment is that lots of potential plastic pollution existed, because the degradation of plastic generated more long-side-chain PAEs than short-side-chain PAEs (Zheng et al. 2014), and long-side-chain PAEs can easily absorbed on the sediment. However, low level of PAEs (21 ng g⁻¹) in sediment but high level in water was

found at site 7, possibly indicating personal care products associated with short-side-chain PAEs might be main sources within this area (Liu et al. 2010).

Furthermore, the distributions of individual PAEs were carried out (Table S5). One of the most dominated PAEs in water was DnBP (1.6×10^2 – 2.9×10^3 ng L⁻¹), contributing 12–68% of total PAEs. Meanwhile, relatively high levels of low molecular weight of PAEs, including DMP (1.0×10^2 – 1.1×10^3 ng L⁻¹), DEP (97 – 9.2×10^2 ng L⁻¹) and DiBP (13 – 9.1×10^2 ng L⁻¹), in water were detected, occupying 3–64, 7.9–22 and 1.2–18% of total PAEs, respectively, whereas for high molecular weight DEHP with more lipophilic property, which is widely used in construction material, clothing, furnishings and polyvinyl chloride plastic (Schettler 2006), only very small proportion of it was found in water (1.1–5.3% of total PAEs, 31–74 ng L⁻¹). In contrast, DEHP in sediment was found with the highest concentration of 11–37 ng g⁻¹, contributing up to 16–85% of total PAEs. This is due to that PAEs with long side chains like DEHP were more lipophilic and likely to be adsorbed onto sediment (Sun et al. 2014). Except for DnBP (9.6×10^{-1} – 47 ng g⁻¹, 3.6–70% of total PAEs), the other short-side-chain PAEs such as DMP (2.0×10^{-1} – 1.6 ng g⁻¹, 0.29–5.5%), DEP (8.0×10^{-2} ng g⁻¹, 0–0.12%) and DiBP (2.9×10^{-1} – 1.9 ng g⁻¹, 1.4–4.3%) presented with very small portion in sediment.

Composition

Furthermore, PAEs were divided into six groups as DMP, DEP, DnBP, DiBP, DEHP and others (the rest of PAEs) and their composition were analyzed (Fig. S6). The highest proportion of PAEs in water is DnBP (12–68% of total PAEs), followed by DMP (3.0–64%), DEP (7.9–22%) and DiBP (1.2–18%). Among them, others showed a high proportion (2.0–39%), while DEHP accounted for low percentage of 1.1–5.3%. In contrast, in sediments, DEHP (accounting for 16–85% of total PAEs) was the main part of PAEs, followed by DnBP (3.6–70%) and others (3.7–41%), whereas the other three groups, DiBP, DMP and DEP, only occupied 1.4–4.3, 0.29–5.5 and 0–0.12%, respectively. The main PAEs in current study were consistent with the previous study (Sun et al. 2014).

Comparison

As well known, six PAEs including DMP, DEP, DBP, BBP, DEHP and DnOP had been categorized as priority pollutants by the USEPA. In the current study, \sum_6 PAEs in water and sediment were calculated as 7.5×10^2 – 5.1×10^3 ng L⁻¹ and 21–71 ng g⁻¹, respectively. Compared with the PAE pollution of other places (Table S8), the concentrations of \sum_6 PAEs in water in present study were lower than Yangtze River (Zhang et al. 2012), riverine outlets of Pearl River Delta (Li et al. 2015c) and Chaohu Lake (He et al. 2013), but much higher than Selangor River (Santhi and Mustafa 2013). However, very low concentrations of \sum_6 PAEs were detected in sediment in this study, which were far below the other studies, including Chaohu Lake (Kang et al. 2016) and riverine outlets of Pearl River Delta (Li et al. 2015c). Furthermore, the pollution levels of \sum_{15} PAEs were also compared with other studies. \sum_{15} PAEs levels in both water and sediment in current study were less than small streams in Pearl River Delta (Sun et al. 2014). However, the \sum_{15} PAEs levels in this study exceeded those in water, but were below in sediment in Shichahai Lake and lakes in Summer Palace (Zheng et al. 2014).

Distributions of PAHs, OCPs and PAEs

The pollution levels of these three SVOCs were also compared. As Fig. 3 shows, along the Xijiang River, the concentration tendency of PAHs and OCPs in water was almost consistent, beginning to increase to the highest levels (PAHs at site 4, OCPs at site 6), then to decrease, finally to increase again. Contrariwise, the PAEs tendency in water was completely different with the above two groups of SVOCs, which may be due to their different sources. Meanwhile, the correlations of PAH, OCPs and PAEs for each other were also analyzed using the software of IBM SPSS statistics. As Table S9 shows, the pollution of PAHs and OCPs has high correlation coefficient, and they are significant at the 0.01 level (two-tailed). The correlations of PAHs and PAEs, or OCPs and PAEs are significance at the 0.05 level (two-tailed). However, this tendency of three compounds in sediment is irregular, and as a result, there is no significance. That is, the source identification of three different SVOCs in both water and sediments is very necessary to be conducted.

Source identification

Principal component analysis (PCA) was also a multivariate analytical tool used to identify the source apportionment, which had been widely applied to source identification of PAHs (Sofowote et al. 2008; Li et al. 2015b), OCPs (Devi et al. 2015) and PAEs (Kong et al. 2013). The IBM SPSS software was also employed to conduct PCA for PAHs, OCPs and PAEs in water and sediment from Xijiang River.

For PAHs, the concentrations of \sum_{16} PAHs in water and sediment were used as variables for the PCA. Three components were extracted and the cumulative variance occupied 92% of total variance in water (Table S10). The first component was highly loaded in Nap, Ace, Dih, Flu, Phe, Ant, Flua and Pry, generally correlated with petroleum-derived residues or coal combustion and wood stoves sources (Sánchez-Avila et al. 2012; Li et al. 2016). The second component showed good loadings for BbF, BkF, BaP, IncdP, DiB and BghiP, with high molecular weight PAHs. Previous study reported that BkF was the tracer of diesel vehicles; BghiP was identified as auto-emissions; and IncdP could be found in both diesel and gas engine emissions (Larsen and Baker 2003). As such, this component was mainly appointed to the mixture of vehicular emission sources. The third component was great correlative with BaA, Chry and Nap in this study. Nap is a characteristic marker of creosote or coal tar volatilization (Zhang et al. 2012). BaA is

considered to the tracer of natural gas combustion (Simcik et al. 1999). BaA plus Chry was the fingerprints of coal combustion (Larsen and Baker 2003). Therefore, the third component was assigned to coal tar volatilization and coal combustions sources. Besides, two components were extracted and the cumulative variance occupied 91% of total variance in sediment. The first component was mainly consistent with four-, five- and six-ring PAHs in sediment. Flua and Pry were also found in wood combustion, besides Flua was consistent with gas-powered vehicles (Larsen and Baker 2003). Therefore, the first component for sediment was mainly consistent with wood combustion and mixture of vehicular emissions sources. The second component was mainly loaded in low molecular weight PAHs like those in water. As such, this component in sediment was mainly assigned to petroleum-derived residues or coal combustion and wood stoves sources.

The concentrations of \sum_{20} OCPs in water and sediment were also applied to PCA for sources apportionment (Table S11). Five components were extracted and the cumulative variance accounted for 84 and 89% of total variance in water and sediment, respectively. For water, the first component was highly loaded in four HCHs, *p,p'*-DDE and γ -chlordane. The presence of α -HCHs, β -HCHs, γ -HCHs and δ -HCHs in the same first component could imply the occurrence status of the pollutants in the current area. Usually, technical HCH consisted of 60–70% of α -HCHs, 5–12% of β -HCHs, 10–12% of γ -HCHs and 6–10% of δ -HCHs (Tan et al. 2009). In addition, the α - to γ -HCHs ratio (Fig. S7) ranged from 0.59 to 3.3 in water in the current study, indicating technical HCHs and lindane were the main sources of HCHs. It is because *p,p'*-DDE is the degradation product of *p,p'*-DDT (Wang et al. 2013). Thus, *p,p'*-DDE plus *p,p'*-DDD to *p,p'*-DDT ratio could infer the sources of *p,p'*-DDTs (Doong et al. 2002). As Fig. 4 shows, the ratios ranged from 0 to 0.64 in water in this study, indicating historical residual was main source for *p,p'*-DDT. γ -Chlordane mainly originated from technical chlordane which was mainly used to control termite, weed and insects (Devi et al. 2015). The second component was mainly correlative with *p,p'*-DDD, heptachlor epoxide, α -chlordane, endrin aldehyde and endrin ketone, indicating endrin aldehyde and endrin ketone might be similar sources of contaminant. The third component was consistent with heptachlor, α -endosulfan and

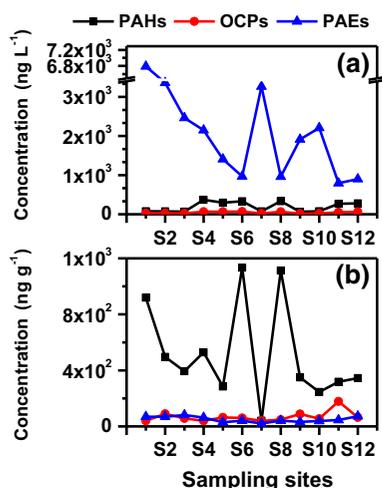


Fig. 3 Distributions of total PAHs, OCPs and PAEs along the sampling sites in water (a) and sediment (b)

methoxychlor, and the fourth component was mainly loaded in *p,p'*-DDT, dieldrin and endrin. The last component was principally consistent with β -endosulfan and aldrin. The results may explain those compounds originated from similar sources. In sediment, the first component was loaded in heptachlor epoxide, α -chlordane and γ -chlordane. The second component showed very high correlations for α -HCHs, γ -HCHs and δ -HCHs. Meanwhile, the α -/ γ -HCHs ratio was obtained as 1.1–28 in sediment, indicating mixture of technical HCHs and lindane, as well as lindane, was major source for HCHs in sediment. The third component was highly loaded in α -endosulfan, β -endosulfan, aldrin and *p,p'*-DDD. Endosulfan is used to protect vegetables and fruits, cotton and ornamental plants (Devi et al. 2015). The last two components were β -HCHs and heptachlor, as well as *p,p'*-DDT and *p,p'*-DDE, respectively. The $(p,p'$ -DDE + *p,p'*-DDD)/DDTs is all above 1, indicating a new input for *p,p'*-DDT in sediment in this area. The reason for fresh DDTs input might be the use of technical DDTs for malaria and mosquito control, additive for antifouling paints for ships (Liu et al. 2009). In a word, source for OCPs was almost independent of each other.

Furthermore, the source identification of PAEs was also carried out using PCA. As Table S12 shows, cumulative variance accounted for 87% of total variance in both water and sediment. Three components were extracted for PAEs in water. The first component was highly loaded in DnBP, DiBP, DEP, BMPP, DAP, BBP, DCHP and DEHP. DEHP is the main PAEs, which is widely used in construction material, clothing, furnishings and polyvinyl chloride plastic, while DEP and DnBP are widely used in

lacquers, coatings, varnishes, cosmetic cosmetics and personal care products (Gomez-Hens and Aguilar-Caballeros 2003; Schettler 2006). Therefore, this component was mainly assigned to plastic, personal care products of urban sewage, and other industrial sources. The second component showed high correlations for DEP, BMEP, BMPP, BBP, DCHP, DnOP, BEEP and DAP, indicating personal care products as their main source due to that they are all short- and middle-side-chain PAEs. The third component was mainly concentrated in DMP, BBEP and DEHP. In addition, four components were extracted for PAEs in sediment. The first component was mainly distributed in middle and high molecular weight PAEs, pointing out plastic pollution as their major source. The second component highly loaded in DMP, DiBP, DnBP and DEHP, indicating mixture sources of plastic and personal care products. BMPP plus DAP and DnNP was the main component in last groups. High molecular weight DnNP and DEHP are also used in construction material, clothing and furnishings (Schettler 2006), which is potential source of PAE for the fourth component. In a word, PAEs in water and sediment mainly originated from plastic and personal care products, as well as industrial activities.

Ecological risk

Potential ecological risks of target compounds to fish, daphnia and green algae at three trophic levels were assessed according to the previous studies (Cristale et al. 2013a, b; Xiong et al. 2015). The $RQ < 1.0$ indicated no significant risk; $1.0 < RQ < 10$ indicated a small potential for adverse effects; $10 < RQ < 100$ indicated significant potential for adverse effects; $RQ > 100$ indicated potential adverse effects should be expected (Cristale et al. 2013a). In this study, as Fig. 5 shows, the risk quotients for three nontarget organisms were all above 1. Meanwhile, it was found that three groups of SVOCs in sediment contributed very little risk quotients. That is, the main contributions for risk quotients were from those compounds in water. It is obvious that RQ of PAHs and OCPs was lower than those of PAEs, indicating that high levels of PAEs were the main contributor for ecological risk in water. For fish, the RQ at site 1 was the highest and exceeded 10, indicating significant potential effects for fish in this area. In addition, the highest RQs were also found at site 1 for daphnia and green algae, which

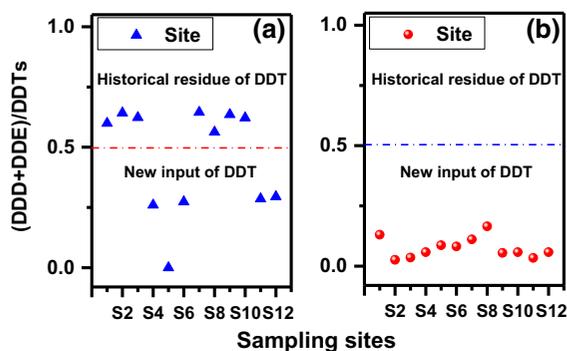


Fig. 4 Source identification of DDTs in water (a) and sediment (b)

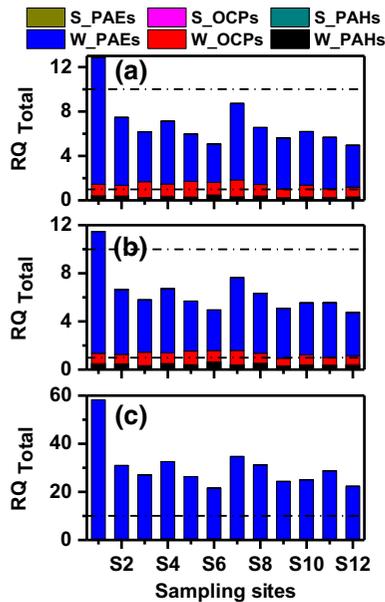


Fig. 5 Risk quotient (RQ) of PAHs, OCPs and PAEs on fish (a), daphnia (b) and green algae (c) in water and sediment

is potentially toxic due to high concentrations of PAEs in this area. The RQ for daphnia was also consistent with those for fish, whereas the RQ for green algae was much higher than that for the other two organisms, which was above 10 in all sampling sites, indicating significant potential for adverse effects to green algae within those areas. The reason for high RQ values is that the EC_{50} or LC_{50} of green algae is lower than that of fish and daphnia.

Conclusions

Higher levels of PAEs than PAHs and OCPs were found in water. In contrast, in sediment, the concentrations of PAHs were significantly high. Low-ring PAHs were dominated in water, while high-ring PAHs were abundant in sediment. HCHs were the main contributor for OCPs in water, whereas DDTs and endosulfans were two main OCPs in sediment. PAEs compositions indicated that short-side-chain PAEs were more soluble in water while more long-side-chain PAEs presented in sediments. Source identification for target compounds using PCA indicated that petroleum-derived residues or coal combustion and wood stoves sources, as well as mixture of vehicular emission, were main sources for PAHs in both water

and sediment. The PCA for OCPs revealed every category was almost independent of each other. PAEs were mainly originated from personal care products of urban sewage, plastic and other industrial sources. Ecological risk assessment caused by PAHs, OCPs and PAEs for fish, daphnia and green algae showed, at all sampling sites, a small potential for adverse effects, while green algae would be undergo a significant potential for adverse effects. Among them, high levels of PAEs were the main contributor for RQ. Actually, there is almost no significant risk caused by PAHs and OCPs, but when integrated three compounds, risk does exist. Therefore, integrated risk of different compounds should be taken into account.

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