

Characterization and sources analysis of polycyclic aromatic hydrocarbons in surface sediments in the Yangtze River Estuary

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Abstract Eighteen polycyclic aromatic hydrocarbons (PAHs), including 16 PAHs selected as priorities for control by the US Environmental Protection Agency, 1-methylnaphthalene and 2-methylnaphthalene, were determined in sediment samples from the Yangtze River Estuary, including the intertidal marshes and the river plume area. Results showed the PAH concentrations in marsh sediments ($316\text{--}792\text{ ng g}^{-1}$) were higher than those in the river plume sediment ($98\text{--}391\text{ ng g}^{-1}$). Further analysis suggested the PAH concentrations are correlated with total organic carbon ($r = 0.71$, $p < 0.05$), as well as water current and industrial activities. However, particle size less affects distribution of PAHs in Yangtze River Estuary. Results also showed a difference in PAHs' compositions between marsh and river plume sediments: PAHs with two rings were more abundant than other PAHs' compositions in river plume sediments, while PAHs with 3–4 rings were dominated in marsh sediments. This distribution pattern suggested different contamination sources between marsh and river plume sediments. The diagnostic ratios of PAH isomers and principal component analysis further demonstrated the PAHs in the marsh sediment came from burning biomass or coal, and those from river plume sediments derived from a mixture of petrogenic and

pyrolytic source. The concentrations of total PAHs in the sediments from Yangtze River Estuary were relatively low in comparison with other estuaries around the world. And ecological risk assessment also suggested that the PAHs in the Yangtze River Estuary sediments present little ecotoxicological risk. However, a risk assessment for chronic exposure to low PAH concentrations should be performed in a further study.

Keywords Polycyclic aromatic hydrocarbons · Yangtze River Estuary · Distribution · Source analysis · Ecological risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs) as an important class of persistent organic pollutants with carcinogenic, mutagenic and degradation-resistant properties are of particular concern. They are widely found in the environment because they can transport over long distances in the atmosphere and deposit in remote areas (Magi et al. 2002; Tsapakis et al. 2010; Barakat et al. 2011; Li et al. 2012). For example, Laender et al. (2011) found that PAHs had become the dominant persistent organic pollutants in the Arctic ecosystem (replacing polychlorinated biphenyls, which dominated until relatively recently). PAHs can be derived from both petrogenic and pyrogenic source, such as the burning of fossil fuels, biomass, the diagenesis of organic matter and crude oil leakage (Ren et al. 2011; Martins et al. 2011; Lang et al. 2012). Once PAHs are released into the environment, they preferentially accumulate in sediments and organisms because of their hydrophobic natures (Vane et al. 2007; Zhang et al. 2011). On one hand, some zoobenthos may directly ingest

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dissolved and particulate PAHs when exposed to sediments contaminated with PAHs (Ruiz et al. 2011). On the other hand, when the environmental conditions (such as pH and salinity) change, PAHs adsorbed on the sediments could be desorbed into water and taken up by organisms (Wang et al. 2010). This means that PAHs in sediments may enter into the food web and be a source of potential risks to organisms. The contamination of sediments with pollutants such as PAHs is, therefore, of great concern. Many studies of the distributions, transfers, and sources of PAHs have been performed in the last 50 years (Hellmann 1977; Tremolada et al. 1996; Tripathi et al. 2009; Zhang et al. 2013).

Estuaries are often exposed to numerous sources of pollutants because of intensive industrial activities and high population densities in the neighboring areas, and have been selected as the primary ecosystem resource category for study by the US Environmental Protection Agency (EPA) (Maruya et al. 1997; Telesh 2004). PAHs mainly enter estuary environments by direct discharges (e.g., from wastewater treatment plants), atmospheric deposition and oil spills and accumulate in the sediments (Fathallah et al. 2012). Moreover, an estuary is a transitional zone between land and ocean systems, having both marine and land influences, including tides, changes in river flow, and dry–wet cycles. The physical and chemical changes are, therefore, more extreme in estuary environments than in many other environments (Churchill et al. 1999). When sediments are exposed to these marine and land processes, PAHs adsorbed on the sediments could be released into water, which thus caused a secondary pollution and then affected population health and ecological environment (Wang et al. 2010). Thus, it has been shown in a number of previous studies focused on the organic pollutant in estuary sediments (Liu et al. 2005; Essien et al. 2011).

The Yangtze River is the third longest river in the world, and is heavily contaminated because of discharges of industrial and urban wastewater and agricultural runoff from the big cities along the river, such as Wuhan and Shanghai. The Yangtze River carries about 480 Mt year⁻¹ of sediment to the sea, half of which is deposited in the estuary, including the intertidal marshes and the river plume area. These sediments may contain PAHs and cause ecological risks in the estuary. Therefore, determining PAH concentration levels in estuary sediments is necessary for risk assessment and evaluation of ecosystem health. There have been several studies on the investigation of PAH levels in the Yangtze River Estuary, including PAHs in surface sediments and intertidal flat core, reflecting the influence of upstream runoff (Yang et al. 2006; Guo et al. 2007; Li et al. 2012). Most studies paid more attention to the river channel or the coastal area in the East China Sea,

few studies focus on the intertidal marsh. However, with fast industrialization and urbanization of Yangtze River Estuary, an amount of anthropogenic PAHs was released into the estuary and then adsorbed on the sediments in the marsh sediments (Chen et al. 2000). And river sediment discharge from the upstream and middle reaches of the Yangtze River has dramatically decreased because of the construction of the Three Gorges Dam (Wang et al. 2012a). All of these might result in differences in distributions, compositions and sources of PAHs in the surface sediments between the marsh and river plume sediments in Yangtze River Estuary. Moreover, there are more than 100 million people living in Yangtze River Estuary; therefore, human health would be threatened seriously by pollutant discharged. Once the characterization of PAHs changed, the risk assessment of PAHs to human health would be re-estimated. However, few studies have been performed on PAH distributions or on the risks associated with the PAHs in intertidal marsh and river plume sediments in Yangtze River Estuary (Liu et al. 2001, 2008). Therefore, it is necessary to comparatively study PAH distribution and sources between the marsh and river plume sediments in Yangtze River Estuary.

A recent study has shown the difference in both concentrations and compositions of PAHs between marsh and river plume sediments in Mississippi River Estuary (Wang et al. 2014). To further illuminate the difference between marsh and river plume sediments, this study was conducted. The goals of this study were to: (1) determine whether the difference in the concentrations and compositions of PAHs is also found between the marsh and river plume sediments from Yangtze River Estuary; (2) analyze the source of PAHs and assess the ecological risks posed by PAHs in study area. Based on previous studies, we hypothesize the similar trend as found in Mississippi River Estuary that (1) the concentrations of PAHs were lower in marsh sediments than those in river plume sediments from Yangtze River Estuary; and (2) pyrolysis source should be the major source in Yangtze River Estuary.

Materials and methods

Study area and sample collection

The Yangtze River Estuary is under subtropical monsoon with a mean annual precipitation of 900–1,050 mm (He et al. 2012). It is a mesotidal, partially mixed estuary characterized by semidiurnal tides, with a mean tidal amplitude of 2.8 m and tidal currents of 1.0–2.0 m s⁻¹. The estuary is separated into a south branch and a north branch by Chongming Island. The southern branch, which receives most incoming water and sediments of the

Yangtze River (95 %) (Chen et al. 2009), was further divided into the south channel and north channel by Changxing Island (Guo et al. 2007). There are three water currents that dominate in the study area: the riverine water flowing mainly southeastwards, the Taiwan Warm Current (TWC) from southeast and the Yellow Sea Coastal Current (YSCC) in the north (Milliman et al. 1985). Our previous study found the PAH concentrations in the sediments from Yangtze River Estuary changed seasonally with higher concentrations in dry season than flood season. Thus, the sampling time was chosen in December (dry season), when the PAHs in the sediments were high and could present the largest potential risk. In winter, the YSCC was strong; it can bring fine sediment from Yellow Sea to the areas of S3 and S4. On the other hand, the TWC was weak but still can strengthen sediments' resuspension, leading to larger sandy particles that remain in the sediments of S5 (Li et al. 2012). What is more, the discharge of the Yangtze River was smaller in dry season than flood season as water impoundment of Three Gorges Dam is often carried out in November and December (Yang et al. 2006; Yuan et al. 2011), affecting S1 and S2 mostly.

Eleven sediment samples were collected from the Yangtze River Estuary in December 2009. Five of the samples were collected from the southern intertidal marsh (sample sites XP, LHK, WSK, BLG, and LC); one sample was collected from the northern intertidal marsh (sample site DXG); and five samples were from the river plume area (sample sites S1, S2, S3, S4, and S5) (Fig. 1; Table 1). Sediment core samples were collected using a coring device, and surface sediments (0–5 cm) were sectioned by a stainless steel knife considering bioturbation. All sediments were stored in pre-combusted glass jars in a freezer (−20 °C) and freeze dried and grounded to achieve homogeneity before analysis.

Total organic carbon contents in the sediment samples

Enough 1–2 M HCl was added to 1–2 g freeze-dried sediment to just cover the sediment and the sample was left for 2 h until no more bubbles were formed. This process was repeated three times to remove all of the carbonates. The sediment sample was then dried at 60 °C for 12 h to remove the HCl. About 50 mg of the sediment sample was reweighed and analyzed in a CHN elemental analyzer, to determine the total organic carbon (TOC) content, as a percentage, in the sediment.

Sample preparation for PAH analysis

Eighteen PAHs, including the US EPA priority PAHs, were analyzed, and these were naphthalene (Nap), 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene (Ace),

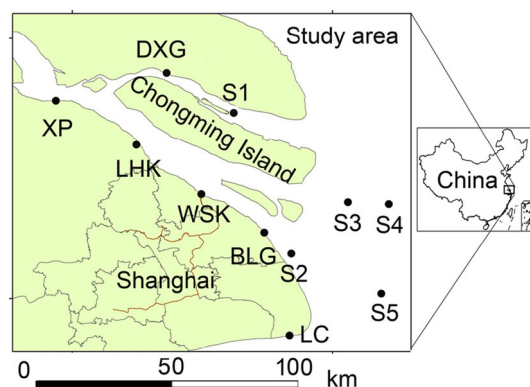


Fig. 1 Sampling sites in the Yangtze River Estuary. Site DXG was in the northern bank marshes, sites XP, LHK, WSK, BLG, and LC were in the southern bank marshes, and sites S1, S2, S3, S4, and S5 were in the river plume area

Table 1 Sampling location and physicochemical properties of waters in Yangtze River Estuary

Station	Location	Salinity (‰)	pH
XP	112°54'E, 31°45'N	0.2	7.30
LHK	121°14'E, 31°31'N	0.5	7.41
WSK	121°29'E, 31°22'N	0.3	7.65
BLG	121°45'E, 31°14'N	1.8	7.54
LC	121°51'E, 30°51'N	19.5	7.78
DXG	121°20'E, 31°52'N	19.2	7.71
S1	121°30'E, 31°42'N	23.6	8.01
S2	121°51'E, 31°12'N	2.4	8.07
S3	122°06'E, 31°21'N	3.6	8.19
S4	122°24'E, 31°15'N	26.2	8.04
S5	112°18'E, 30°54'N	27.7	7.94

acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (An), fluoranthene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k,j]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP). BbF and BkF were measured together because they were not able to be chromatographically separated. A standard mixture of the 18 PAHs and standards of five deuterated PAHs (D₈-Nap, D₁₀-Ace, D₁₀-Phe, D₁₂-Chr, and D₁₂-Per), which were used as internal standards, were purchased from Dr. Ehrenstorfer (Augsburg, Germany). All of the organic solvents were of HPLC grade and were purchased from J&K (Beijing, China).

The PAHs were extracted from the sediment samples using previously published method (Wang et al. 2012b). In brief, sediment samples (5 g dry weight) were extracted with a 1:1 (v/v) mixture of acetone and dichloromethane in an accelerated solvent extraction system (ASE-300;

Dionex, Sunnyvale, CA, USA). The final temperature and pressure in the extraction cells were 100 °C and 1,500 psi, respectively, and these conditions were maintained for 5 min; then the cells were flushed with a 60 % flush volume and a 90-s purge time. The final extracts were of approximately 30–40 mL, and they were concentrated to about 1 mL, and exchanged into pure *n*-hexane, using a rotary evaporator. Each concentrated extract was cleaned by passing it through a chromatographic column containing silica gel (8 g, 100–200 mesh, activated at 160 °C for 16 h then partially deactivated with 10 % water, by weight) topped with 1 g of anhydrous sodium sulfate (baked at 450 °C for 4 h). The column was cleaned with 20 mL hexane; then the concentrated extract was added. The column was first eluted with 15 mL hexane (to remove alkanes), which were discarded, then with 70 mL of a 3:7 (v/v) mixture of dichloromethane and hexane, which were collected for further processing. The volume of the collected solution was decreased to 1 mL using a rotary evaporator; then it was transferred to a 2-mL vial and stored in a freezer at –18 °C until it was analyzed by gas chromatography/mass spectrometry (GC/MS).

PAH analysis

The GC/MS instrument used to analyze the PAHs in the extracts was fitted with an HP-5 MS capillary chromatography column (30 m long, 0.25 mm i.d., 0.25 µm film thickness; Agilent Technologies, Santa Clara, CA, USA). The carrier gas was helium, and it was used at a flow rate of 1.0 mL min^{–1}. The oven temperature program began at 40 °C, which was held for 4 min, then increased at 10 °C min^{–1} to 280 °C, which was held for 4 min, then increased 10 °C min^{–1} to 300 °C, which was held for 5 min. The injection volume was 1 µL, and splitless injection mode was used. The injector and detector temperatures were 250 and 280 °C, respectively. The mass spectrometer was used in selective ion monitoring mode. No PAHs were detected in the method blanks, which were prepared using the same procedure as was used for the samples to measure background contamination. The recoveries from spiked blank tests were 50–150 %. An internal standard method was used to quantify the PAHs.

Results and discussion

PAH concentrations in the Yangtze River Estuary sediment

The PAH concentrations in the intertidal marsh sediment samples from the Yangtze River Estuary were

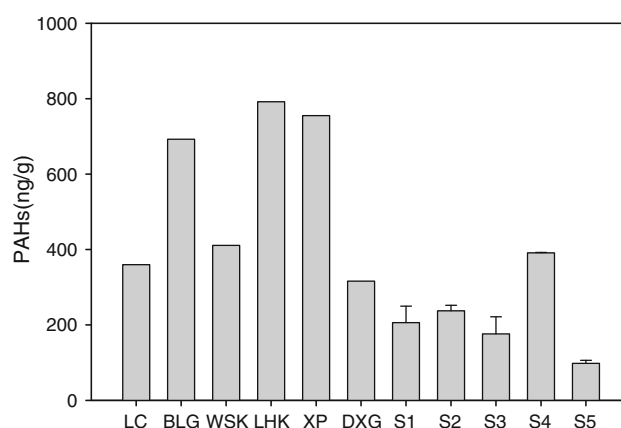


Fig. 2 Total polycyclic aromatic hydrocarbon (PAH) concentrations in the sediment samples from the Yangtze River Estuary. The error bars indicate one standard deviation (from duplicate sample analyses)

316–792 ng g^{–1}, and the concentrations in the river plume sediment samples were lower, in the range of 98–391 ng g^{–1} (Fig. 2). Although there is a great deal of industrial activity and a high population in the Yangtze River Estuary area, which would be expected to cause high PAH concentrations in the sediments, the PAH concentrations found were much lower than those in highly polluted sites, such as the Lenga Estuary (290–6,118 ng g^{–1}) (Pozo et al. 2011), the Yellow River Estuary (111–205 ng g^{–1}) (Hu et al. 2014), and the Jiulong River Estuary (280–1,074 ng g^{–1}) (Tian et al. 2008). Overall, the PAH concentrations in the Yangtze River Estuary were classified as low to moderate, consistent with a recent study, which suggested an increasing trend of the PAH values with the descending distance from the estuary to the adjacent sea (Li et al. 2012). In this study, the concentrations of PAHs in sediments from the southern and northern bank and river plume were further compared.

The PAH concentrations in the river plume sediment samples were half those found in the intertidal marsh sediment samples, providing insights into the factors that affect the PAH concentrations. Certain sediment properties, such as the TOC and clay contents, can affect the distributions and concentrations of PAHs. For example, PAH concentrations tend to be higher in sediment with a high TOC content than in sediment with a low TOC content because organic matter has a high sorption capacity for PAHs (Chiou et al. 1998; Xia and Ball 1999). A significant correlation between the TOC contents and the PAH concentrations in the sediment samples was found in this study ($r = 0.71$, $p < 0.05$; Fig. 3), suggesting TOC plays an important role in distribution of PAHs in study area. Mineral surfaces also affected the distribution of PAHs in sediment, because PAHs can sorb directly to a mineral surface or to organic matter coating the mineral surface

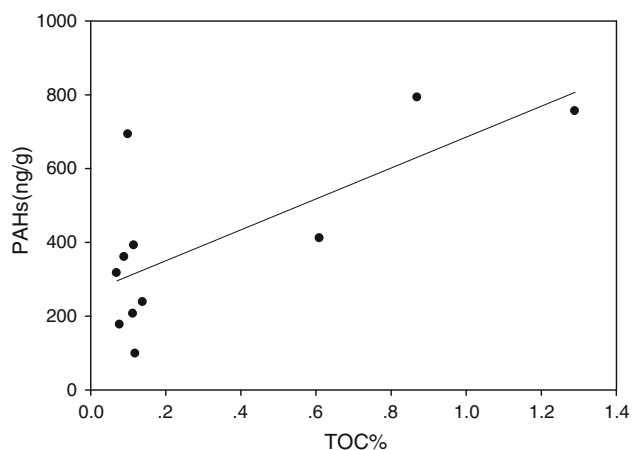


Fig. 3 Relationship between the polycyclic aromatic hydrocarbon (PAH) concentrations and the total organic carbon (TOC) contents in the sediments, showing a significant positive correlation ($r = 0.71$, $p < 0.05$)

(Warren et al. 2003). Minerals with smaller particle sizes would have higher specific surface areas, and these would sorb more organic pollutants than will minerals with larger particle sizes. However, there were many studies that also suggested no relationship between particle size and PAH concentrations (Wang et al. 2001). Zhu et al. (2011) had found the grain size distribution was consistent in different parts of the Yangtze River Estuary, indicating that the particle size would not have affected the PAH distribution in the Yangtze River Estuary sediments (Li et al. 2012). The phenomenon can likely be resulted from the different types of TOC in the whole estuary (Wang et al. 2014). Moreover, different flocculation rates of particles in different sampling sites might also have attributed to the differences in sedimentary PAH loads because of different water conditions at various areas, such as salinity and pH (Table 1). Kucklick et al. (1997) suggested the proximity to industrial activity (i.e., the distance from the contaminant source to the sediment) also affected the PAH concentrations in the sediment. For example, higher PAH concentrations were found at the southern bank of the estuary, where there are more industrial activities, than at the northern bank. In addition, the water current was often considered to affect the distribution of PAHs significantly in estuary. The inflow of multiple tributaries, such as Liuhe River and Huangpu River, carried a large amount of pollutant into southern branch, resulting in higher PAH concentrations in southern branch (Wang et al. 2012a). In contrast, the lower PAH concentrations in river plume sediments indicated that relatively small amounts of PAHs were input into the estuary via the upper and middle reaches of the Yangtze River. As water impoundment of Three Gorges Dam, the runoff volume and suspended particles in the lower reach of the watershed declined

drastically, resulting in less PAHs in the upper reach would transport and precipitate in the estuary (Yang et al. 2006; Yuan et al. 2011). Therefore, the PAHs in Yangtze River Estuary were mainly of local source rather than long-distance transportation. This distribution pattern of PAH between marsh and river plume sediments were different from Mississippi River Estuary (Wang et al. 2014), which showed higher PAH concentrations in river plume sediments than marsh sediments. This might be explained by different sediment properties, water current and industry distribution between two estuaries.

PAH profiles and source analysis

The 18 PAHs were divided into three groups, the two-ring (2-ring) PAHs, the three- and four-ring (3- to 4-ring) PAHs, and the five- and six-ring (5- to 6-ring) PAHs; and these groups can be assumed to represent petroleum sources, low-medium temperature thermal reactions of organic matter sources, and high temperature combustion sources, respectively (Soclo et al. 2000; Zaghden et al. 2007). The 3- to 4-ring PAHs were dominant in the intertidal sediment samples, accounting for more than 70 % of the total PAH concentrations, while the 2-ring PAHs accounting for 10–30 % of the total PAH concentrations. However, the 2-ring PAHs accounted for 50–80 % of the total PAH concentrations in the river plume sediment samples, with the 3- to 4-ring PAHs contributing 15–35 %. The 5- to 6-ring PAHs contributed less than 18 % of the total PAH concentrations in the estuary sediment samples (Fig. 4a). Phe and Flua contributed the most to the total PAH concentrations in the intertidal marsh sediment samples, accounting for more than 30 % and about 10 % of the total PAH concentrations, respectively, while 2-methylnaphthalene contributed the most (more than 20 %) to the total PAH concentrations in the river plume sediment samples (Fig. 4b). The differences in the PAH composition profiles indicated that there were different PAH sources for the intertidal marsh sediment samples and for the river plume sediment samples, because different sources produce the different PAH composition profiles found (Kim et al. 2008).

The concentration ratios of specific PAH isomers were used to attempt to identify the PAH contamination sources, because different PAHs have different thermodynamic stabilities (Yunker and Macdonald 1995). Yunker et al. (2002) suggested that the PAHs with molecular masses of 202 and 276 Da can be used to identify the difference between petroleum and combustion sources because the isomers with these masses have a relatively broad range of stabilities. The InP to 276 Da (InP and BgP) ratio and the Flua to 202 Da (Flua and Pyr) ratio were used to identify different PAH sources in this study. As is shown in Fig. 5a,

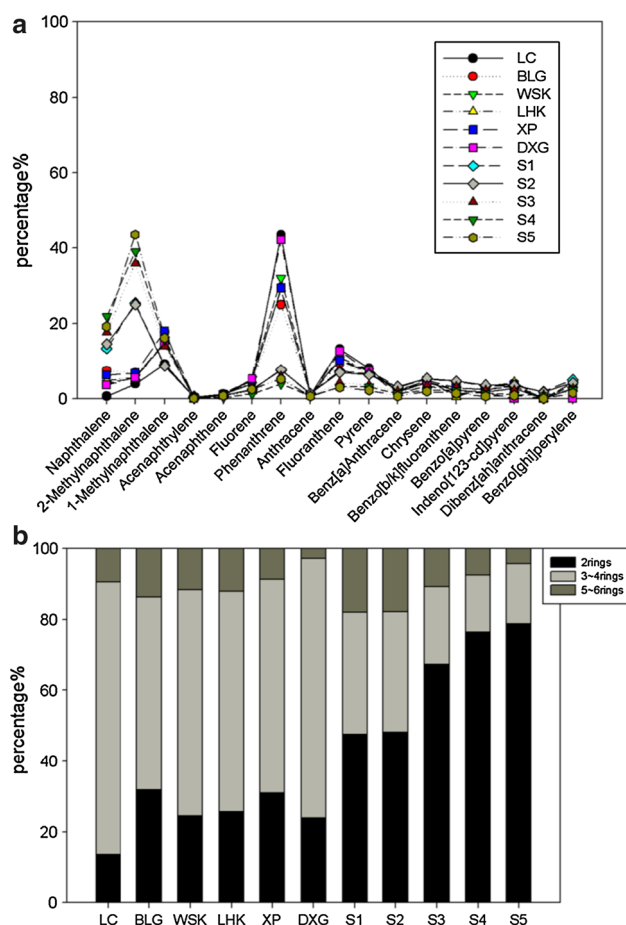


Fig. 4 Distribution of **a** individual polycyclic aromatic hydrocarbons (PAHs) and **b** 2-ring, 3- to 4-ring, and 5- to 6-ring PAHs in the Yangtze River Estuary sediment samples

the InP to 276 Da ratios were higher than 0.5 in the intertidal marsh sediment samples and 0.2–0.5 in the river plume sediment samples, which indicates that the PAHs in the marsh sediment samples came from coal or biomass combustion and that the PAHs in the river plume sediment samples came from other fossil fuel combustion sources (Yunker et al. 2002; Li et al. 2006). The Flua to 202 Da ratios were higher than 0.5 in all of the samples, indicating that the PAHs came from coal and biomass combustion (Yunker et al. 2002). The combustion-derived PAH (ComPAHs) concentrations [Flua, Pyr, BaA, Chr, BbF, BkF, BaP, InP, DBA, and BgP (Prah and Carpenter 1983)] significantly correlated with the total PAH concentrations ($r = 0.96$, $p < 0.05$; Fig. 5b), further suggesting that pyrogenic PAH sources are important in the Yangtze River Estuary. Overall, the ratios of specific PAH isomers suggested the PAHs in the marsh sediment samples appear to have come from coal or biomass combustion, while the PAHs in the river plume sediment samples appear to have come from a mixture of coal and petroleum combustion.

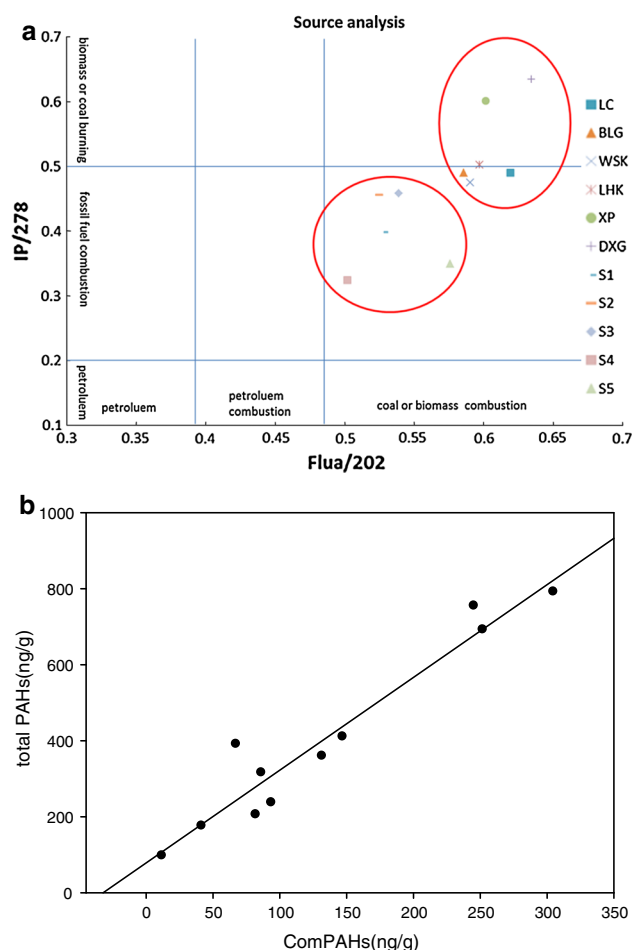


Fig. 5 **a** Diagnostics for distinguishing polycyclic aromatic hydrocarbon (PAH) sources in the Yangtze River Estuary and **b** the relationship between the total PAH and combustion-derived PAH (ComPAH) concentrations in the sediment samples, showing a significant positive correlation ($r = 0.96$, $p < 0.05$)

However, the sediment samples from river plume area were separated from marsh area, suggesting the pyrogenic source might be not the only source (Fig. 5a). Unlike the PAHs in marsh sediments, the PAHs in river plume sediments were not only from the discharge from industry, runoff from upstream and atmospheric deposition, but also from the direct discharges from shipping or from oil or petroleum product leakages in the area (Robertson 1998; Liu et al. 2008). This can be inferred from the results of PAH compositions in the river plume sediment that the presence of alkyl-substituted naphthalenes accounted for more than 30 % of the total PAH concentrations, which are characteristically associated with unweathered petroleum. Thus, the petrogenic source might be another source in Yangtze River Estuary, especially in river plume sediments. These results indicated that the mixed source of PAHs may alter the ratios of specific PAH isomers, suggesting that the diagnostic ratios can be used to identify

potential contamination sources, but cannot give conclusive data.

Principal component analysis

As mentioned above, the diagnostic ratios can only be used to qualitatively identify PAH sources. Principal component analysis (PCA), however, can usually be used to semi-quantitatively describe the contributions of the main PAH sources (Simcik et al. 1999; Ingalls et al. 2006; Li et al. 2012; Wang et al. 2012b). PCA can be used to identify the main factors that describe the variability in the PAH data and to group the sampling sites by the relationships between their PAH concentration profiles. The PAH concentrations were standardized before performing PCA by dividing the individual PAH concentrations by the total PAH concentrations, to avoid the concentration of any particular PAH being too high to be useful in the PCA (e.g., by dominating the variability).

Two principal components (PCs) were extracted, and they accounted for 70 and 16 % of the variability in the data, respectively (Fig. 6). If the PAH composition contributed more than 70 % to one principal component it could be assumed to be the main factor in that PC (Golobocanin et al. 2004). The score plot for the samples (Fig. 6) showed that the intertidal marsh sediment samples and the river plume sediment samples were separated in PC1, indicating that they had different PAH sources. The intertidal marsh sediment samples were enriched in 1-methylnaphthalene, Acy, Ant, Flu, Phe, Flua, Pyr, BaA, Chr, and BaP relative to the sediment samples from the other sites. Most of these components are 3- to 4-ring PAHs, which are usually derived from vehicular emissions

(May and Wise 1984; Harrison et al. 1996). In contrast, the river plume sediment samples were enriched in Nap and 2-methylnaphthalene, which are usually thought to be derived from petroleum (Yunker et al. 1996; Robertson 1998). Therefore, the PAHs in marsh sediments were mainly from atmospheric deposition, while the PAHs in river plume sediments mainly came from shipping process and oil leakage. This source analysis again indicated the PAHs in Yangtze River Estuary were less influenced by river sediments from river flow because of less sediments carried out in December due to impoundment of Three Gorges Dam.

Taking the PCA and diagnostic ratio results together, pyrolysis was the major source of PAHs in the marsh sediments, such as coal and biomass burning, and both pyrolysis and petrogenic source contributed to the PAHs in the river plume sediments. This conclusion was consistent with the distribution of PAHs in Yangtze River Estuary. As the particles from pyrolysis often have significant adsorption ability for PAHs (Cornelissen et al. 2005), and the PAHs from petrogenic might be easier to release into water, resulting in more PAHs found in marsh sediments than river plume sediments. These results suggested the PAHs from different sources have different fates after accumulated into sediments. For example, the pyrolysis PAHs preferred to be resistant in the particles, while petrogenic PAHs might be released into aqueous phase easily.

The sources of PAHs in Yangtze River Estuary were partially consistent with hypothesis, suggesting both pyrolysis and petrogenic source contributed to the PAHs in Yangtze River Estuary. This difference indicated the shipping process cannot be neglected while considering the source of PAHs in estuary.

Ecological risk assessment

PAHs can enter the food web by being absorbed from sediment by plants and animals. There is, therefore, an ecological risk associated with the presence of PAHs in an estuary (Liu et al. 2009). Long et al. (1995) suggested that the parameters called the “effects range low” (ERL) and the “effects range median” (ERM) could be used to evaluate risks associated with the presence of organic pollutants. The ERL (which was $4,022 \text{ ng g}^{-1}$ for the total PAH concentration) and the ERM (which was $44,792 \text{ ng g}^{-1}$ for the total PAH concentration) are the concentrations at which the likelihood of ecological effects occurring are 10 and 50 %, respectively. The ERL and ERM have been used as ecological risk guidelines in recent studies (Lang et al. 2012). The total PAH concentrations and the individual PAH concentrations were all below the ERLs in our study, indicating that the ecological risks from PAHs in the Yangtze River Estuary were low. However, Kalf et al.

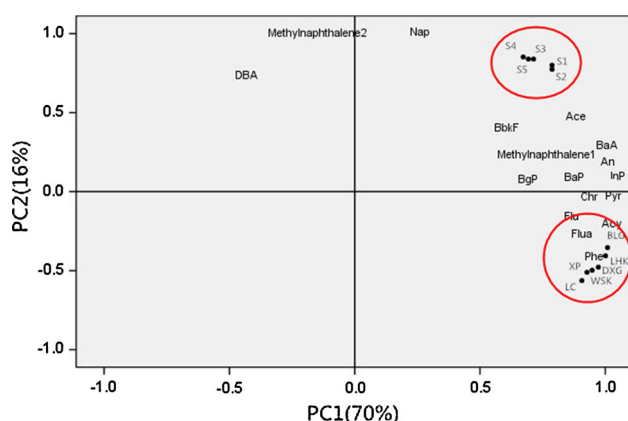


Fig. 6 Principal component analysis (PCA) of the polycyclic aromatic hydrocarbon (PAH) concentrations in the sediment samples from the Yangtze River Estuary. PC1 explained 70 % of the variance in the data and PC2 explained 16 % of the variance. The intertidal marsh sediment samples were clearly separated from the river plume sediment samples

(1997) proposed another method for assessing ecological risks from organic pollutants, using a risk quotient (RQ). Cao et al. (2010) further improved this approach using toxic equivalency factors, and this improved method was found to be more accurate and scientific than the previous methods (Cao et al. 2010; Liu et al. 2013). This improved method was used to assess the risks associated with the presence of PAHs in the Yangtze River Estuary. The RQs for different PAHs were calculated using the equations

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV(NCs)}}$$

and

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV(MPCs)}},$$

where C_{PAHs} and C_{QV} are the actual concentration of a specific PAH in a sediment and the concentration that gives a specific effect, respectively. Negligible concentrations (“NCs”) are the concentrations below which adverse effects are negligible, and maximum permissible concentrations (“MPCs”) are the concentrations above which adverse effects on the ecosystem are unacceptable. RQ_{NCs} of less than 1.0 indicate that the PAH of interest can be disregarded, and RQ_{MPCs} of more than 1.0 indicate that the PAH of interest poses a severe risk. RQ_{NCs} of more than 1.0 and RQ_{MPCs} of less than 1.0 indicate that the PAH of interest could cause moderate risks to the ecosystem. The RQ_{NCs} and RQ_{MPCs} values used in this study were reported by Kalf et al. (1997) and are shown in Table 2. The RQ_{NCs} and RQ_{MPCs} for all of the PAHs (i.e., for the total PAH concentrations) are the sums of the RQ_{NCs} and RQ_{MPCs} of the individual PAHs that are each not lower than 1.

The RQ_{NCs} for most of the individual 2- to 4-ring PAHs were higher than 1.0, especially for Nap, while the RQ_{NCs} for the individual 5- to 6-ring PAHs were lower than 1.0. All of the RQ_{MPCs} for the individual PAHs were lower than 1.0. These results indicate that there was a moderate level of ecological risks associated with the low–medium molecular weight PAHs in the Yangtze River Estuary, and this risk may come from petroleum emissions and from low–medium temperature thermal reactions of coal or biomass, as discussed earlier. In terms of the total PAH concentrations, the RQ_{NCs} were higher in the intertidal marsh sediment samples than in the river plume sediment samples, indicating that there were higher ecological risks associated with PAHs in the intertidal marsh sediments (Fig. 7). The differences between the effect ranges and the risk quotients in the ecological risk assessments suggest that, even though organisms in the Yangtze River Estuary will be exposed to relatively low PAH concentrations, there might be potential ecological risks to organisms over long exposure times.

Table 2 NCs and MPCs of individual PAHs in sediments (ng/g)

PAHs	NCs	MPCs	PAHs	NCs	MPCs
Nap	1.4	104	BaA	3.6	360
Ace	1.2	120	Chr	107.0	10,700
Acy	1.2	120	BbF	3.6	360
Flu	1.2	120	BkF	24.0	2,400
Phe	5.1	510	BaP	27.0	2,700
An	1.2	120	DBA	27.0	2,700
Flua	26.0	2,600	InP	59.0	5,900
Pyr	1.2	120	BgP	75.0	7,500

Negligible concentrations (NCs) are the concentrations below which the adverse effects could be negligible concern and maximum permissible concentrations (MPCs) are the concentration above which the adverse effects are unacceptable to ecosystem. The value were reported by Kalf et al. (1997)

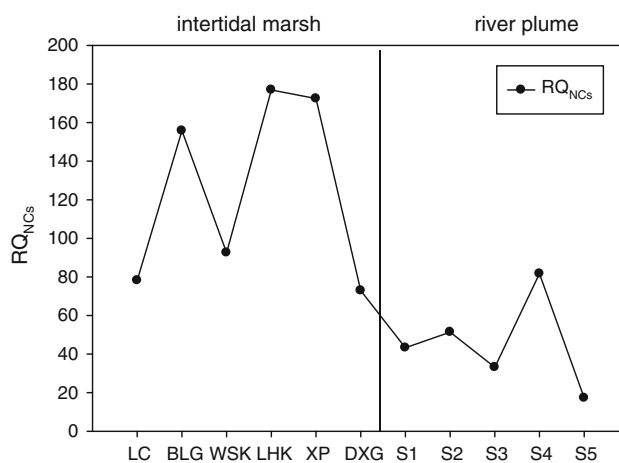


Fig. 7 Negligible concentration risk quotients (RQ_{NCs}) for the total polycyclic aromatic hydrocarbons (PAHs) in sediments from the Yangtze River Estuary

Conclusions

The PAH distributions in surface sediments from the Yangtze River Estuary were analyzed and the sources of the PAHs were identified. The Yangtze River Estuary sediment samples contained low–medium levels of PAH concentrations in the range of 98–792 ng g^{−1}. The differences in the PAH concentrations between the intertidal marshes and river plume sediment samples were caused by a number of factors, such as total organic carbon, the water current and industrial activities. The 3- to 4-ring PAHs dominated the marsh sediment samples, while the 2-ring PAHs dominated the river plume sediment samples. Source analyses showed that vehicular emissions were the main sources of PAHs in the intertidal marsh sediment samples but that petroleum cannot be neglected while considering

the source of PAHs in the river plume sediment samples. PCA further divided all sampling stations into two groups by PAH compositions, again suggesting different PAHs' sources between them. Both distributions of PAH concentrations and compositions in Yangtze River Estuary were different from that in Mississippi River Estuary, which can be explained by different water currents, TOC distribution and industry activities. Ecological risk assessments suggested that there is a moderate level of ecological risk from PAHs in the Yangtze River Estuary, especially in the intertidal marshes.

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References

- Barakat AO, Mostafa A, Wade TL, Sweet ST, El Sayed NB (2011) Distribution and characteristics of PAHs in sediments from the Mediterranean coastal environment of Egypt. *Mar Pollut Bull* 62(9):1969–1978
- Cao ZG, Liu JL, Luan Y, Li YL, Ma MY, Xu J, Han SL (2010) Distribution and ecosystem risk assessment of polycyclic aromatic hydrocarbons in the Luan River, China. *Ecotoxicology* 19(5):827–837
- Chen ZY, Song BP, Wang ZH, Cai YL (2000) The late quaternary evolution of the subaqueous Yangtze Delta, China: stratigraphy, sedimentation, palynology and deformation. *Mar Geol* 162(2–4):423–441
- Chen JL, Wong YS, Tam NPY (2009) Static and dynamic sorption of phenanthrene in mangrove sediment slurry. *J Hazard Mater* 168(23):1422–1429
- Chiou CT, McGroddy SE, Kile DE (1998) Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. *Environ Sci Technol* 32(2):264–269
- Churchill JH, Blanton JO, Hench JL, Luettich RA, Werner FE (1999) Flood tide circulation near Beaufort Inlet, North Carolina: implications for larval recruitment. *Estuaries* 22(4):1057–1070
- Cornelissen G, Gustafsson O, Bucheli TD, Jonker MTO, Koelmans AA, van Noort PCM (2005) Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ Sci Technol* 39(18):6881–6895
- Essien JP, Eduok SI, Olajire AA (2011) Distribution and ecotoxicological significance of polycyclic aromatic hydrocarbons in sediments from Iko River estuary mangrove ecosystem. *Environ Monit Assess* 176(1–4):99–107
- Fathallah S, Medhioub MN, Kraiem MM (2012) Photo-induced toxicity of four polycyclic aromatic hydrocarbons (PAHs) to embryos and larvae of the carpet shell clam *Ruditapes decussatus*. *B Environ Contam Toxicol* 88(6):1001–1008
- Golobocanin DD, Skrbic BD, Miljevic NR (2004) Principal component analysis for soil contamination with PAHs. *Chemometr Intell Lab* 72(2):219–223
- Guo ZG, Lin T, Zhang G, Zheng M, Zhang ZY, Hao YC, Fang M (2007) The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River estuary coastal sea for the past century. *Sci Total Environ* 386(1–3):33–41
- Harrison RM, Smith DJT, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environ Sci Technol* 30(3):825–832
- He YL, Li XZ, Guo WY, Ma ZG (2012) Division of labor in rhizomatous species: comparative performance of native and invasive species in the tidal marshes of the Yangtze River estuary, China. *J Exp Mar Biol Ecol* 422:122–128
- Hellmann H (1977) Fluorimetric determination of polycyclic aromatic-hydrocarbons in leaves, blooms and phytoplankton. *Fresen Z Anal Chem* 287(2–3):148–151
- Hu NJ, Huang P, Liu JH, Ma DY, Shi XF, Mao J, Liu Y (2014) Characterization and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in sediments in the Yellow River Estuary, China. *Environ Earth Sci* 71:873–883
- Ingalls AE, Liu ZF, Lee C (2006) Seasonal trends in the pigment and amino acid compositions of sinking particles in biogenic CaCO_3 and SiO_2 dominated regions of the Pacific sector of the Southern Ocean along 170 degrees W. *Deep Sea Res Part I* 53(5):836–859
- Kalf DF, Crommentuijn T, Vandeplasseche EJ (1997) Environmental quality objectives for polycyclic aromatic hydrocarbons (PAHs). *Ecotoxicol Environ Saf* 36(1):89–97
- Kim M, Kennicutt MC, Qian Y (2008) Source characterization using compound composition and stable carbon isotope ratio of PAHs in sediments from lakes, harbor, and shipping waterway. *Sci Total Environ* 389(2–3):367–377
- Kucklick JR, Sivertsen SK, Sanders M, Scott GI (1997) Factors influencing polycyclic aromatic hydrocarbon distributions in South Carolina estuarine sediments. *J Exp Mar Biol Ecol* 213(1):13–29
- Laender FD, Hammer J, Hendriks AJ, Soetaert K, Janssen CR (2011) Combining monitoring data and modeling identifies PAHs as emerging contaminants in the Arctic. *Environ Sci Technol* 45(20):9024–9029
- Lang YH, Wang NN, Gao HW, Bai J (2012) Distribution and risk assessment of polycyclic aromatic hydrocarbons (PAHs) from Liaohu estuarine wetland soils. *Environ Monit Assess* 184(9):5545–5552
- Li GC, Xia XH, Yang ZF, Wang R, Voulvoulis N (2006) Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environ Pollut* 144(3):985–993
- Li BH, Feng CH, Li X, Chen YX, Niu JF, Shen ZY (2012) Spatial distribution and source apportionment of PAHs in surficial sediments of the Yangtze Estuary, China. *Mar Pollut Bull* 64(3):636–643
- Liu M, Hou LJ, Yang Y, Zou HX, Lu JH, Wang XR (2001) Distribution and sources of polycyclic aromatic hydrocarbons in intertidal flat surface sediments from the Yangtze estuary, China. *Environ Geol* 41(1–2):90–95
- Liu GQ, Zhang G, Li XD, Li J, Peng XZ, Qi SH (2005) Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River Estuary, South China. *Mar Pollut Bull* 51(8–12):912–921
- Liu Y, Chen L, Zhao JF, Huang QH, Zhu ZL, Gao HW (2008) Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environ Pollut* 154(2):298–305
- Liu AX, Lang YH, Xue LD, Liao SL, Zhou H (2009) Probabilistic Ecological Risk Assessment and Source Apportionment of Polycyclic Aromatic Hydrocarbons in Surface Sediments from Yellow Sea. *B Environ Contam Toxicol* 83(5):681–687
- Liu F, Liu JL, Chen QY, Wang BB, Cao ZG (2013) Pollution characteristics and ecological risk of polycyclic aromatic

- hydrocarbons (PAHs) in surface sediments of the southern part of the Haihe River system in China. *Chin Sci Bull* 58(27):3348–3356
- Long ER, MacDonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuary sediments. *Environ Manag* 19(1):81–97
- Magi E, Bianco R, Ianni C, Di Carro M (2002) Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environ Pollut* 119(1):91–98
- Martins CC, Bicego MC, Mahiques MM, Figueira RCL, Tessler MG, Montone RC (2011) Polycyclic aromatic hydrocarbons (PAHs) in a large South American industrial coastal area (Santos estuary, Southeastern Brazil): sources and depositional history. *Mar Pollut Bull* 63(5–12):452–458
- Maruya KA, Loganathan BG, Kannan K, McCumber-Kahn S, Lee RF (1997) Organic and organometallic compounds in estuarine sediments from the Gulf of Mexico (1993–1994). *Estuaries* 20(4):700–709
- May WE, Wise SA (1984) Liquid-chromatographic determination of polycyclic aromatic-hydrocarbons in air particulate extracts. *Anal Chem* 56(2):225–232
- Milliman JD, Beardsley RC, Zuo-Sheng Y, Limeburner R (1985) Modern Huanghe-derived muds on the outer shelf of the East China Sea: identification and potential transport mechanisms. *Cont Shelf Res* 4(1–2):175–188
- Pozo K, Perra G, Menchi V, Urrutia R, Parra O, Rudolph A, Focardi S (2011) Levels and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Lengua Estuary, central Chile. *Mar Pollut Bull* 62(7):1572–1576
- Prahl FG, Carpenter R (1983) Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediment. *Geochim Cosmochim Acta* 47(6):1013–1023
- Ren HF, Kawagoe T, Jia HJ, Endo H, Kitazawa A, Goto S, Hayashi T (2011) Continuous surface seawater surveillance on polycyclic aromatic hydrocarbons (PAHs) and mutagenicity of East and South China Seas. *Estuar Coast Shelf Sci* 86(3):395–400
- Robertson A (1998) Arctic Monitoring, Assessment Programme. AMAP Assessment Report: Arctic Pollution Issues, Oslo, 666
- Ruiz Y, Suarez P, Alonso A, Longo E, Villaverde A, Juan FS (2011) Environmental quality of mussel farms in the Vigo estuary: pollution by PAHs, origin and effects on reproduction. *Environ Pollut* 159(1):250–265
- Simcik MF, Eisenreich SJ, Liroy PJ (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos Environ* 33(30):5071–5079
- Soclo HH, Garrigues P, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Mar Pollut Bull* 40(5):387–396
- Telesh IV (2004) Plankton of the Baltic estuarine ecosystems with emphasis on Neva Estuary: a review of present knowledge and research perspectives. *Mar Pollut Bull* 49(3):206–219
- Tian Y, Liu HJ, Zheng TL, Kwon KK, Kim SJ, Yan CL (2008) PAHs contamination and bacterial communities in mangrove surface sediments of the Jiulong River Estuary, China. *Mar Pollut Bull* 57(6–12):707–715
- Tremolada P, Burnett V, Calamari D, Jones KC (1996) Spatial distribution of PAHs in the UK atmosphere using pine needles. *Environ Sci Technol* 30(12):3570–3577
- Tripathi R, Kumar R, Mudiam MKR, Patel DK, Behari JR (2009) Distribution, sources and characterization of polycyclic aromatic hydrocarbons in the sediment of the River Gomti, Lucknow, India. *B Environ Contam Toxicol* 83(3):449–454
- Tsapakis M, Dakanali E, Stephanou EG, Karakassis I (2010) PAHs and *n*-alkanes in Mediterranean coastal marine sediments: aquaculture as a significant point source. *J Environ Monitor* 12(4):958–963
- Vane CH, Harrison I, Kim AW (2007) Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, UK. *Sci Total Environ* 374(1):112–126
- Wang XC, Zhang YX, Chen RF (2001) Distribution and partitioning of polycyclic aromatic hydrocarbons (pahs) in different size fractions in sediments from Boston harbor. *Mar Pollut Bull* 42(11):1139–1149
- Wang HS, Zhang C, Liang P, Shao DD, Kang Y, Wu SC, Wong CK, Wong MH (2010) Characterization of PAHs in surface sediments of aquaculture farms around the Pearl River Delta. *Ecotoxicol Environ Saf* 73(5):900–906
- Wang Y, Li X, Li BH, Shen ZY, Feng CH, Chen YX (2012a) Characterization, sources, and potential risk assessment of PAHs in surface sediments from nearshore and farther shore zones of the Yangtze estuary, China. *Environ Sci Pollut Res* 19(9):4148–4158
- Wang ZC, Liu ZF, Yang Y, Li T, Liu M (2012b) Distribution of PAHs in tissues of wetland plants and the surrounding sediments in the Chongming wetland, Shanghai, China. *Chemosphere* 89(3):221–227
- Wang ZC, Liu ZF, Xu KH, Mayer LM, Zhang ZL, Kolker AS, Wu W (2014) Concentrations and sources of polycyclic aromatic hydrocarbons in surface coastal sediments of the northern Gulf of Mexico. *Geochem Trans* 15:2
- Warren N, Allan IJ, Carter JE, House WA, Parker A (2003) Pesticides and other micro-organic contaminants in freshwater sedimentary environments – a review. *Appl Geochem* 18(2):159–194
- Xia GS, Ball WP (1999) Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environ Sci Technol* 33(2):262–269
- Yang Z, Wang H, Saito Y, Milliman JD, Xu K, Qiao S, Shi G (2006) Dam impacts on the Changjiang (Yangtze) River sediment discharge to the sea: the past 55 years and after the Three Gorges Dam. *Water Resour Res* 42(4):W04407
- Yuan W, Yin D, Finlayson B, Chen Z (2011) Assessing the potential for change in the middle Yangtze River channel following impoundment of the Three-Gorges Dam. *Geomorphology* 147–148:27–34
- Yunker MB, Snowdon LR, MacDonald RW, Smith JN, Fowler MG, Skibo DN, McLaughlin FA, Danyushevskaya AI, Petrova VI, Ivanov GI (1996) Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environ Sci Technol* 30(4):1310–1320
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33(4):489–515
- Yunker MB, Macdonald RW (1995) Composition and origins of polycyclic aromatic-hydrocarbons in the mackenzie river and on the beaufort sea shelf. *Arctic* 48(2):118–129
- Zaghen H, Kallel M, Elleuch B, Oudot J, Salot A (2007) Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea. *Mar Chem* 105(1–2):70–89
- Zhang K, Zhang BZ, Li SM, Zeng EY (2011) Regional dynamics of persistent organic pollutants (POPs) in the Pearl River Delta, China: implications and perspectives. *Environ Pollut* 159(10):2301–2309
- Zhang L, Qin YW, Zheng BH, Lin T, Li YY (2013) Polycyclic aromatic hydrocarbons in the sediments of Xiangjiang River in south-central China: occurrence and sources. *Environ Earth Sci* 69(1):119–125
- Zhu C, Wang ZH, Xue B, Yu PS, Pan JM, Wagner T, Pancost RD (2011) Characterizing the depositional settings for sedimentary organic matter distributions in the Lower Yangtze River-East China Sea Shelf System. *Estuar Coast Shelf S* 93(3):182–191