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RESEARCH ARTICLE

Characterization, sources, and potential risk assessment of PAHs in surface sediments from nearshore and farther shore zones of the Yangtze estuary, China

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Abstract The assessment of polycyclic aromatic hydrocarbons (PAHs) contamination in surface sediments from the Yangtze estuary which is a representative area affected by anthropogenic activity (rapid industrialization, high-population density, and construction of dams upstream) in the world was systematically conducted. Fifty-one samples were analyzed by high-performance liquid chromatography (HPLC). The ∑PAHs in all sediments varied from 76.9 to 2,936.8 ng g^{-1}. Compared with other estuaries in the world, the PAH levels in the Yangtze estuary are low to moderate. Phenanthrene, acenaphthylene, fluoranthene, and pyrene were relatively abundant. The ∑PAH levels and composition varied obviously in different estuarine zones due to different sources. The highest ∑PAHs concentration was observed in the nearshore of Chongming Island. The PAH composition showed that four to six ring PAHs were mainly found in the nearshore areas, while two to three ring PAHs were in the farther shore zones. The PAHs in the Yangtze estuary were derived primarily from combustion sources. A mixture of petroleum combustion and biomass combustion mainly from coal combustion and vehicle emission was the main source of PAHs from the nearshore areas, while the spill, volatilization, or combustion of petroleum from shipping process and shoreside discharge were important for PAHs in the farther shore areas. The result of potential ecotoxicological risk assessment based on sediment quality guidelines indicated low PAH ecological risk in the Yangtze estuary. The study could provide foundation for the protection of water quality of the Yangtze estuary by inducing main sources input.

Keywords Yangtze estuary · Sediments · Polycyclic aromatic hydrocarbons · Isomeric ratios · Multivariate statistics · Ecotoxicological risk assessment

Introduction

The Yangtze estuary, situated in east China, is one of the world's largest estuaries (Hui et al. 2009) and is also an important commercial and industrial center in China. In the past two decades, the economy and the population density of the region developed quickly. Many enterprises, such as smelting plants, paper mills, and wiring disassembly factories, were built in many ambient towns and villages. Energy used in many of these plants is generated from coal leading to substantial environmental degradation if the gases and wastes are discharged without appropriate treatment. With the development of economy, crop straw has been replaced as a domestic fuel by fossil fuels in some regions, and most crop residues are burned in the open air after the crops are harvested. What's more, the number of cars has doubled during the past two decades, and many gas stations are located in this region. These would increase atmospheric depositional fluxes of pollutants such as polycyclic aromatic hydrocarbons (PAHs). Besides, the population densities of Jiangsu Province and the city of Shanghai, are which located around the Yangtze estuary, are over 700 and 2,600 people km^{-2}, respectively, which are obviously higher than the

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world average. Heavy population density would also increase the amount of sewage discharge into the estuary. Therefore, fast economic development and heavy population density would make the distribution of pollutants in the Yangtze estuary differ from that in the past decades.

PAHs, a typical class of persistent organic pollutants, are prevalent in the environment. Due to their characteristics, like toxicity, persistence, carcinogenicity, and mutagenicity, the distribution and sources of PAHs have been the focus of numerous investigations (Wang et al. 2011b; Rajput et al. 2011; Li et al. 2012). PAHs are mainly derived from combustion activities including the burning of fossil fuels, biomass, municipal wastes, and the other sources like diagenesis of organic matter in the sediments and crude oil leakage, and thus they are ubiquitous in the environment and recalcitrant to biodegradation (Ren et al. 2011; Martins et al. 2011). Sixteen PAHs have been recommended as the priority pollutants by the United States Environmental Protection Agency (USEPA). The PAHs are likely to accumulate in sediments for lots of years because of their hydrophobicity and persistence (Fang et al. 2009). As a result, sediments may be an important reservoir for PAHs. When the environmental conditions (such as pH and salinity) change, PAHs adsorbed on the sediments could desorb into water, which thus caused a secondary pollution and then affected population health and ecological environment (Wang et al. 2010).

There are several reports on the PAH levels in the Yangtze estuary, including PAHs in surface sediments and intertidal flat core, reflecting the influence of upstream runoff (Yang et al. 2006; Guo et al. 2007) and the nearby regions. In their studies, they paid more attention on the river channel or the coastal area in the East China Sea. In recent years, due to fast industrialization and urbanization of the ambient regions, a tremendous amount of anthropogenic PAHs was carried into the estuary and then adsorbed on the sediments in the nearshore (Chen et al. 2000). What's more, flow rate 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. All of these would make the influence of the side discharges on PAH distribution in the Yangtze estuary become more prominent, which might lead to differences in distributions, compositions, sources, and potential risks of PAHs in the surface sediments between the nearshore and the farther shore zones of the Yangtze estuary. Therefore, it is necessary to comparatively study PAH distribution and sources between nearshore and father shore areas in the Yangtze estuary.

In this paper, the Yangtze estuary was chosen as study area because of its very fast economic development, heavy population density, and construction of great dam on the upstream Yangtze River, making this region a representative area affected by anthropogenic activity in Asia and even in the world. What's more, more than 100 million people live around there, and some sections of the river are used as drinking water sources. Once PAH accumulation occurred, human health would be threatened and biota species would change. Thus, it is essential that comparative studies of contents, sources, and potential ecotoxicological risks of PAHs in the surface sediments from the nearshore areas and the farther shore areas of the Yangtze estuary be systematically conducted. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used as statistical ways. The results obtained here could provide foundation for future remediation as well as protection of water quality of the Yangtze estuary.

Materials and methods

Study area and sampling

The Yangtze River, historically the world's fifth largest river in water discharge and the fourth largest one in sediment discharge (Yang et al. 2009), carries about $9{,}200\times10^6$ t of water and 480×10^6 t of sediments into the transitional area between the East China Sea and the Yellow Sea. The continental shelf of the Yellow Sea and East China Sea is one of the largest and most productive shelves in the world. In the Yangtze estuary, the Yangtze River is divided into two large river systems (southern branch and northern branch) by Chongming Island (Yang et al. 2006; Guo et al. 2007). The southern branch, which receives most incoming water and sediments of the Yangtze River, had developed into a regular bifurcated delta. The main stream of the southern branch is divided into the south channel and north channel by Changxing Island (Guo et al. 2007). There are more than 30 branches in the Yangtze estuary, such as Baimao River, Yanglintang River, Liuhe River, Gujing River, Huangpu River, Xinjianghai River, and so on. The longest branch is Huangpu River. The annual average flux of the estuary is 10 billion m^3. The sedimentation rate of the Yangtze estuary is 6.3–6.6 cm yr^{-1}.

The climate in the Yangtze estuary is subtropical monsoon with four distinct seasons. Annual average temperatures range from 16 to 18 °C, and annual average rainfall ranges from 800 to 1,600 mm. What's more, the environment of the Yangtze estuary is dynamic and complex. The effects of tides, waves, coastal current, monsoon, and topographical evolution would influence the transport and transformation of PAHs jointly (Li et al. 2012).

The sample sites are illustrated in Fig. 1a. The study area is 4,600 km^2. According to the spatial distribution, 33 samples from the nearshore areas (southern branch (NSB, N1–N17), northern branch (NNB, N18–N23), and Chongming Island (NCM, N24–N33)) of the Yangtze estuary, 18 samples from the farther shore areas (the river channel (RC, R1–

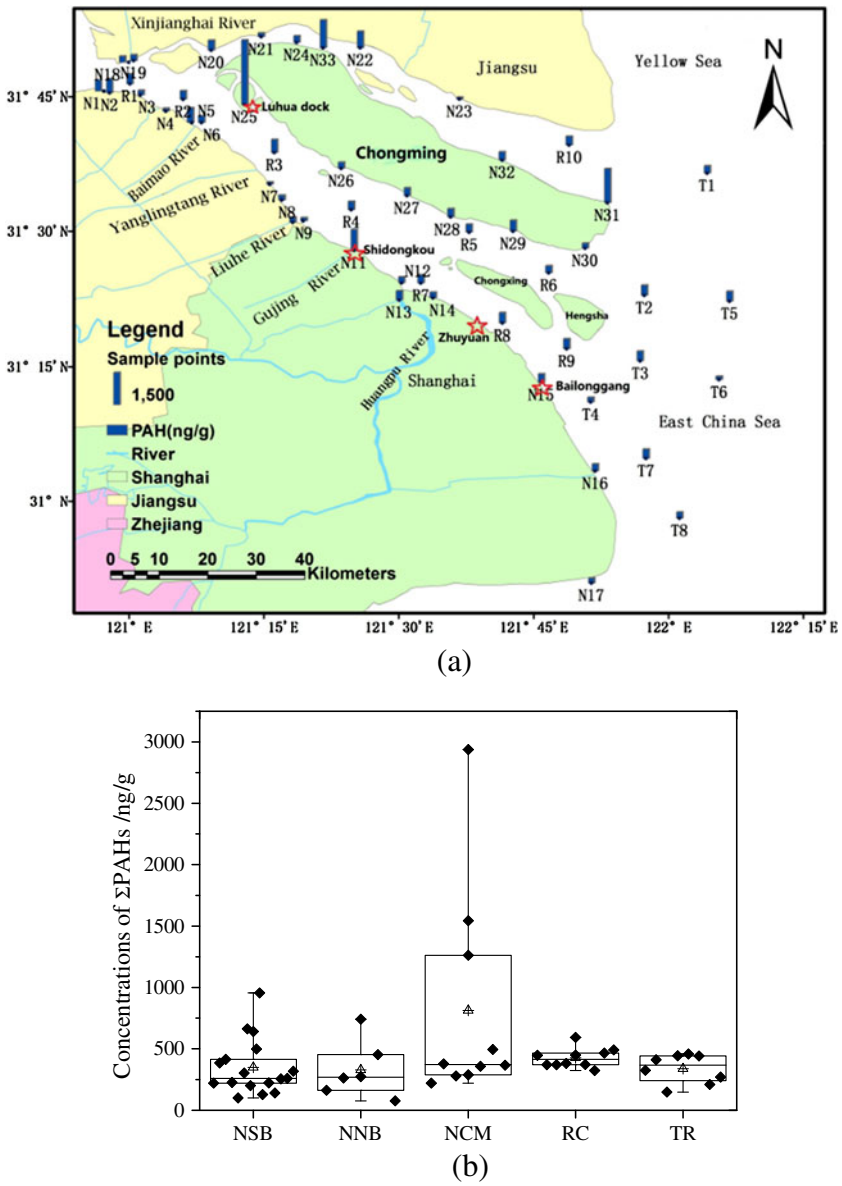

Fig. 1 **a** The ΣPAHs concentrations in the sediment samples from the nearshore areas of southern branch (NSB, N1–N17), the nearshore areas of northern branch (NNB, N18–N23), the nearshore areas of Chongming Island (NCM, N24–N33), the river channel (RC, R1–R10), and the transition regions (TR, T1–T8) of the Yangtze estuary. **b** The comparison of concentration range, median, and mean of ∑PAHs in the surface sediments from the five zones of the Yangtze estuary

R10) and the transition regions zone between river channel and coastal areas (TR, T1–T8)) were collected in May and August 2010. The surface sediments were sampled to a depth of 0–2 cm using a Van Veen stainless steel grab sampler (Eijkelamp, Netherlands).

Chemicals

Standard PAHs (the reference number of 16 USEPA priority compounds is Z-013-17; each is diluted to 200 ng μL^{-1} with methanol and dichloromethane (v:v = 1:1)) were obtained from AccuStandard Reference Materials (New Haven, USA). All solvents in this study were of high-performance liquid chromatography (HPLC) grade and obtained from J. T. Baker (USA). Silica gel and anhydrous sodium sulfate (analytical grade) were baked at 450 °C for 4 h prior to use.

Analytical methods

Five grams of freeze-dried sample was extracted with 1:1 mixture of n-hexane and acetone (66 mL) by an accelerated solvent extractor (Dionex ASE 300). The process was carried out in 2 cycles with 5-min heating followed by 5-min static extraction. Then, the extract was purged using N_2 and reduced to 1–2 mL by a rotary evaporator (Li et al. 2012). The concentrated extract was passed through a 2:1 silica/Na_2SO_4 polytetrafluoroethylene column (1 cm i.d.) with 8-mL hexane and then eluted with 10 mL dichloromethane/n-hexane (v:v = 1:1). Finally, the elution containing the PAHs was concentrated to 1 mL, exchanged the solvent with methanol, and was then concentrated to 1.0 mL for HPLC analysis (Niu et al. 2003).

PAHs were analyzed by a Dionex U-3000 HPLC system (Dionex, USA). Separation was carried out on an Ultimate

PAH column (4.6×250 mm, particle size 5 μm, Varian, USA) at a constant solvent flow rate of 1.0 mL min^{-1} using a gradient elution program which was employed starting with 75 % methanol followed by a 17.2-min linear gradient to 100 % methanol for 25 in. A linear gradient (1 min) back to starting conditions was followed by a 3-min prerun to achieve equilibration for each subsequent run. Acenaphthylene was quantified by a UV detector at 229 nm, and the other 15 PAHs were identified by a fluorescence detector.

Quality assurance and quality control

Quantifications of PAHs were done using external standards, with correlation coefficients for calibration curves all higher than 0.999. Before onset of the extraction and analysis program, recovery experiments were done by spiking the 16 PAHs standard solution with sediment samples. The six parallel experiments indicated that recoveries for the 16 PAHs were 60 %–120 % for sediments (except NAP, 30± 5 %), respectively. Each batch of 12 sediment samples, containing a method blank (solvent), a spiked blank (standards spiked into solvent), and a sample duplicate, was processed. The respective relative standard deviations (RSDs) ranged from 3.13 % to 16.06 % for all samples. Distribution characteristics of PAH detection limits for the 16 PAHs ranged from 0.34 to 4.05 ng g^{-1} for sediments. Method blanks operation showed no detectable amounts of PAH contamination.

Data analyses

PCA was performed using SPSS 13.0 for Windows. A multiple linear regression analysis (MLRA) was calculated by using total concentrations of PAHs and PCA factor scores as dependent and independent variables, respectively. Natural groupings of 16 kinds of individual PAHs were emphasized by HCA using SPSS 13.0. The data were normalized.

Results and discussion

Spatial distribution of PAHs

The concentrations of PAHs

The 16 target PAHs were detected in all sediments from the Yangtze estuary. The total amount of PAHs (∑PAHs) varied from 76.9 to 2,936.8 ng g^{-1} dry weight, with a mean concentration of 449.8±442.6 ng g^{-1}. Phe, Acy, Fla, and Pyr were relatively abundant, representing 19.8 %, 11.8 %, 10.9 %, and 9.9 % of ∑PAHs, respectively. Table 1 showed a comparison of PAHs in the Yangtze estuary with other estuaries in the world. Compared with sediments from James Ross Island, Antarctica, the degree of sediment contamination by PAHs from the Yangtze estuary obviously increased. However, PAH concentrations in the Yangtze estuary are less than those in some areas of highly urbanized estuaries, such as Santos Estuary, Boston Harbor, San Francisco Bay, and so on. Therefore, the PAH levels in the sediments from the Yangtze estuary are low to moderate.

Figure 1b showed the concentration range, median, and mean of ∑PAHs in the surface sediments from the five zones of the Yangtze estuary. The mean concentrations of ∑PAHs were 812.9±872.5, 419.7±76.2, 349.1±226.6, 338.5±118.7, and 328.8±238.1 ng g^{-1} dry weight for NCM, RC, NSB, TR, and NNB zones, respectively. The order was NCM > RC > NSB > TR > NNB. The mean concentration of PAHs in the nearshore areas (485.96± 544.6 ng g^{-1}) was higher than that in the farther shore areas (382.14±102.4 ng g^{-1}), which might be due to the discharge of industrial and domestic wastewater from the nearshore areas.

As expected, the mean concentration of ∑PAHs in the sediments from NCM zone was far higher than that from the other four zones. Chongming Island is the third largest island in China and the largest alluvial island in the world (Li et al. 2009). The town industry, agriculture, tourism, and shipping are developing rapidly on that island, which may cause an amount of PAHs discharged into the estuary from industrial wastewater and shipping (Meng et al. 2011). Additionally, an amount of PAHs which was carried by sediments from upstream accumulated around Chongming Island. Besides, because of south wind in summer, PAHs carried by suspended particles in air from Shanghai City would move to Chongming Island (Feng et al. 2006). Therefore, atmospheric deposition may be another reason for the high level of PAHs there. The concentrations of ∑PAHs in the sediments from the north side (N24, N31–N33) of Chongming Island were higher than that from the south side (except site N25), which may be because the Yangtze River and tidal current that spilled over from the north branch mixed at the north side and more complex hydrological and hydraulic conditions, such as low flow rate, high salinity, and more sand precipitation (Li et al. 2012), might lead to higher PAH levels there.

At the NCM zone, higher concentrations of ∑PAHs were observed at sites N25 (2,936.8 ng g^{-1}), N31 (1,543.0 ng g^{-1}), and N33 (1,261.7 ng g^{-1}). The site N25 is near the Luhua dock. According to the isomeric ratio of PAHs (Martins et al. 2011), the ratios of anthracene/anthracene + phenanthrene (An/178), fluoranthene/fluoranthene + pyrene (Fl/Fl + Py) and indene[1,2,3-c,d]pyrene/indene [1,2,3-c,d]pyrene + benzo[g,h,i]perylene (IP/IP + Bghi) were 0.16, 0.54, and 0.37, respectively, which indicated that the sources of PAHs in site N25 were a mixture of petroleum combustion and sewage, and biomass and coal combustion.

Table 1 Comparison of PAHs in surface sediments from the Yangtze estuary with worldwide areas

Location	Range (ng g^{-1})	Mean (ng g^{-1})	Reference
James Ross Island, Antarctica	1–205		Klánováa et al. (2008)
The Gulf of Mexico, North America	52–403	305	Wang et al. (2011a)
Mersey Estuary, U.K	626–3,766		Vane et al. (2007)
Santos Estuary, São Paulo, Brazil	4,000–7,550		Martins et al. (2011)
Boston Harbor, USA	7,300–358,000		Wang et al. (2001)
San Francisco Bay, USA	2,653–27,680	7,457	Pereira et al. (1996)
Mediterranean coast of Egypt	13.5–22,600		Barakat et al. (2011)
Manukau Harbour, New Zealand	16–5,300	820	Holland et al. (1993)
Chao Phraya River Estuary, Thailand	6–8,399	2,290	Ruchaya et al. (2006)
Masan Bay, Korea	41.5–1,100	353	Khim et al. (1999)
Pearl River Delta, China	156–10,811	2,057	Mai et al. (2002)
Yellow River Estuary, China	10.8–252	91.2	Hui et al. (2009)
Liaodong Bay, China	144.5–291.7	184.7	Hu et al. (2011)
Yangtze estuary, China	76.9–2,936.8	449.8	This study

This result may be due to the burning and leakage of fossil fuel, and the discharge of sewage during shipping process. The site N31 (Dongwangsha sluice) is near the TR zone. Site N33 is located at the entrance of northern branch where the Yangtze River and saltwater that spilled over from the north branch joined in summer. Special hydrology conditions, such as low flow rate and high salinity, were observed in N31 and N33 sites. So, depositing and salting-out effects lead to higher PAH levels (Li et al. 2012).

The mean concentration of ∑PAHs in the sediments from RC zone was higher than that from the other areas except NCM. It was found that higher PAH levels in many sites in the RC zone were more related with the input from the ambient nearshore zone (such as site R3). However, there was no increasing trend of PAH values with descending distance from the estuary to the adjacent sea. So, the influence of shoreside discharge on PAH distribution in the RC zone is more important than that of the runoff from the upper and middle reaches. Additionally, the shipping industry is another reason for PAH accumulation in the river. The ∑PAH levels in the south channel of Changxing Island (R7, R8, and R9) were higher than that in the north channel (R5 and R6) because the south channel is the main seaward channel and near two large wastewater outlets (Zhuyuan and Bailong-gang) of Shanghai City.

The mean concentration of ∑PAHs in the surface sediments from NSB was higher than that from NNB and TR zones (Fig. 2). This result might be related to the inflow of multiple tributaries such as Gujing River, Liuhe River, and Huangpu River. These tributaries flow through Shanghai City and thus, carry a large number of pollutants into the southern branch. Additionally, the industry at the nearshore areas of the southern branch, such as petrochemistry and wharfs, is more prosperous (Chen et al. 2000). So, the discharge of industrial sewage was another reason. The highest level of ∑PAHs in NSB occurred at site N11 (Shidongkou) where industry developed quickly. Shidongkou is also one of three biggest sewage discharge outlets in Shanghai. So, the discharge of industrial wastewater and domestic sewage caused the PAH accumulation there. Comparably, the lowest level of ∑PAHs in the NNB zone may be attributed to fewer tributary input and undeveloped industry.

As known, the environment of transition zone is very complex. Special hydrological and chemical conditions are observed. For example, when freshwater flows into the sea, salinity in water changes. Tidal current variation results in the redistribution of finer sediment. Several dominant coastal currents are in the Yangtze estuary: Taiwan warm current, Subei coastal current, and Fujian–Zhejiang coastal current. In summer, the impacts of Taiwan warm current and Fujian–Zhejiang coastal current are stronger than Subei coastal current (Yuan et al. 2008), which result in more PAHs that

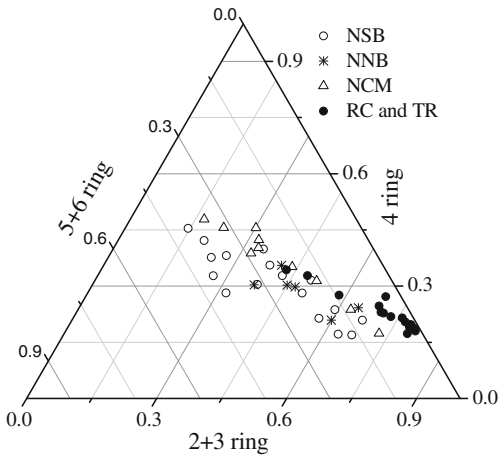

Fig. 2 Ternary plot showing PAH compositions in the sediments from the nearshore areas (*NSB*, *NNB*, and *NCM*) and the farther shore areas (*RC* and *TR*) of the Yangtze estuary

moved to the north and settled there. So, the mean of PAH concentration in the north area (T1, T2, T3, T5, and T6) (363.2±148.8 ng g^{-1}) was higher than that in the south area (T4, T7, and T8) (297.3±71.0 ng g^{-1}). As a result, the accumulation of ∑PAHs in the TR zone might be due to the combined effect of ocean dilute, and tidal and coastal currents. In addition, at the transition regions, the mean concentration of ∑PAHs at the mouth of the Yangtze estuary (T5, T6, T7, and T8) was higher than that at the sites (T1, T2, T3, and T4) farther away from the Yangtze estuary. At the mouth of the Yangtze estuary, Yangtze runoff floats on sea water because of lower density, which formed pinnate circulation and pinnate crest (Bouloubassi et al. 2001). The pinnate crest areas with an intensely dynamic process, as a dynamic barrier, could obstruct the conveyance of momentum, sediment, and environment pollutant to the open sea. Therefore, the concentrations of ∑PAHs were higher at the mouth of the Yangtze estuary.

The compositions of PAHs

The compositions of PAHs in the sediments from the Yangtze estuary were shown in Fig. 2. The two-to-three-ring, four-ring, and five-to-six-ring PAHs, representing low, medium, and high molecular weight PAHs (LM-, MM-, and HM-PAHs) (Amoako et al. 2011), accounted for 14–81 %, 16–45 %, and 1–40 % of ∑PAHs, respectively. The mean values of the two-to-three-ring PAHs (LM-PAHs) and four-to-six-ring PAHs (MM- and HM-PAHs) were 52±20 % and 48±20 % (the data were analyzed statistically with a *t* test by SPSS 13.0). Both of $t_{\text{nearshore}}$ (=0.099) and $t_{\text{farther shore}}$ (=0.060) were lower than $t(50, 0.05)$, which indicated that the data were reliable. What's more, in 74 % samples of the Yangtze estuary, the concentration of two-to-three-ring PAHs was higher than that of four-ring PAHs or five-to-six-ring PAHs. This result indicated that the dominant components of PAHs in the Yangtze estuary were two-to-three-ring PAHs (LM-PAHs).

In the sediments from the three zones of the nearshore areas (NSB, NNB, and NCM), the levels of two-to-three-ring (LM-PAHs) and four-to-six-ring (MM-, HM-PAHs) were 40–49 % and 51–64 % of ∑PAHs, respectively. The concentration ratios of two-to-three-ring and four-to-six-ring in 70 % samples were lower than 1. The result suggested that the sediment samples from the nearshore zones were characterized by four-to-six-ring PAHs. Differently, at the farther shore zones (RC and TR), a higher ratio of two-to-three-ring PAHs in ∑PAHs (around 71 %) were observed. The levels of two-to-three-ring PAHs were higher than those of four-to-six-ring PAHs in 88 % samples from the farther shore zones. It showed that the sediment samples from the farther shore zones were characterized by lighter molecular weight PAHs. As known, LM-PAHs (two-to-three-ring PAHs) may be derived from a petrogenic source as fossil fuel combustion, but also major constituents of petroleum, whereas MM- and HM-PAHs are generated mainly by pyrogenic sources (high-temperature combustion) (Fernandes et al. 1997). Therefore, pyrogenic sources might be the common sources of PAHs in nearshore areas, while petrogenic sources were dominant in the farther shore areas.

In recent years, due to the rapid increase of industrialization and vehicles in the ambient regions of the Yangtze estuary, more PAHs from combustion and exhaust emission were discharged into the nearshore areas of the Yangtze estuary. What's more, it was well known that PAHs were inclined to adsorb on the sediments with ring number increase. So, four-to-six-ring PAHs (MM-PAHs and HM-PAHs) were the dominant components in the sediments from the nearshore areas. Comparably, developed shipping process may be an important reason for low LM-PAHs accumulation in the farther shore zones. Besides, more two-to-three-ring PAHs in the nearshore zones may be diffused or absorbed on suspended particles and then deposited in the farther shore areas. Four-to-six-ring PAHs adsorbed on the suspended sediments in the nearshore areas may be biodegraded by microorganisms to two-to-three-ring PAHs which would also move to the farther shore areas.

The sources of PAHs

The isomeric ratios of PAHs

Diagnostic ratios of PAHs, such as anthracene/anthracene + phenanthrene (An/178); fluoranthene/fluoranthene + pyrene (Fl/Fl + Py) and indene[1,2,3-c,d]pyrene/indene[1,2,3-c,d] pyrene + benzo[g,h,i]perylene (IP/IP + Bghi), can identify the possible sources of PAHs (Yunker and Macdonald 2003). In general, a ratio of An/178 >0.1 suggests a dominance of combustion, while a ratio <0.1 indicates petroleum origin (Yunker and Macdonald 2003). A ratio of Fl/(Fl + Py) < 0.4 is consistent with a petroleum source; a value between 0.4 and 0.5 indicates petroleum combustion; and a ratio >0.5 implies sewage, biomass, and coal combustion. For IP/(IP + Bghi), low ratios (<0.20) is consistent with petroleum source, intermediate ratios (0.20–0.50) implies petroleum combustion, whereas ratios >0.50 indicates combustion of coal and biomass (grass and wood) (Martins et al. 2011).

To determine the sources of PAHs in sediments from the Yangtze estuary, Fl/(Fl + Py) against An/178 and IP/IP + Bghi were plotted (Fig. 3). At the Yangtze estuary, the source of PAHs in 90 % sediment samples was combustion, and in 10 % sediment samples was petroleum (Fig. 3). The result suggested that combustion might be the dominant source in the Yangtze estuary. The source of PAHs in 59 % sediment samples was a mixture of petroleum combustion and biomass combustion, and the source of PAHs in 20 % sediment samples was petroleum combustion.

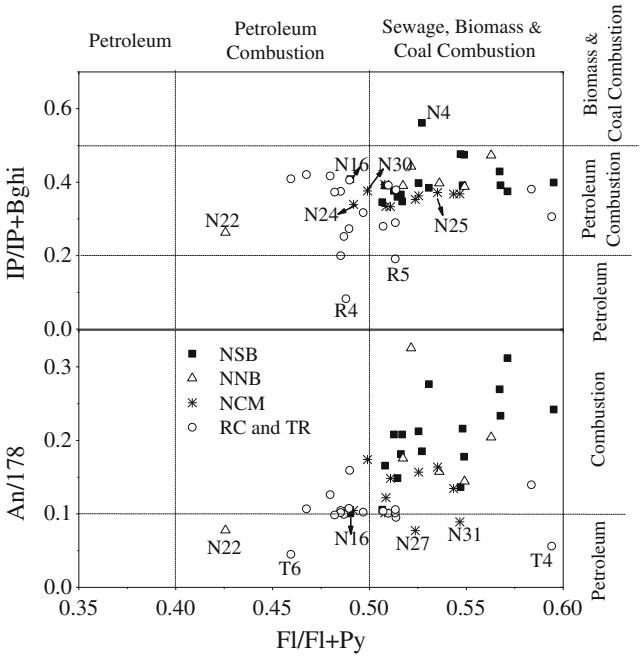

Fig. 3 Isomeric ratios of Fl/Fl + Py vs. An/178 and Fl/Fl + Py vs. IP/IP + Bghi in the sediments from the nearshore areas (*NSB*, *NNB*, and *NCM*) and farther shore areas (*RC* and *TR*) of the Yangtze estuary

At the nearshore areas, the main sources of PAHs in 79 % sediments were a mixture of petroleum combustion and sewage, biomass, and coal combustion (Table 2). For the other 21 % samples, the origin of PAHs was scattering. Overall, petroleum combustion and sewage, biomass, and coal combustion were the main sources of PAHs in the nearshore areas. The result was consistent with that in "The compositions of PAHs".

The source of PAHs in the sediments from the farther shore areas (RC and TR) was scattering. According to Fig. 3 and Table 2, five kinds were defined: petroleum combustion; a mixture of petroleum and petroleum combustion; a mixture of petroleum combustion and sewage, biomass, and coal combustion; a mixture of petroleum and sewage, biomass, and coal combustion; and a mixture of petroleum, petroleum combustion and sewage, biomass, and coal combustion. The results suggested that the sources of PAHs in the farther shore areas were complicated and multiplex, which might be due to the river channel receiving the pollutants from the nearshore areas and the runoff from upstream, atmospheric deposition, and shipping process (Li et al. 2012). More analyses about the dominant sources of PAHs in the farther shore areas will be discussed in "Principal component analysis (PCA)".

Principal component analysis (PCA)

The data of 16 PAHs from the nearshore areas (NSB, NNB, and NCM) and the farther shore areas (RC and TR) of the Yangtze estuary were analyzed using PCA. The three factors accounted for 95.79 % and 91.11 % of the total variance, respectively. Due to the weak correlation of PC3 (7.10 % and 8.36 % of the total variance, respectively), PC3 was not discussed in this study. For the nearshore areas (Fig. 4a), PC1 was heavily weighted by three-ring PAHs-Ace, Flu, Phe, and Ant; four-ring PAHs-Fla, Pyr, BaA, and Chr; and five-to-six-ring PAHs-BbF, BkF, BaP, DahA, BghiP, and IndP which were consistent with the emission characteristics of PAHs from mixture sources such as petroleum combustion and biomass combustion. According to literatures (Li et al. 2007; Zhang et al. 2009; Wang et al. 2010), Ace, Fla, Chr, and Pyr were related with the emission characteristics of PAHs from coal combustion. BbF, BkF, BaP, BghiP, and IndP have been suggested to indicate vehicle emission. Thus, coal combustion and vehicle emission make a greater contribution to PC1. PC2 had a significant positive loading of Acy which could be attributed to petrogenic sources (Soclo et al. 2000).

Table 2 The PAH source analysis by isomeric ratios of An/178, Fl/Fl + Py, and IP/IP + Bghi in the sediments from the nearshore areas (NSB, NNB, and NCM) and farther shore areas (RC and TR) of the Yangtze estuary

	Station numbers/the ratio of station numbers and total station numbers			
Source		A	B	C
A	Nearshore	0/0		
	Farther shore	0/0		
B	Nearshore	2/6 % (N16, N22)	2/6 % (N24, N30)	
	Farther shore	4/22 % (R4, R7, T5, T6)	7/39 % (R6, R8, R9, T3, T7, T8, T1)	
C	Nearshore	0/0	26/79 %	1/3 % (N4)
	Farther shore	1/6 % (R5)	4/22 % (R1, R2, R10, T2)	0/0
Mix of A, B, and C	Nearshore	2/6 % (N27, N31)		
	Farther shore	2/11 % (R3, T4)		

A petroleum, *B* petroleum combustion, *C* sewage, biomass and coal combustion

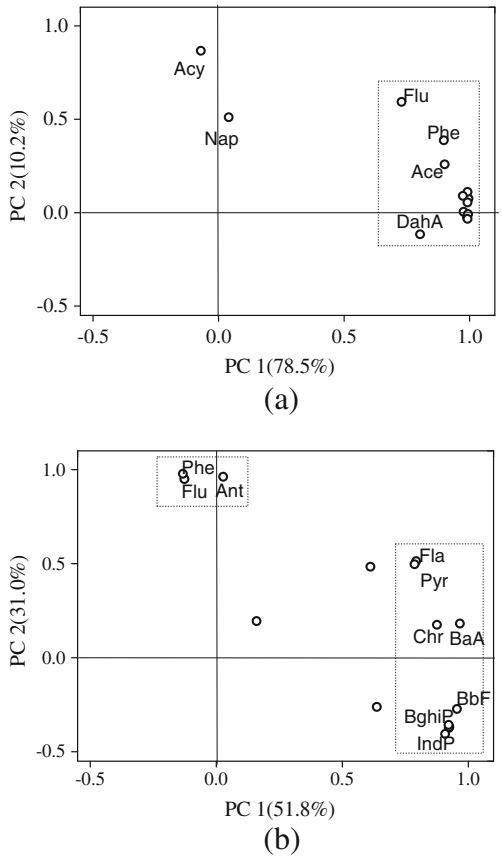

Fig. 4 Rotated principal components of 16 PAHs from the nearshore areas (**a**) and the farther shore areas (**b**) of the Yangtze estuary

For the farther shore areas (Fig. 4b), PC1 was heavily weighted by Fla, Pyr, BaA, Chr, BbF, BkF, BaP, BghiP, and IndP, which indicated PC1 was related to the combustion sources (Qin et al. 2011). PC2 had a heavily loading of three-ring PAHs (Flu, Phe, and Ant). This factor is suggested to be indicative of spill, volatilization, or combustion of petroleum (Soclo et al. 2000).

Percentage contributions of different PAH sources were quantified by MLRA method. By performing a stepwise procedure, PC1-3 for the (a) nearshore and (b) farther shore areas were regressed against the normal standard deviation of ∑PAH. The contribution of each PAH source was estimated by Eqs. 1 and 2, respectively:

$$\sum \mathrm{PAH}_{(a)} = 0.972\mathrm{PC1} + 0.205\mathrm{PC2} + 0.091\mathrm{PC3}; R^2 = 0.995, p < 0.001 \quad (1)$$

$$\sum \mathrm{PAH}_{(b)} = 0.486\mathrm{PC1} + 0.836\mathrm{PC2} + 0.148\mathrm{PC3}; R^2 = 0.948, p < 0.001. \quad (2)$$

The calculation revealed that 76.65 % of mixture sources of petroleum combustion and biomass combustion mainly included coal combustion and vehicle emission, and 16.17 % of petrogenic sources contributed to the PAH source in the nearshore areas. For the farther shore areas, 33.06 % for combustion source and 56.87 % for spill, volatilization, or combustion of petroleum composed the PAH source apportion. Therefore, petroleum combustion and biomass combustion mainly from coal combustion and vehicle emission made much contribution to the PAHs in the nearshore area sediments because industrialization and the number of cars increased quickly around the estuary. The spill, volatilization, or combustion of petroleum was the main input of PAHs in the farther shore area sediments. This result may be due to the very developed shipping process in the Yangtze estuary. In addition, because the result of PAH distribution demonstrated that the nearshore discharge makes much contribution to PAH accumulation in the farther shore areas, PAHs from the nearshore areas may diffuse or absorb on suspended particles and then deposit in the farther shore areas.

Hierarchical cluster analysis (HCA)

In this study, HCA was used to identify the homogeneous groups of individual PAHs in the sediments from Group A (the nearshore areas) and Group B (the farther shore areas) of the Yangtze estuary. For Group A, the result of HCA presented in the hierarchical dendogram (Fig. 4) distinguished the 16 individual PAHs into two major groups. The first group included the high-molecular-weight PAHs with four to six rings (Fla, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, BghiP, and IndP) and some three-ring PAHs as Ace, Flu, Phe, and Ant. The first group, which consisted of the result of PCA of the nearshore areas (PC1), mainly derived from coal combustion and vehicle emission. The second group was composed of Nap and Acy (PC2) which might be due to petrogenic sources. For Group B, the result (Fig. 5b) distinguished the 16 individual PAHs into two major groups. The first group was composed of Ace, Flu, Phe, and Ant which also was consistent with the result of PCA of the farther shore areas (PC2). The low-molecular-weight PAHs with three rings were mainly from spill, volatilization, or combustion of petroleum. The second group could be divided into two subgroups. The first subgroup consists of Acy, BaP, BbF, BkF, InP, DahA, and BghiP, most of which constitute the high-molecular-weight PAHs with five to six rings. The second subgroup contains Nap, Fla, Pyr, BaA, and Chr, most of which are four-ring PAHs. The second group was consistent with PC1, which indicate that both subgroups usually were from combustion sources. From the above statistical analysis, the PAHs in the nearshore areas could be attributed to mix sources of petroleum combustion and biomass combustion mainly from coal combustion and vehicle emission. The spill, volatilization, or combustion of petroleum was the main sources of PAHs in the farther shore areas.

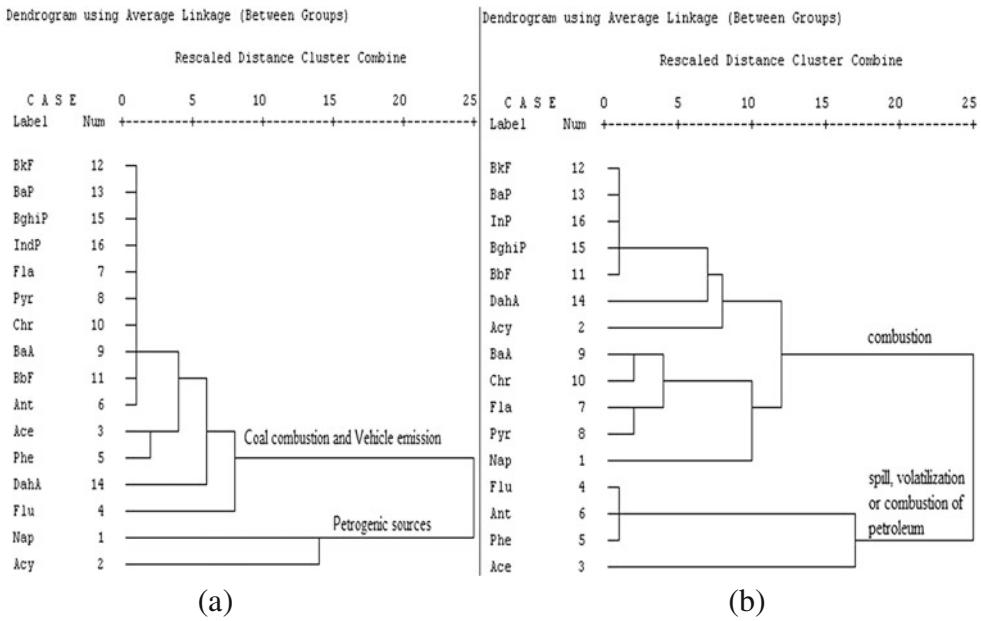

Fig. 5 Hierarchical dendogram for 16 PAHs in the nearshore areas (**a**) and the farther shore areas (**b**) of the Yangtze estuary sediments

Ecotoxicological risk assessment

The sediment quality guideline calculations are used to evaluate sediment quality in relation to possible adverse effects of PAH levels (Perra et al. 2011; Wang et al. 2009). Concentrations below the effects range low (ERL) value suggest the minimal adverse effects range. Concentrations of PAHs above the ERL, but below the effects range median (ERM), represent the possible adverse effects range. Concentrations above the ERM value represent the probable value effects range (Long et al. 1995). Additionally, once the BbF, BkF, BghiP, and InP exist, the ecotoxicological risk would occur (Chapman et al. 1999). In our study, BbF, BkF, BghiP, and InP occurred in all sediments of Yangtze estuary.

Table 3 presented the ERL and ERM values of 12 PAHs proposed by the sediment quality guideline and the number of stations over ERL in the Yangtze estuary. In our study, the ∑PAHs in all samples were below the ERL value, indicating that the ∑PAH levels in the Yangtze estuary were within minimal effects ranges. The values of 12 PAHs in all sediments were lower than ERL, except Acy, Flu, Phe, and BaA. This suggested that most PAH levels in the Yangtze estuary were in the minimal adverse effects range, and Acy, Flu, Phe, and BaA levels in some sites were within possible

Table 3 SQG values for PAHs, over ERL station numbers and the total station numbers in the sediments from the nearshore areas (NSB, NNB, and NCM) and the farther shore areas (RC and TR) of the Yangtze estuary

PAHs	SQG[a] (ng g^{-1} d.w.)		Over ERL station numbers/the total station numbers			
			Nearshore areas			Farther shore areas
Compound	ERL	ERM	NSB	NNB	NCM	RC and TR
Nap	160	2,100	0	0	0	0
Acy	44	640	9/17	5/6	6/10	4/18
Ace	16	500	0	0	0	0
Flu	19	540	2/17	2/6	6/10	15/18
Phe	240	1,500	0	0	2/10	1/18
Ant	853	1,100	0	0	0	0
Flu	600	5,100	0	0	0	0
Pyr	665	2,600	0	0	0	0
BaA	261	1,600	0	0	1/10	0
Chr	384	2,800	0	0	0	0
BaP	430	1,600	0	0	0	0
DahA	63	260	0	0	0	0
∑PAHs	4,000	44,792	0	0	0	0

[a]SQG values taken from Long et al. (1995)

adverse effects range. The potential ecological risk of Acy in the nearshore areas was higher than that in the farther shore areas, while Flu in the farther shore areas was higher than that in the nearshore areas.

Conclusions

PAHs in surface sediments from the nearshore areas and the farther shore areas of the Yangtze estuary were investigated in this study. Even though anthropogenic sources of PAHs in sediments from the Yangtze estuary are obvious, PAH levels in the Yangtze estuary are low to moderate in comparison with other estuaries in the world. Four-to-six-ring PAHs were mainly found in the nearshore areas. However, samples from the farther shore zones were characterized by lighter molecular weight PAHs. Most PAHs in the Yangtze estuary derived primarily from combustion. Coal combustion and vehicle emission made much contribution to the PAHs in the nearshore area sediments, while the spill, volatilization, or combustion of petroleum was the main input of PAHs in the farther shore areas sediments. Additionally, tributary discharge, air deposition, water currents, and special environmental conditions of the estuary result in different PAH distribution. The study provided important data on the pollution status and distribution characteristics of PAHs in the sediments of the Yangtze estuary. Although the potential ecotoxicological risk assessment of PAHs suggested that the ∑PAH levels in the Yangtze estuary were within minimal effects ranges, caution should be taken in some zones (the nearshore of Chongming and South branch) where there are industrial enterprises and wastewater outlets around.

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