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ORIGINAL ARTICLE

Characterization and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in sediments in the Yellow River Estuary, China

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Abstract Concentrations and sources of polycyclic aromatic hydrocarbons (PAHs) were investigated in surface sediments of the Yellow River Estuary (YRE). The isobath-parallel tidal and residual currents play important roles in the variation of PAH distribution, such that the contamination level of PAHs in fine-grained sediments is significantly higher than in the relatively coarse grain size sediments. Both diagnostic ratios and principal component analysis (PCA) with multivariate linear regression (MLR) were used to apportion sources of PAHs. The results revealed that pyrogenic sources are important sources of PAHs. Further analysis indicated that the contributions of coal combustion, traffic-related pollution and mixed sources (spills of oil products and vegetation combustion) were 35, 29 and 36 %, respectively, using PCA/MLR. Pyrogenic sources (coal combustion and traffic-related pollution) contribute 64 % of anthropogenic PAHs in sediments, which indicates that energy consumption could be a predominant factor in PAH pollution of YRE. Acenaphthylene and acenaphthene are the two main species of PAHs with more ecotoxicological concern in YRE.

Keywords PAHs · Surface sediment · Risk assessment · Source apportionment · PAH isomer ratio · PCA/MLR

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of environmental significance owing to their widespread distribution in water (Li et al. 2006; Wang et al. 2009), sediment/soil (Hu et al. 2010a, b; Liang et al. 2011; Ruiz-Fernández et al. 2012), and air (Guo et al. 2003; Gong et al. 2011), and potential toxicity to living organisms. Because of their low solubility and hydrophobic nature, PAHs tend to associate with particulates and they are widely transported through atmospheric routes (Ohkouchi et al. 1999). The deposition of suspended particles carried by rivers can also contribute to the local accumulation of PAHs. Once deposited in sediments, these compounds are less susceptible to photochemical and biological oxidation, and thus tend to persist for longer periods and accumulate in high concentrations (Guzzella and De Paolis 1994).

Estuaries are biologically productive and receive considerable pollutant inputs from land-based sources via river runoff and sewage outfalls (Wang et al. 2007b; Ni et al. 2008; Guan et al. 2009), which are then transported to the sea. As a result, sediments in estuaries are one of the most important records to demonstrate the degree of interaction between land and sea, as well as industrial pollution. Furthermore, PAHs in coastal sediments can serve as effective tracers of materials transport from land-to-sea (Fang et al. 2009). Hence, investigations of PAHs in estuary sediments

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can provide useful information for further understanding of environmental processes and material transport. The Yellow River Estuary (YRE), as a major region for fisheries in China and one of the most plentiful and biodiverse zones in the world, is situated at the south of the Bohai Sea and has a warm-temperate monsoon climate. The Yellow River, flowing across nine provinces in Northern China, has the second largest sediment load (of rivers) in the world with annual sediment loading of 0.8×10^9 t (IRTCES 2005; Wang et al. 2007a). Because the 1970s large scale economic reforms were undertaken, increasing development activities (industrial and agricultural) have resulted in a large volume of wastewater emptying into and causing pollution of the Yellow River (Li et al. 2006; Xu et al. 2007, 2009; Wang et al. 2009). Recent studies revealed that chlorinated and non-chlorinated hydrocarbons were detectable in water samples and suspended particulate matter of the YRE (Xu et al. 2007; Wang et al. 2007c) due to anthropogenic impacts. Mollusks and shellfish collected from the YRE have been found to be contaminated by PAHs and polybrominated diphenyl ethers (Liu et al. 2007; Jin et al. 2008). However, not much is known about the sources and concentrations of PAHs in the YRE sediments.

Sediment chemistry data alone do not provide an adequate basis for assessing the hazards posed by sediment-associated contaminants to aquatic organisms. Sediment quality guidelines (SQGs) provide a scientific tool for evaluating the potential effects of sediment-associated contaminants on aquatic organisms (Long and MacDonald 1998; Pekey et al. 2004; Cardellicchio et al. 2007). Generally, the primary purposes of SQGs are to protect the aquatic biota from the deleterious effects associated with sediment-bound contaminants, to rank and/or prioritize contaminated areas or chemicals of concern for further investigation (Long and MacDonald 1998), to evaluate the spatial patterns of sediment contamination and direct monitoring programs (Farkas et al. 2007). Among the various SQGs developed during the past decade, the effects range low value (ERL) and effects range median value (ERM) guidelines (Long et al. 1995) as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines (CCME 2002) were widely used to assess the potential biological risk of contaminants in sediments (Pekey et al. 2004; Cardellicchio et al. 2007; Hu et al. 2010a, b).

The objectives of this study are to determine the distribution and concentration of the 16 EPA priority PAHs in YRE sediments; to identify the possible sources of PAHs using diagnostic ratios and PCA; to carry out quantitative sources apportionment of PAH pollution based on the PCA with MLR; and to assess the potential biological risk of these compounds based on the SQGs.

Materials and methods

Sample collection, storage, and preparation

Twenty-one surface sediments were collected with a stainless steel grab sampler during a cruise onboard the R/V Kan407 of the Shanghai Bureau of the marine geology survey from 16 to 26 August, 2007. All surface samples (0–3 cm) were wrapped in aluminum foil and then immediately stored at −20 °C. The sampling stations (Fig. 1) were located in the YRE. Their water depth ranged from 3.8 to 18.4 m, with mean value 11.1 m. A differential global positioning system (DGPS) was used to record the field sampling positions. The samples were freeze-dried and ground to pass through a 40-mesh sieve, then stored at −20 °C until analyzed.

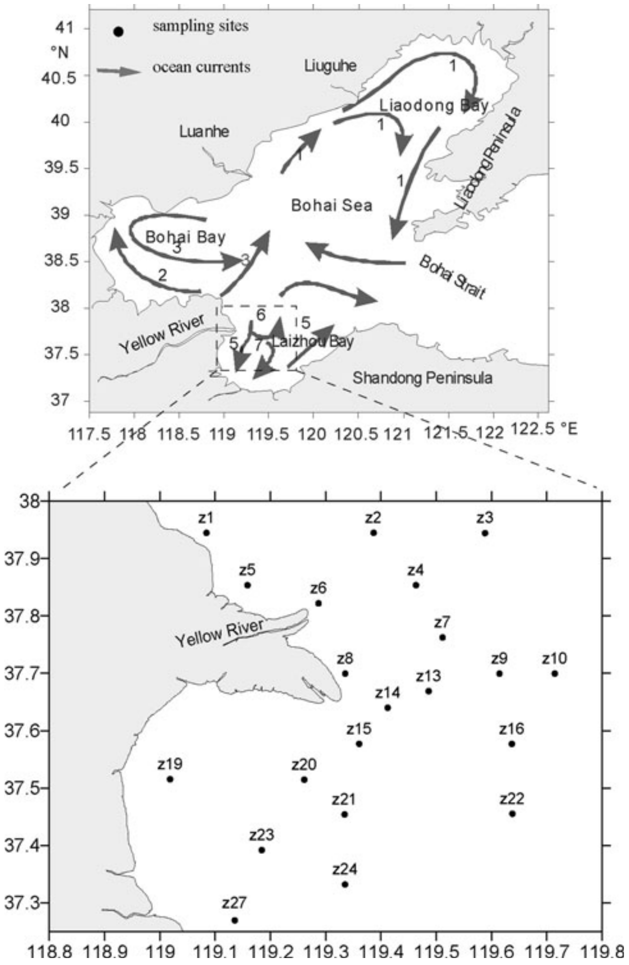

Fig. 1 The study area and locations of sampling sites in the YRE. Current circulation system (from (Huang and Su 2002; Mao et al. 2008): 1—clockwise circulation in Liaodong Bay; 2, 3—anti-clockwise and clockwise circulation in the northern and southern part of Bohai Bay; 4—anti-clockwise circulation of Laizhou Bay; 5, 6—anti-clockwise and clockwise circulations off the river mouth

Sample extraction and cleanup

Determination of PAHs in surface sediment samples was conducted following the methods described in the literature (Mai et al. 2001; Hu et al. 2010a, b). In brief, freeze-dried and meshed sediment samples (5 g) were extracted with 100 mL dichloromethane for 48 h in Soxhlet extractors, and then concentrated by a rotary evaporator. The concentrated extracts were charged to a 1:2 alumina:silica chromatographic column (8 g of 100–200 mesh fully activated silica gel, 4 g of 50–200 mesh fully activated alumina, 0.5 g of activated copper powder, topped with 1 g of anhydrous sodium sulfate) for purification and fractionation. The first fraction was eluted with 15 mL hexane and discarded. The second fraction, containing PAHs, was collected by eluting 5 mL hexane then 70 mL of dichloromethane:hexane (30:70, v:v). The PAH fraction was concentrated to 1 mL with a gentle nitrogen flow.

PAH analysis

The PAH fraction was analyzed with a Finnigan trace DSQ gas chromatograph/mass spectrometer (GC/MS). The separation was carried out on a 50 m × 0.25 mm i.d. DB-5MS (film thickness 0.25 μm) silica fused capillary column. Column temperatures were programmed at 100 °C increasing at 5 °C min^{-1} to 280 °C, and holding for 20 min at 280 °C. Helium was the carrier gas at a flow of 1 mL min^{-1}. PAHs were analyzed using selected ion monitoring (SIM). The mass spectrometer was operated in scan mode with electron impact ionization of 70 eV, electron multiplier voltage of 1,288 V, and ion source at 230 °C. The samples were analyzed in the splitless mode, and the head column pressure was 30 kPa.

Identification of PAHs was quantified based on the retention time and ion m/z ratio of an authentic PAH mixed standard (Accu Standard, USA) containing the 16 US EPA priority PAHs (Zhang et al. 2006; Hu et al. 2010a, b). The 16 PAH compounds were naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)-fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), inde(1, 2, 3)pyrene (IcdP), dibenz(a, h)anthracene (DahA) and benzo(g, h, i)perylene (BghiP). Quantification was performed by the external standard method. Regression coefficients for calibration curves were all higher than 0.993.

Quality control

All data were subjected to strict quality control procedures. Two surface sediments were selected for a recovery study. Five grams of sediment (freeze-dried) was weighed into an extraction vessel with 1.0 mL of spiking solution of the standard mixture (10 and 50 ng g^{-1} of each PAH; Accu Standard, USA, Z-013-17) and dried overnight in a dark room. PAHs in spiked sediments were extracted and analyzed as described in "Sample extraction and cleanup" and "PAH analysis". Recoveries were 86 % for NAP, 91 % for ACY, 97 % for ACE, 84 % for FLO, 92 % for PHE, 105 % for ANT, 87 % for FLA, 97 % for PYR, 91 % for BaA, 88 % for CHR, 89 % for BbF, 101 % BkF, 97 % for BaP, 94 % for IcdP, 93 %for DahA and 84 % for BghiP, respectively. All of the samples taken were analyzed in duplicate, and the relative difference for individual PAHs was <15 %. The detection limits were 0.16–1.23 ng g^{-1} for a 5 g sample. The results of blanks extracted under the same conditions were below detection limits and sample results without blank correction are presented.

Sediment physical and chemical analyses

Twenty-one samples (about 40 mg for each sample) were analyzed for TOC with an Elemental analyzer (Vario EL III) after they were freeze-dried, pulverized and treated with 1 M HCl to remove carbonate. The standard deviation of the measurement was ±0.006 % based on the replicate standard analyses. Grain sizes of sediments were determined using a laser grain size analyzer (Mastersizer 2,000) after the samples were processed with 30 % H_2O_2 and 3 M HCl to remove organic matter and biogenic carbonate, respectively. The classification of sediment type followed Shepard (1954).

Statistical analyses

Principal component analysis (PCA) and multivariate linear regression (MLR), applied to apportion PAH sources in sediments, were conducted using SPSS 11.5 for Windows (SPSS Inc., Chicago, Illinois). PCA was performed on 15 US EPA priority PAHs except BghiP which was not detectable at many sites. Before statistical analysis of the data, the non-detectable values were reassigned with concentration values one half the detection limits (Zaghden et al. 2007). Then the raw data matrix was Z-score standardized to eliminate the influence of different units and make each determined variable have an equal weighting in the PCA (Yunker et al. 1995). Principal components were rotated using the Varimax rotation method, and eigenvalue >1 were retained. MLR was performed using the PCA factor scores and normalized total PAH concentrations as independent and dependent variables, respectively (Larsen and Baker 2003). The regression was run using a stepwise method. The contribution of source *i* is the ratio of the regression coefficient for factor *i* to the sum of all the regression coefficients, according to the description in the literature (Larsen and Baker 2003; Zuo et al. 2007). The adjusted R^2 value for MLR was 0.985 and the P values for the regression coefficients were <0.05.

Results and discussion

Sediment characteristics

As shown in Table 1, the surface sediment types in the YRE varied from sand to clayey silt, with mean grain size between 3.6 and 7.7 Φ. The clayey silt sediments were mainly restricted to the northern and southern regions of the YRE, which form two mud patches on two sides of the YRE. The sandy silt sediments were mainly concentrated in the central region.

TOC contents in the surface sediments were in the range of 0.10–0.67 %, with mean value 0.34 %. In general, sandy sediments have higher permeability and porosity than fine sediments (Suguio 1973), which allows greater water circulation among sediment particles and therefore less accumulation of organic matter. However, fine sediment particles have larger relative surface areas than coarse particles and can adsorb colloidal and dissolved organic matter (Sharp 1973). In this study, the distribution of TOC followed the distribution of fine sediment fractions, and the TOC content had positive and significant correlations with silt and clay contents ($r = 0.57$ and 0.82, $p < 0.01$). TOC correlated well with sediment grain size, indicating the influence of hydrodynamic effects on the sediment organic matter (SOM) accumulation in the YRE.

PAH distribution

As shown in Fig. 2a, the maximum concentration (204.8 ng g^{-1}, dry weight) was at site z1, near the Chengdao offshore oilfield, a part of the land-based Shengli Oilfield (the second largest one in China). Thus, this reflected the importance of PAH input from the offshore oilfield. There were two enriched PAH zones in both northern and southern mud patches of the YRE, consisting mostly of fine-grained silt and clayey silt sediments. This distribution pattern of PAHs in the YRE agreed well with the dispersion of Yellow River-derived sediments, and the distribution of suspended particles (Qiao et al. 2009),

Table 1 Some properties of surface sediments in the Yellow River Estuary

Site	Sand (%)	Silt (%)	Clay (%)	S.T[a]	Mz (Φ)	Sorting (Φ)	TOC (%)
z1	13.9	65.6	20.5	cSi	6.2	2.0	0.25
z2	9.5	70.7	19.7	cSi	6.3	1.9	n.d.
z3	11.0	70.4	18.6	cSi	6.1	1.9	0.39
z4	11.9	60.2	27.8	cSi	6.7	2.3	0.51
z5	0.6	58.5	41.0	cSi	7.7	1.5	n.d.
z6	1.0	72.2	26.8	cSi	7.0	1.6	0.58
z7	3.5	66.9	29.7	cSi	7.1	1.7	0.42
z8	2.1	72.0	25.9	cSi	6.9	1.7	n.d.
z9	21.7	63.2	15.1	saSi	5.6	2.0	0.28
z10	20.1	66.7	13.3	saSi	5.5	1.9	0.27
z13	10.7	73.1	16.2	cSi	6.0	1.8	0.28
z14	18.1	66.3	15.7	saSi	5.7	2.0	0.21
z15	15.7	69.8	14.5	saSi	5.7	1.9	0.21
z16	39.1	52.3	8.5	saSi	4.8	1.8	0.16
z19	26.5	61.3	12.2	saSi	5.4	1.9	0.37
z20	21.7	64.8	13.5	saSi	5.5	1.9	0.23
z21	2.9	76.2	20.9	Si	6.6	1.7	0.67
z22	15.6	63.1	21.4	cSi	6.2	2.1	0.25
z23	2.5	72.1	25.4	cSi	6.8	1.7	0.53
z24	11.1	70.5	18.4	cSi	6.1	2.0	0.33
z27	83.0	15.1	1.8	Sa	3.6	1.2	0.10

[a] Sediment type based on Shepard (1954), *Sa* sand, *Si* silt, *saSi* sandy silt, *siSa* silty sand, *cSi* clayey silt, *Mz* mean grain size, *n.d.* no data

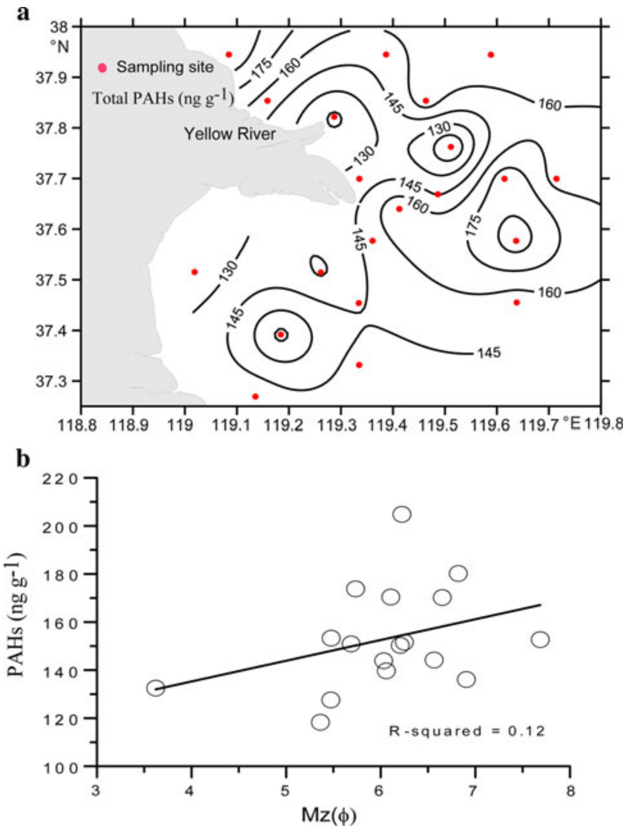

Fig. 2 Spatial distributions of PAHs in the surface sediments of the Yellow river estuary (**a**) and correlation between PAHs and mean grain size (**b**)

which indicates that sediments in the YRE could be the sink of Yellow River-derived PAHs. Thus, PAHs associated with suspended particles are transported southward and northward under the control of the isobath-parallel tidal currents, and a large amount of suspended sediments are entrapped by residual current circulations (Fig. 1) (Wang et al. 2007a; Qiao et al. 2009). High concentrations of PAHs were observed in fine-grained sediments, while low concentrations of PAHs were found in relatively coarse grain size sediments, and there was a positive correlation between PAHs and mean grain size (except z6, z7, z9 and z16) (Fig. 2b). This may indicated that the distribution of sedimentary PAHs in the YRE is associated with hydrodynamic effects.

The status of PAH contamination in this work was compared with those in other estuaries, bays, and coastal regions (Table 2). The concentrations of PAHs in YRE were similar to the data reported for Liaodong Bay of Bohai Sea, China (Hu et al. 2010b) and several coastal regions around the world, such as Kyeonggi Bay, Korea; Chao Phraya River Estuary, Thailand; and Niger Delta, Nigeria. The levels of PAHs in this study were slightly higher than those found in White Sea, Russia, but much lower than detected in Liaohe River Estuary of Bohai Sea, and Kaohsiung, Taiwa. In particular, the values in this study were about 10-, 20-, 40-, and 50-folds lower than detected in Lenga Estuary, Chile; northern continental shelf, Spanish and Casco Bay, USA; Kaohsiung, Taiwa, and San Francisco Bay, USA, respectively. In general, PAH contamination does exist in YRE but the pollution level is well below that of the highly polluted coastal areas mentioned above.

As shown in Table 3, two widely used SQGs, i.e., ERL and ERM (Long et al. 1995) as well as TEL and PEL (CCME 2002) were applied to evaluate the possible eco-toxicological risks of PAHs in the study area. Both sets of SQGs were derived using statistical analyses of matching chemistry and biological data compiled from numerous field, laboratory, and modeling studies performed throughout North America (Long and MacDonald 1998), and were generally used to prioritize contaminated areas and chemicals of potential concern (Pekey et al. 2004; Hu et al. 2010b; Panagiotopoulos et al. 2010). Compounds that occur at concentrations below the low-range SQGs (ERL or TEL) and remain low in concentrations in both toxic and non-toxic samples should be identified as relatively low-priority chemicals. Those compounds whose concentrations exceed the low-range SQGs (ERL or TEL), but do not equal or exceed the mid-range SQGs (ERM or PEL) should be ranked as chemicals of low-to-moderate concern. Compounds that equal the mid-range SQGs or exceed them by a moderate amount should be viewed as chemicals of high concern (Long and MacDonald 1998). The level of each PAH compound was lower than the ERL value, except for ACE at site z1.Concentration of DahA was over the TEL value at four sites (z10, z14, z15, z23), whereas they were below the PEL value. This suggested that the concentration levels of DahA at most sites were lower than the values that

Table 2 Comparison of PAH concentrations in surface sediment of Yellow River Estuary and other coastal areas in the world (ng g^{-1} dry weight)

Location	∑PAH[a]	Mean	References
Asia			
Yellow River Estuary	97.2–204.8 (16)	152.2	This study
Liaohe River Estuary	277–1607 (16)	743	Men et al. (2009)
Yangtze River Estuary	107–633 (16)	309	Liu et al. (2008)
Liaodong Bay, China	144.5–291.7 (16)	184.7	Hu et al. (2010b)
Kyeonggi Bay, Korea	9.1–1400 (24)	120	Khim et al. (1999)
Masan Bay, Korea	41.5–1100 (16)	353	Khim et al. (1999)
Chao Phraya River Estuary, Thailand	30–724 (17)	179	Boonyatumanond et al. (2007)
Kaohsiung Harbor, Taiwan	472–16201 (17)	5,764	Chen and Chen (2011)
America			
San Francisco Bay, USA	2636–27510 (16)	7,406	Pereira et al. (1996)
Casco Bay, USA	16–21000 (23)	2,900	Kennicutt et al. (1994)
Lenga Estuary, Chile	290–6118 (16)	2,025	Pozo et al. (2011)
Estuarine of Guaratuba Bay, Brazil	78.5–3270 (14)	899	Pietzsch et al. (2010)
Europe			
Arcachon Bay, France	32–4120 (16)	1918	Baumard et al. 1998
White Sea, Russia	13–208 (27)	61	Savinov et al. (2000)
Northern continental shelf, Spanish	37–34085 (13)	2708	Viñas et al.(2010)
Africa			
Niger Delta, Nigeria	65–331 (28)	168	Sojinu et al. (2010)

[a] The numbers in parenthesis indicate the number of PAH compounds studied

Table 3 Concentrations of PAHs in sediments of the Yellow river estuary (ng g^{-1} dry weight)

PAH	Max[a]	Min[b]	Mean	Med[c]	SD[d]	TEL[e]	ab-TEL (%)[i]	PEL[f]	ab-PEL (%)[i]	ERL[g]	ab-ERL (%)[i]	ERM[h]	ab-ERM (%)[i]
NAP	20.3	6.3	10.5	8.7	4.3	34.6	0	391	0	160	0	2,100	0
ACY	12.1	n.d.[j]	8.3	8.2	2.9	5.87	91	128	0	44	0	640	0
ACE	16.2	5.7	8.9	7.6	2.9	6.71	71	88.9	0	16	4.8	500	0
FLO	17.7	4.2	9.0	8.7	2.9	21.2	0	144	0	19	0	540	0
PHE	17.5	4.9	9.0	7.7	3.6	86.7	0	544	0	240	0	1,500	0
ANT	19.0	7.2	13.5	13.5	3.3	46.9	0	245	0	85.3	0	1,100	0
FLA	26.4	10.2	16.0	15.6	3.5	113	0	1,494	0	600	0	5,100	0
PYR	25.1	10.8	15.8	15.6	3.5	153	0	1,398	0	665	0	2,600	0
BaA	25.2	7.5	14.9	15.7	5.0	74.8	0	693	0	261	0	1,600	0
CHR	17.2	7.7	11.3	10.5	2.6	108	0	846	0	430	0	1,600	0
BbF	8.7	5.4	7.2	7.1	0.8	–	–	–	–	–	–	–	–
BkF	10.9	4.1	7.9	8.0	1.6	–	–	–	–	–	–	–	–
BaP	8.1	n.d.[c]	6.4	7.0	1.7	88.8		763	0	384	0	2,800	–
IcdP	8.2	n.d.	5.3	5.5	1.9	–	–	–	–	–	–	–	–
DahA	7.0	n.d.	4.9	4.9	1.6	6.22	19.1	135	0	63.4	0	260	–
BghiP	7.0	n.d.	3.3	3.8	2.3	–	–	–	–	–	–	–	–
PAH$_{16}$[k]	204.8	97.2	152.2	150.9	27.9	1684	0	16770	0	0	0	0	0

[a] Maximum concentration

[b] Minimum concentration

[c] Median concentration

[d] Standard deviation

[e] Threshold effect level

[f] Probable effect level

[g] Effect range-low value

[h] Effect range-median value

[i] Percentage of samples above the corresponding levels

[j] Under the limit of detection

[k] The concentration of total 16 PAHs

may cause adverse biological risk. For ACY and ACE, although not exceed than ERL and PEL values, 91 and 71 % of total sites in the study area are higher than TEL values, respectively, suggesting that the exposure of ACY and ACE may cause ecological risk on the benthic organisms. Therefore, ACY and ACE could be the two main species of PAHs with low-to-moderate ecotoxicological concern in YRE, while other PAHs in surface sediments would be less possible to cause adverse biological effect.

PAH composition

Table 3 shows the concentration of individual PAH in YRE sediments. Individual PAH concentrations of most samples were above the limits of detection (LOD) with the exception of ACY and IcdP at one station, and BghiP at five stations. Although both BghiP and DahA were detected at most stations, their concentrations were relatively low. FLA and PYR were the most dominant components, accounting for 10.5 ± 1.0 and 9.9 ± 2.5 % of the total concentration, respectively. In addition, the simplest low molecular weight PAH, NAP, was found at relatively high level (accounting for approximately 7 %) in all of the sediments investigated, especially in z1, z2, z3, z4, and z5. Yunker et al. (2002) found high NAP concentrations in sediments were due to the contamination of fresh oil. The Chengdao offshore oilfield, a part of the land-based Shengli Oilfield (the second largest oilfield in China) is in the north YRE. Thus, detecting the petroleum-derived NAP in this area was reasonable. It also has been reported that NAP was the major PAH produced in vegetation fires (Kim et al. 2003; Lemieux et al. 2004). Biomass burning is an important energy source in the villages in north China (Streets et al. 2001). It is believed that, therefore, vegetation fires and petroleum make a large contribution to elevated NAP levels in the sediments of the north of YRE. The sources of PAHs are further discussed in relation to other experimental evidence in the following section.

The composition pattern of PAHs by ring size in sediments was dominated by 4-ring PAHs (76.0–43.3 ng g^{-1} and mean of 57.1 ± 9.6 ng g^{-1}), accounting for 37.9 ± 4.4 % of the total concentrations (Fig. 3). The 3-ring (32.0–76.0 ng g^{-1} and mean of 48.7 ± 11.9 ng g^{-1}) and 5-ring (13.9–39.1 ng g^{-1} and mean of 31.61 ± 5.0 ng g^{-1}) PAHs were also highly abundant, accounting for 31.8 ± 3.0 and 21.0 ± 2.7 %, respectively, of the total PAHs. Overall, the high molecular weight PAHs (≥4 rings) accounted for a large fraction of the total PAHs in these sediments owing to their resistance to degradation and migration (Yunker et al. 2002; Larsen and Baker 2003).

Source identification using isomer ratios

In general, low molecular weight (LMW, with two or three rings) PAHs originate from petrogenic sources, while pyrogenic procedures mainly generate high molecular weight (HMW, with four or more rings) PAHs (Yuan et al. 2001; Huang and Su 2002). Consequently, pyrogenic sources led to LMW/HMW ratios <1, while petrogenic sources gave LMW/HMW ratio >1 (Yunker et al. 2002; Liu et al. 2008). In the present study, the LMW/HMW ratios in most locations were <1 (Fig. 4a), indicating that pyrogenic sources were the primary sources of sedimentary PAHs in the YRE. For some locations (z1, z2, z3, z4, and z5) in the north YRE, LMW/HMW ratios were in the range 0.8–0.9, suggesting that the contributions from petroleum and combustion may be significant and comparable. As discussed above, there are oilfield drilling platforms in the north YRE. Thus, detecting petroleum-based PAHs in this area was not unexpected. In fact, the result of an unresolved complex mixture (UCM, an indicator of chronic/degraded petroleum contamination) also indicated that sediments this area were contaminated by petroleum (Hu et al. 2009).

Ratios of PAHs with similar molecular weights have been used as indices for source apportionment (Yunker et al. 1996, 2002). The ratio BaA/(BaA + CHR) is often used to distinguish between combustion and petroleum

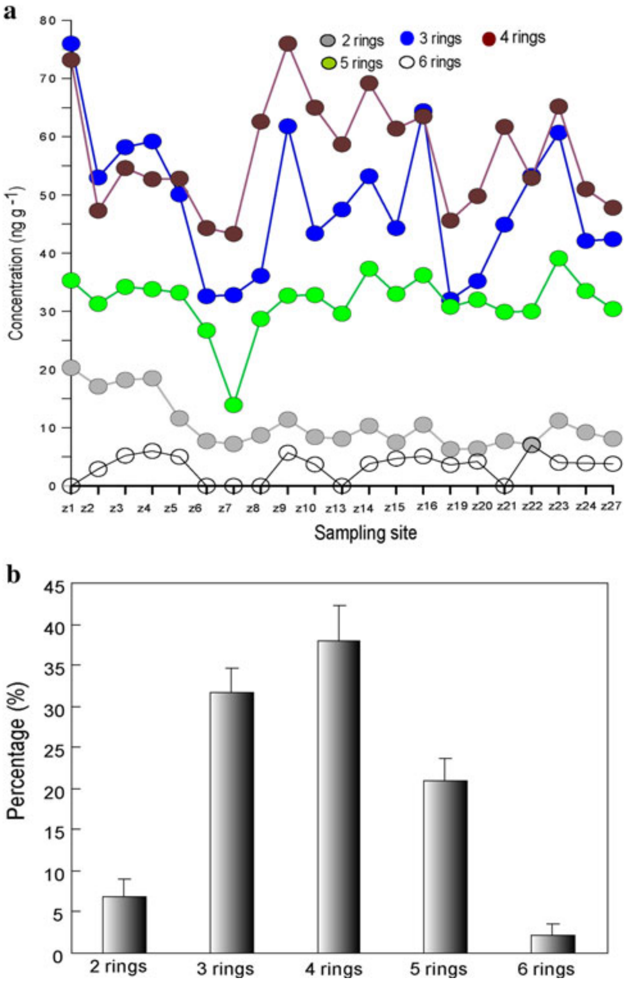

Fig. 3 Profile of PAH concentrations of ring group PAHs (**a**) and percentage of two-, three-, four-, five-, and six-rings to the 16 PAHs (**b**) in sediments of the YRE

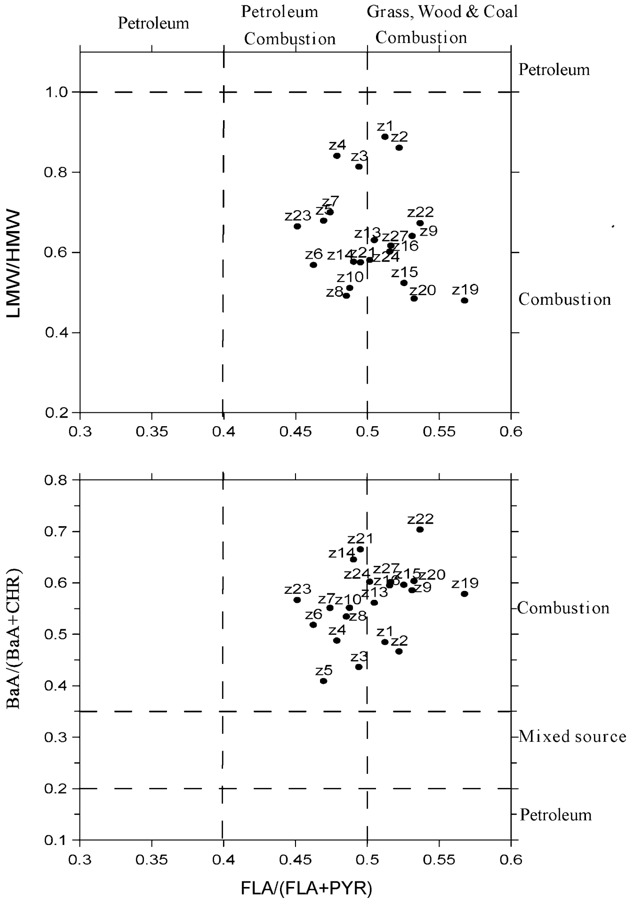

Fig. 4 PAH cross-correlations for the ratios **a** LMW/HMW, **b** BaA(BaA + CHR) vs. FLA/(FLA + PYR)

sources. In general, BaA/(BaA + CHR) < 0.2 indicates a petrogenic source, while BaA/(BaA + CHR) > 0.35 a pyrogenic source is suggested (Baumard et al. 1998; Yunker et al. 2002). In this study, BaA/(BaA + CHR) was the range 0.44–0.67, further confirming the importance of pyrogenic sources (Fig. 4b). This is consistent with the previous observations on sediments of Bohai Bay (Liu et al. 2007; Hu et al. 2010a) and Bohai Strait (Wu and Zhang, 2001). However, the values of the BaA/(BaA + CHR) ratio for several sites in north YRE (z1, z2, z3, z4, and z5) were near the boundary of mixed sources (petrogenic and pyrogenic PAHs), which suggests that these sediments could be contaminated by both petrogenic and pyrogenic PAHs. This is in agreement with the results from the LMW/HMW ratios, as discussed in the above section.

Yunker et al. (2002) and Mai et al. (2001) reported that a FLA/(FLA + PYR) ratio <0.4 can possibly be attributed to a petrogenic source, between 0.4 and 0.5 to liquid fossil fuel (vehicle and crude oil) combustion, while ratios > 0.5 are characteristic of coal, grass and wood combustion. Figure 4 suggests that PAHs in the samples originated from both petroleum combustion and incomplete combustion of coal or biomass. In the past three decades, there has been a drastic increase in the combustion of petroleum products in China, and this is reflected in the depositional records in the Pearl River Delta sediment close to South China (Mai et al. 2001). However, coal is still one of the main energy sources in China, especially in the north of China. For example, the energy consumption for 2000 was 69.0 % coal, 22.3 % oil and 2.5 % natural gas (NBSC 2005). In addition, the sampling site is influenced by regions in North China that use extra coal for space heating in winter that the PAHs in the winter aerosols are 14-fold higher than in the summer in the North China coastal city (Guo et al. 2003).Thus, as compared to Southern China, coal is expected to contribute more to the sediments (Mai et al. 2001). All of those factors support the hypothesis that petroleum combustion, and burning of coal or biomass are the dominant origins of the PAHs in the YRE samples.

Source identification using principle component analysis

Principal component analysis (PCA) was performed on 15 US EPA priority PAHs except BghiP that was not detectable at many sites. The first three principal components (PCs) were responsible for 78.7 % of the total variance (Table 4). PC1, responsible for 33.5 % of the total variance, was heavily weighted by NAP, ACE, FLO, PYR and IcdP, with moderate loading of FLA and ACY. In previous studies, NAP and FLO were identified as a typical tracer of a petroleum source (Yunker et al. 2002; Larsen and Baker 2003). ACY and PYR were the major PAHs produced in vegetation fires (Duval and Friedlander 1981; Venkatesan and Kaplan 1982). Spilled petroleum from the Chengdao oilfield located in the north of YRE was absorbed into suspended particles and accumulated in sediments. Furthermore, the petroleum products leaking from cargo vessels and ships in Dongying harbor (located in the north of the YRE) also play an important role as a PAH contributor, and should not be neglected in the discussion of sedimentary PAHs. Wang et al. (2009) reported that burning of vegetation and agricultural straw in the open air in the Yellow River Delta contributed the elevated PAH in the water and suspended particles in the river delta, and biomass combustion was a major source of PAHs in sediments and suspended particles of Yellow River (Li et al. 2006). Based on this information, PC1 was selected to represent the mixed source of petrogenic and vegetation burning.

Table 4 Principal component loading of principal components 1–3

PAH	PC1	PC2	PC3
NAP	0.94	0.02	0.09
ACE	0.91	−0.06	0.18
FLO	0.89	0.09	−0.12
IcdP	0.73	−0.10	0.09
Pyr	0.70	0.52	0.29
Fla	0.63	0.51	0.39
ACY	0.61	0.36	0.58
CHR	−0.05	0.91	0.07
PHE	0.45	0.79	0.05
BaA	−0.46	0.75	0.26
BbF	0.12	0.67	0.46
DahA	0.04	0.00	0.91
BaP	0.32	0.17	0.82
ANT	0.14	0.50	0.65
BkF	−0.38	0.41	0.60
Variance (%)	33.5	23.9	21.3

PC2, accounting for 23.9 % of the total variance, had a highly positive loading of CHR, PHE, BaA and BbF with moderate loading of BkF and ANT, which were typical indicators for coal combustion. As discussed previously, it appears that coal is the most important energy as well as PAH source in China (Xu et al. 2006). Especially, industrial and domestic coal consumption has continually increased from 610.1 million tons in 1985 to 1,376.8 million tons in 1995 and 2,586.4 million tons in 2007 (NBSC 1996, 2008), causing a high percentage contribution of coal combustion for PAHs. For example, coal combustion was found to be a major PAH source of emission in most cities of northern China (Xu et al. 2006). PAHs in the middle and low reaches of the Yellow River were also mainly derived from coal and wood combustion (Li et al. 2006). Therefore, this factor is believed to be the contribution of coal combustion.

PC3, contributing 21.3 % of total variance, was characterized by a high loading of DahA and BaP. DahA predominates in gasoline engine exhaust tar (Cambridge Isotope Laboratories. The standard 2002). BaP has been identified as a tracer of vehicular emissions because it was found to be enriched in a traffic tunnel along with BghiP (Harrison et al. 1996; Cambridge Isotope Laboratories 2002; Larsen and Baker 2003; Boonyatumanond et al. 2007). Consequently, PC3 was selected to represent traffic-related source of PAHs.

Contribution of PAH sources

In the previous studies, researchers have successfully applied PCA and multivariate linear regression (MLR) to apportion sources of PAH in soils, sediments and urban atmosphere (Harrison et al. 1996; Larsen and Baker 2003). In the present study, MLR results show that the contributions are 36 % for the mixed source, 35 % for coal combustion, and 29 % for petrogenic combustion. There might be some uncertainty resulting from PCA/MLR as an estimation method to apportion PAH sources. Therefore, in future, the source apportionment should be determined using multiple techniques, such as PMF (Stout and Graan 2010) and UNMIX (Larsen and Baker 2003), to reduce weaknesses in individual method and compare results among methods.

Conclusion

Sixteen priority polycyclic aromatic hydrocarbons (PAHs) were measured in surface sediments from the YRE. The distribution pattern of PAHs in the YRE agreed well with the dispersion of Yellow River-derived sediments, and distribution of suspended particles, indicating that sediments in the YRE could be the sink of Yellow River-derived PAHs. Contamination levels of sedimentary PAHs in this area were low compared with other coastal sediments over the world. Based on the sediment quality guidelines, ACY and ACE would be more concerned for the ecotoxicological risk in the YRE.

Source identification indicated that the PAH inputs could be mainly attributed to coal combustion, traffic-related pollution, spills of oil products and vegetation burning. Further analysis using PCA/MLR showed that the contributions of coal combustion, traffic-related pollution and mixed sources (spills of oil products and vegetation burning) were 35, 29 and 36 %, respectively. Pyrogenic sources (coal combustion and traffic-related pollution) contribute 64 % of anthropogenic PAHs to sediments, which indicated that energy consumption may be a predominant factor in PAH pollution in the YRE.

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