# **Pollution assessment and source identifications of polycyclic aromatic hydrocarbons in sediments of the Yellow River Delta, a newly born wetland in China**

**Zhifeng Yang · Lili Wang · Junfeng Niu · Jingyi Wang · Zhenyao Shen**

Received: 23 June 2008 / Accepted: 30 September 2008 / Published online: 30 October 2008 © Springer Science + Business Media B.V. 2008

**Abstract** The levels and possible sources of 16 priority polycyclic aromatic carbons (PAHs) in the sediments from the Yellow River Delta (YRD) were investigated. The total PAH concentrations ranged from 23.9 to 520.6  $\mu$ g kg<sup>-1</sup> with a mean value of 150.9 μg kg<sup>-1</sup>, indicating low or medium levels compared with reported values of other deltas. The concentrations of the 16 individual PAHs presented varied profiles among different regions. The ecological risk assessment of PAHs showed that adverse effects would rarely occur in the sediments of the YRD based on the effect range-low quotients and the probability risk assessment. The PAH compositions and the principal component analysis (PCA) with multiple linear regression (MLR) uniformly presumed the mixed sources of pyrogenic- and petrogenicderiving PAHs in the YRD. By PCA with MLR, the contributions of major sources were quantified as 36.4% from oil burning, 33.1% from biomass combustion, and 30.5% from diesel emission sources.

**Keywords** Yellow River Delta **·** Polycyclic aromatic hydrocarbons (PAHs) **·** Distribution **·** Ecological risk assessment **·** Principal component analysis (PCA) with multiple linear regression (MLR)

# **Introduction**

The Yellow River Delta (YRD), one of the most active regions of land–ocean interaction among the large river deltas in the world, is a newly born wetland. With an abundance of wetland vegetation and aquatic biological resources, the YRD provides the birds with an appropriate habitat for breeding, migrating, and wintering. Seven species of birds listed as first priority for national conservation and 33 species listed as the second have been observed here (Xu et al[.](#page-10-0) [2004](#page-10-0)). Thus, the YRD is considered to be an important stopover region in the inland of Northeast Asia and around the western Pacific Ocean for bird migration. Due to its unique environmental condition and ecological sensitivity, the YRD is widely concerned both in domestic and abroad. Therefore, protecting the delicate ecology in this region is of great significance.

However, as the YRD consists of the estuary of the current course of the Yellow River at the Bohai Sea, it admits the incoming water from the middle and lower reaches of the Yellow

Z. Yang  $(\boxtimes)$   $\cdot$  L. Wang  $\cdot$  J. Niu  $\cdot$  J. Wang  $\cdot$  Z. Shen State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, People's Republic of China e-mail: zfyang@bnu.edu.cn

River, where national petrochemical industry plants, mines, metallurgy factories, and many other pollution sources are located (Li et al[.](#page-9-0) [2006\)](#page-9-0). Moreover, the YRD developed rapidly in modern industry due to the exploitation of the Shengli Oil Field (Chen et al[.](#page-8-0) [2007](#page-8-0); Xu et al[.](#page-10-0) [2004;](#page-10-0) Yue et al[.](#page-10-0) [2004\)](#page-10-0), and as a newly born wetland, the YRD has become a major region for the development of agriculture and fisheries (Chen et al[.](#page-8-0) [2007](#page-8-0); Fang et al[.](#page-8-0) [2005](#page-8-0); Xu et al[.](#page-10-0) [2004\)](#page-10-0). The rapidly economic development here probably results in significant pollution to aquatic environment, especially to the sediment which acts as a natural repository for hydrophobic organic compounds (HOCs). Recent studies on different organic pollutants in sediments have been launched in some coastal areas of China. However, most of them concentrated on the southern sea areas (Chen et al. [2006](#page-8-0); Mai et al. [2002](#page-9-0); Yuan et al. [2001](#page-10-0)). On the other hand, most contaminant studies on the YRD focused on distributions of heavy metals, nitrogen, and phosphorus (Chen et al[.](#page-8-0) [2007;](#page-8-0) Li et al[.](#page-9-0) [2001](#page-9-0); Son[g](#page-10-0) [2000\)](#page-10-0), but few studies on polycyclic aromatic hydrocarbons (PAHs), which have toxic effects on aquatic lives and show a probable carcinogenicity to human beings (Bihari et al[.](#page-8-0) [2007;](#page-8-0) Gevao et al[.](#page-9-0) [2007\)](#page-9-0).

PAHs are a class of diverse compounds that consist of two or more fused aromatic rings. They are mainly derived from incomplete combustion, petroleum leakage/evaporation, and early diagenesis of organic matter (Chen et al[.](#page-8-0) [2006;](#page-8-0) Shi et al[.](#page-9-0) [2007\)](#page-9-0). Sixteen PAH compounds have been recommended as priority pollutants by the United States Environmental Protection Agency (USEP[A](#page-10-0) [1993\)](#page-10-0). Owing to their ubiquitous distribution and toxic characteristics, some of the PAHs have been studied widely all over the world (Chen et al[.](#page-8-0) [2001](#page-8-0); IAR[C](#page-9-0) [1987\)](#page-9-0). As one of the major sinks of PAH contamination, aquatic ecosystem has received much attention for PAH investigations (Tao et al[.](#page-10-0) [2003](#page-10-0)). PAHs are introduced into the aquatic environment through atmospheric deposition, surface runoff, oil leakage, industrial, and residential wastewater discharge (Gevao et al[.](#page-9-0) [1998;](#page-9-0) Ping et al[.](#page-9-0) [2007\)](#page-9-0). Owning to their hydrophobic characteristics, PAHs have great tendency to associate with solid phase matrix in aquatic systems (Bihari et al[.](#page-8-0) [2007;](#page-8-0) Chiou et al[.](#page-8-0) [1998;](#page-8-0) Tolosa et al[.](#page-10-0) [2004](#page-10-0)). Recent studies on delta, estuaries, coastal reaches, and continental shelves showed that sediments in these areas often contained high concentrations of PAHs (Chen et al. [2006;](#page-8-0) Liu et al. [2006](#page-9-0)). Therefore, studies on PAH concentration characteristics and their ecological risk assessment in the YRD would be very informative.

The objectives of the present work were to investigate the concentrations and compositional characteristics of PAHs in sediments in the YRD, and to provide data for comparison with other deltas in order to assess potential ecotoxicological effect here. Moreover, possible PAH sources were identified by principal component analysis with multiple linear regression operation.

## **Materials and methods**

Study area and sample collection

The Yellow River Delta is situated in the northern part of Shandong Province, China. It lies on the south side of the Bohai Sea, spanning from 118°07' E to 119°18′ E, and from  $36°55'$  N to  $38°12'$  N, with an area of 6,010 km<sup>2</sup>. The area has a monsoon climate of the warm-temperate zone which receives continental cold airflow (Asian monsoons) blowing down to South China coastal regions in winter, and is also influenced by marine climate in summer time. The average annual temperature in the YRD is 11.7–12.6◦C and average annual precipitation is 530–630 mm, of which 70% is rainfall during summer (Chen et al[.](#page-8-0) [2007;](#page-8-0) Liu et al[.](#page-9-0) [2005a\)](#page-9-0).

Sediments were collected from 30 sampling sites in the YRD during May to August in 2007 (Fig. [1\)](#page-2-0). Among them, seven sites were located around the coastal reaches, nine in the inhabited area, four near drilling platforms, and the other ten were collected from marsh area in the YRD. Top 5-cm surface sediments were taken using a Van Veen stainless steel grab sampler (Eijkelamp, Netherlands). The samples were then immediately transferred to a pre-cleaned stainless steel cylinder and stored at −20◦C for further analysis.

<span id="page-2-0"></span>

**Fig. 1** Sampling sites in the Yellow River Delta

Chemicals

Sixteen PAH compounds were selected as target analytes, i.e., naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), 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), indeno[1,2,3-*cd*]pyrene (IcdP), dibenzo[*a*,*h*]anthracene (DahA), and benzo[*g*,*h*,*i*] perylene (BghiP). Standard PAHs (16 USEPA priority compounds, each at 100 mg  $l^{-1}$  in acetonitrile) were obtained from Dr. Ehrenstorfer, Reference Materials (Augsburg, Germany). All solvents in this study (i.e., methanol, acetone, dichloromethane, *n*-hexane) were HPLC grade and obtained from Dikma (USA). The working standard solutions were prepared by diluting appropriate volumes of the standard PAH mixture with methanol solution. Silica gel (reagent grade, Qingdao Ocean Chemical Reagent Co., China) and anhydrous sodium sulfate (analytical grade, Beijing Chemical Reagent Co., China) were baked in a furnace oven at 650◦C for 6 h prior to use. Water was prepared from a Milli-Q system (Millipore, Bedford, MA, USA) with a specific resistivity of 18.2 M $\Omega$  cm.

# Sample analysis

The samples were freeze dried, and then grinded and homogenized in a mortar. One gram of dry sediment sample was mixed with 30 ml hexane/acetone mixture  $(1:1, v/v)$  and left to settle overnight. After extracted in an ultrasonic bath (KQ-502B, Kunshan Ultrasonic Instruments, China) for 1 h, the sample was centrifuged at 4,000 rpm for 20 min. Then the supernatant was concentrated and solvent-exchanged to *n*-hexane using a rotary evaporator (RV 05 basic, IKA, Germany). The *n*-hexane extract was subject to a column filled with 2.0 g silica gel and 1.0 g anhydrous sodium sulfate for cleanup and fractionation. Elution was performed with 8 ml hexane first and then 10 ml hexane/dichloromethane  $(1:1, v/v)$ . The second fraction containing the PAHs was reduced to 1–2 ml, subject to a solvent exchange to methanol, and concentrated to 1.0 ml by the rotary evaporator prior to HPLC analysis (Niu et al. [2004](#page-9-0)).

PAHs were analyzed by a Waters 1525 highperformance liquid chromatography (HPLC) system (Waters, USA) with Waters 1525 binary HPLC pump, a 474 scanning fluorescence detector, and a 2347 double beam UV detector. The injector was a Rheodyne 7725 high-pressure manual injector valve with a 20-μl injection loop. Separation was carried out using a ChromSep guard column (10  $\times$  4.6 mm, particle size 5  $\mu$ m, Varian, USA) followed by a ChromSep  $C_{18}$  Column (250  $\times$  4.6 mm, particle size 5  $\mu$ m, Varian). The HPLC separation of the analytes was operated at a flow rate of 1.0 ml min<sup>-1</sup> using a gradient elution program in which methanol–water was used as mobile phase. A linear gradient (1 min) back to starting conditions followed by a 7-min

**Table 1** The detection limits and recoveries of PAHs in sediments

<b>PAHs</b>	Detection limit	Recovery	RSD	
	$(\mu g kg^{-1})$	( %)	(%)	
Nap	4.0	45.8	8.9	
Acy	1.5	61.5	11.9	
Ace	0.8	66.0	14.2	
Flu	1.0	77.3	8.4	
Phe	1.2	92.6	16.7	
Ant	0.8	86.2	6.2	
Fla	0.9	83.6	8.6	
Pyr	0.7	95.0	10.9	
BaA	0.8	85.0	9.3	
Chr	0.8	89.8	6.4	
BbF	0.9	91.8	8.6	
BkF	0.4	82.7	7.1	
BaP	0.5	85.6	7.1	
DahA/BghiP	0.6	86.7	8.9	
IcdP	1.1	86.4	10.6	

prerun allowed the separation column to equilibrate prior to each subsequent run. Acenaphthylene, which was weakly fluorescent, was identified by UV detector at 229 nm. The other 15 PAHs were quantified by fluorescence detector based on fluorescence properties of individual PAH.

# Quality control

All analytical operations were conducted under quality control guidelines. Before the onset of the extraction and analysis program, recovery experiments were undertaken by spiking the 16 PAHs standard solution with sediment samples. The six parallel experiments indicated that recoveries for the PAHs were 60–95% except for NAP, while the respective relative standard deviations (RSDs) ranged from 6% to 17% (shown in Table 1). Method blanks operation showed no detectable amounts of PAH contamination except for naphthalene. The detection limits of the procedure were 0.4–4.0  $\mu$ g kg<sup>-1</sup> for each PAH.

# Probability risk assessment

A probability risk assessment (PRA) procedure, being implemented by the USEPA (USEPA [2000a,](#page-10-0) [b\)](#page-10-0), was adopted in this study to estimate PAH probabilistic ecological risk. In this method, both uncertainty and stochastic properties of exposures and responses can be fully considered Solomon et al. [2000](#page-9-0); Wang et al. [2002.](#page-10-0) Exposure and toxicity data with log-normal distributions are plotted on the same axes for PRA, and the extent of overlap between the curves indicates the probability of ecological risk. Conceptually, there is always some degree of overlap between the two distributions. In addition, joint probability curve (JPC) which uses dual probability lines with concentration of the residue as the common variable was applied to describe the nature of risks. In this method, an associated concentration can be determined for any level of effect and a probabilistic value of risk can be calculated for any concentration (Che[n](#page-8-0) [2005;](#page-8-0) Solomon et al[.](#page-9-0) [2000](#page-9-0)). In this study, the software package Matlab 7.0 was used for PRA analysis.

# Principal component analysis with multiple linear regression

In order to enhance the accuracy of source identification and quantitatively apportion the contribution percentage of each possible PAH source, principal component analysis (PCA) followed by multiple linear regression (MLR) was applied to analyze the data set. In this method, PCA was related to the information of source composition and MLR was used to quantify the source contribution (Larsen and Bake[r](#page-9-0) [2003](#page-9-0)). The original individual PAH concentrations in each sample were arranged in matrix after being standardized. In the matrix, columns correspond to individual PAH components and rows represent the sampling sites. Source groupings were determined by PCA with varimax rotation and only factors with eigenvalues >1 were retained as PCs. After that, MLR was operated and the regression coefficients obtained indicated the PAH source contributions. In this study, the software package SPSS 11.5 was used for PCA and MLR analysis.

## **Results and discussion**

# PAH concentrations

All 16 PAHs in each sediment sample were quantified, and concentrations of PAHs were summarized in Table 2. Owning to the relatively high indoor temperature during HPLC operations, DahA and BghiP were not individually detected. These two compounds were analyzed together as DahA/BghiP in this study. As shown in Table 2, the concentrations of total PAHs  $(\sum$ PAHs) in sediments of the YRD varied from 23.9 to 520.6  $\mu$ g kg<sup>-1</sup> with a mean value of 150.9  $\mu$ g kg<sup>−</sup><sup>1</sup>. The general level of PAHs in the study area was lower than the corresponding concentrations of the Mississippi River Delta (Santschi et al[.](#page-9-0) [2001\)](#page-9-0), the Pearl River Delta (Mai et al[.](#page-9-0) [2002\)](#page-9-0), and the Yangtze River Delta (Ping et al[.](#page-9-0) [2007\)](#page-9-0), but was higher than that of the Niger Delta (Olajire et al[.](#page-9-0) [2005](#page-9-0)) and the middle and lower reaches of the Yellow River (Li et al[.](#page-9-0) [2006](#page-9-0)). In general, concentrations of PAHs in sediments of the YRD were at low or medium levels compared with other reported deltas. By comparing the PAH average levels among different regions, the sampling sites with the lowest concentration of PAHs were found to be situated in the coast reach areas, and the other three regions (i.e., inhabited areas, drilling platforms, and marsh areas) pre-

**Table 2** PAHs concentrations ( $\mu$ g kg<sup>-1</sup>, dw) in sediments of the Yellow River Delta

<b>PAHs</b>	Min <sup>a</sup>	Max <sup>b</sup>	Mean	Mid <sup>c</sup>	CV(%) <sup>d</sup>
Nap	ND	84.5	16.4	10.9	123.9
Acy	ND	32.9	13.1	9.5	88.5
Ace	2.8	55.3	16.8	11.7	77.9
Flu	1.4	76.2	10.9	5.6	136.9
Phe	3.5	90.0	29.4	19.9	87.7
Ant	ND	5.4	1.5	1.2	82.8
Fla	1.7	37.6	12.0	8.0	81.0
Pyr	1.2	29.0	9.6	6.4	79.0
BaA	ND	52.2	9.2	5.2	118.9
Chr	1.2	47.6	6.7	4.6	122.6
BbF	1.7	21.2	5.4	4.7	62.9
BkF	0.5	29.1	4.5	3.0	130.6
BaP	0.7	22.6	4.8	4.0	82.5
DahA/BghiP	0.7	26.5	4.3	3.4	102.3
IcdP	1.3	13.8	6.0	5.3	50.9
$\Sigma$ PAHs	23.9	520.6	150.9	124.2	66.2

<sup>a</sup>*Min* minimum concentrations

<sup>b</sup>*Max* maximum concentrations

<sup>c</sup>*Mid* median concentrations

<sup>d</sup>*CV* coefficient of variation

*ND* not detectable

sented similar PAH concentrations with relatively high levels. The highest  $\Sigma$ PAH concentration was found at the site I6, likely because oil wells located nearby it and population density here was relatively high. The median concentrations of individual PAHs with the range of 1.2–19.9 μg kg<sup>-1</sup> were basically lower than the corresponding average concentrations (1.5–29.4  $\mu$ g kg<sup>-1</sup>), mathematically indicating that majority of the sites contained relatively low PAH concentrations. Coefficients of variation (CV) of all PAHs were near or over 50.0% and even some of them exceeded 100%, suggesting great variation in the concentrations of PAHs in different samples.

#### Ecological risk assessment

In this study, potential ecological risks were evaluated on the basis of two guideline values, i.e., effects range-low (ERL) and effects rangemedian (ERM), introduced by Long et al[.](#page-9-0) [\(1995](#page-9-0)) in view of 12 PAHs (see Fig. 2). According to Long et al[.](#page-9-0)  $(1995)$ , the concentrations of three classes of PAHs (total low-ring, total high-ring, and total) and all of individual PAHs remarkably influenced the incidence of adverse effects in sediments. Based on PAH concentrations in this study, ERL quotients of three classes of PAHs and all of individual PAHs were calculated as shown in Fig. 2. The concentrations of



**Fig. 2** Effects range-low (*ERL*) quotients of individual PAH species for all sediments and the mean ERL quotients of PAHs in different sampling sites (*upper embedded plot*) in the Yellow River Delta

three classes of PAHs and all of individual PAHs were far below the ERM, indicating no frequent acute adverse biological effect would happen in the YRD. However, some of the individual PAHs were in excess of ERL which implied possible acute adverse biological effects. As DahA and BghiP were detected together in this study, concentrations of DahA/BghiP were used to compare with the ERL and ERM of DahA. The result indicated that concentrations of DahA/BghiP in all sampling sites were under ERL. As shown in Fig. 2, the concentrations of Ace and Flu in some sampling sites exceeded their corresponding ERL values, suggesting occasional adverse effects may occur in the study area (Long et al[.](#page-9-0) [1995\)](#page-9-0).

However, as the above method does not have any environmental relevance, PRA procedure was further employed in this study to evaluate the probabilistic risk of PAHs in the YRD. In addition, the integral PAH effects was evaluated by calculating the BaP equivalency  $(BaP_{eq})$  of PAHs based on the toxic equivalency factors (TEF) for individual PAHs (Nisbet and LaGo[y](#page-9-0) [1992\)](#page-9-0). The range of  $BaP_{eq}$  in sediment samples were 1.1–32.2, and based on this, the probability risk assessment was adopted for PAH risk evaluation. By employing Jarque–Bera method, the distribution of data for exposure concentrations ( $p =$ 0.41) and toxicological effects on sensitive species  $(p = 0.73)$  were found to be log-normal distributed ( $p > 0.05$ ). Figure [3](#page-6-0) presents the probability density curves (Fig. [3a](#page-6-0)) and joint probability curves (Fig. [3b](#page-6-0)) of the  $BaP_{eq}$  in the sediments of the YRD. The overlap area of 8.02  $\times$  10<sup>-4</sup> in Fig. [3a](#page-6-0) was quantified by Matlab 7.0, indicating a very low probability of toxic effect. From Fig. [3b](#page-6-0), it can be seen that the JPC of  $BaP_{eq}$  are very close to the axes, indicating little probability of adverse effect (Solomon et al[.](#page-9-0) [2000](#page-9-0); Wang et al[.](#page-10-0) [2002\)](#page-10-0). The proportion of species was calculated to be affected by 0.00057% of the current observations in the sediments when 1% of species will be affected. This result further indicated that the ecological risk of PAHs in the YRD was rather low that adverse environmental events were supposed to rarely happen by PAH exposure in the YRD. However, as neither the probability of overlap in PRA nor the JPC point is very useful as quantitative predictors of risk (Solomon et al[.](#page-9-0) [2000\)](#page-9-0),

<span id="page-6-0"></span>

**Fig. 3** Probability density curves (**a**) and joint probability curves (**b**) for the exposure concentrations and toxicity data of the BaPeq in the sediments from the Yellow River Delta

the result could only provide the information on relative risk of PAHs in the YRD.

#### PAH composition and source identification

For further discrimination of PAH distribution and primary identification of PAH sources, the composition profiles of PAHs by different benzene rings in four areas were investigated (see Fig. 4). The results indicated that the coast reach showed different PAH composition comparing with the other three areas. The profile in the coast reach was dominated by four- to six-ring PAHs, accounting for 69.4% of  $\sum$ PAHs. Whereas the



**Fig. 4** Compositional profile of PAHs by ring size in sediments from the Yellow River Delta

fractions of two- to three-ring PAHs presented as predominance in the inhabited area, drilling platform, and marsh area, ranging from 51.9% to 63.0% of the total concentrations of PAHs.

As relative concentrations of individual PAH compounds are usually used to distinguish between PAHs for petrogenic and pyrogenic origin (Dahle et al[.](#page-8-0) [2003](#page-8-0); Liu et al[.](#page-9-0) [2006\)](#page-9-0), the main sources of PAHs in different regions could primarily be identified from Fig. 4. Generally, lowring PAHs (i.e., two to three rings) derive from petroleum products, incomplete combustion of fossil fuels, and biomass at low to moderate temperature and natural diagenesis, while pyrogenic sources are abundant in high-ring PAH components with four or more rings (Fernandes et al[.](#page-8-0) [1997;](#page-8-0) Liu et al[.](#page-9-0) [2006;](#page-9-0) Tolosa et al[.](#page-10-0) [2004\)](#page-10-0). Moreover, as low-ring PAHs are prone to be desorbed or degraded greatly in the sediments during transportation process, they are more lost during transport, and the composition of PAHs tends to shift to high-ring PAHs when undergoing transport progress (Li et al[.](#page-9-0) [2006;](#page-9-0) Ping et al[.](#page-9-0) [2007\)](#page-9-0). In this study, relative values of high-ring PAHs with four or more rings account for more than 50% in sediments of coast reach, indicating a dominance of combustion or relatively long-term transport process. Besides PAH physicochemical properties, the characteristics of sediments (Dahle et al[.](#page-8-0) [2003](#page-8-0); Ghosh et al[.](#page-9-0) [2000;](#page-9-0) Luo et al[.](#page-9-0) [2006](#page-9-0)) and hydrodynamic conditions (Liu et al[.](#page-9-0) [2005b;](#page-9-0) Mai et al[.](#page-9-0) [2001\)](#page-9-0) also played important roles in

PAH distributions. The yellow river in the YRD admitted the water from its middle and lower reaches with the contained PAHs; however, the PAH level in the river sediment in the YRD was not as high as its upper reaches. This is possibly the result of sediment characteristics and hydrodynamic conditions. The sediments in yellow river were composed primarily of sandy grains with a relatively small proportion of the readily available PAH fractions, which is due to the weak sorption of PAHs (Ghosh et al[.](#page-9-0) [2000\)](#page-9-0). In addition, when being entrained into the coast areas, sediments were diluted by clean seawater due to the tidal interactions.

In the regions of inhabited areas, drilling platforms, and marsh areas, low-ring PAHs presented as the major compositions of PAHs  $(>50\%)$ . According to the regional characteristics, mixed sources of fossil fuels and biomass combustion at low to moderate temperature and anthropogenic oil leakage were presumed as main PAH origins in these three regions. Moreover, marsh areas were located in intertidal flat regions, where PAHs are prone to accumulate in the sediments (Xu et al[.](#page-10-0) [2001\)](#page-10-0). Among the four different regions, the composition of four-ring PAHs showed similar quantities, primarily implying a common distribution of four-ring PAH fractions in the YRD.

To provide insight into the accuracy and quantification of source apportion, principal component analysis (PCA) followed by multiple linear regression (MLR) was applied to analyze the data set. The results of PCA analysis of PAH concentrations in the sediments from the YRD are tabulated in Table 3. Three principal components (PCs) were extracted and the accumulative variance accounted for 81.2% of the total variance. For each PC, the PAH with relatively high loading values (exceeding 0.7) (Fang et al. [2006;](#page-8-0) Golobocanin et al. [2004](#page-9-0)) were marked with bold numbers.

Each type of PAH source may provide an individual profile or signature. As shown in Table 3, PC1 was heavily loaded on Flu, BaA, Chr, BbF, BaP, and DahA/BghiP. According to the literature, this source appears as oil combustion procedure in nature. Flu and Chr are typical markers of petroleum combustion, and BaA, BaP, and BghiP were found to be enriched in oil burning emission

**Table 3** Rotated component loadings of three principal components (PCs) for PAH compositions in the sediments of the Yellow River Delta

<b>PAHs</b>	PC <sub>1</sub>	PC <sub>2</sub>	PC <sub>3</sub>
Nap	0.69	0.12	
Acy	0.38	0.25	0.53
Ace	0.26	0.90	0.15
Flu	0.81	0.44	
Phe	0.12	0.87	0.34
Ant		0.95	
Fla	0.15	0.88	0.24
Pyr	0.55	0.78	
BaA	0.88		
Chr	0.97		
<b>BbF</b>	0.90	0.22	0.17
BkF		0.13	0.90
BaP	0.96	0.15	0.12
DahA/BghiP	0.96		0.15
IcdP	0.65		
Explained variance (%)	50.3	22.7	8.2

PCA loading values lower than 0.1 are not presented and those higher than 0.7 are in bold

(Harrison et al[.](#page-9-0) [1996;](#page-9-0) Larsen and Bake[r](#page-9-0) [2003;](#page-9-0) Yang et al[.](#page-10-0) [1998\)](#page-10-0). In the YRD, oil wells spread over the estuary with petroleum waste combusted evermore. Thus, it is reasonable to assign oil combustion as an important PAH source contributor here.

PC2 was composed of high loadings of Ace, Phe, Ant, Fla, and Pyr, which were related to source of wood combustion (Duval and Friedlander [1981](#page-8-0)). Since bulrush and wood burning in marsh area and straw burning in agriculture field are ubiquitous in the YRD, biomass combustion is supposed to be a responsible source of PAHs.

The factor of PC3 had high loadings on BkF, which was reported to be dominant as tracers for diesel combustion (Larsen and Bake[r](#page-9-0) [2003;](#page-9-0) Venkataraman et al[.](#page-10-0) [1994](#page-10-0)). This is supposedly attributed to the oil exploitation in the Shengli Oil Field by oil extraction machines located in the YRD. Accordingly, PC3 is inferred to indicate a diesel combustion source of PAHs.

Percent contribution of different PAH sources were quantified by MLR analysis. By performing stepwise procedure, PC1 to PC3 representing oil burning, biomass combustion, and diesel emission <span id="page-8-0"></span>sources were regressed against the sum of PAHs. The MLR equation is:

$$
\sum PAHs = 0.941 PC1 + 0.855 PC2 + 0.788 PC3
$$
\n(1)

The mean contribution of each PAH source was estimated from Eq. 1, i.e., 36.4% for oil burning, 33.1% for biomass combustion, and 30.5% for diesel emission from machines.

Emission inventory of PAH sources gave rise to complex mixtures of PAHs in the sediments of the YRD. The PCA represented accordant results with the diagnostic ratios of PAHs which presumed the mixed sources of pyrogenic- and petrogenic-deriving PAHs in the YRD.

## **Conclusions**

In this study, PAH distribution, possible adverse ecological effects, and their possible sources were identified in the sediments from the YRD. Compared with other reported deltas, the YRD presented generally low or medium PAH levels. Among the four regions (i.e., coast reach, inhabited areas, drilling platforms, and marsh areas) of the YRD, the lowest concentrations of PAHs were observed in the coast reach areas. The spatial distribution of PAHs was site specific, i.e., highring PAHs dominated the profiles in the coast reach, whereas low-ring PAHs presented as major fractions in the inhabited area, drilling platform, and marsh area. Ecological risk assessment for PAHs indicated that adverse effects would rarely occur in the sediments of the YRD. PAH source identification qualified the complex mixtures of PAH sources in the YRD, including oil burning (36.4%), biomass combustion (33.1%), and diesel emission sources (30.5%).

**Acknowledgements** The research was supported by the National Basic Research Program of China (973 Project, 2006CB403303) and the National Science Foundation for Distinguished Young Scholars (50625926). We gratefully acknowledge project 40701166 supported by the National Natural Science Foundation of China.

#### **References**

- Bihari, N., Fafandel, M., & Piskur, V. (2007). Polycyclic aromatic hydrocarbons and ecotoxicological characterization of seawater, sediment, and mussel *Mytilus galloprovincialis* from the Gulf of Rijeka, the Adriatic Sea, Croatia. *Archives of Environmental Contamination and Toxicology, 52*, 379– 387. doi[:10.1007/s00244-005-0259-5.](http://dx.doi.org/10.1007/s00244-005-0259-5)
- Chen, C. S. (2005). Ecological risk assessment for aquatic species exposed to contaminants in Keelung River, Taiwan. *Chemosphere, 61*, 1142–1158. doi[:10.1016/j.chemosphere.2005.02.077.](http://dx.doi.org/10.1016/j.chemosphere.2005.02.077)
- Chen, S. J., Luo, X. J., Mai, B. X., Sheng, G. Y., Fu, J. M., & Zeng, E. Y. (2006). Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the Northern South China Sea. *Environmental Science & Technology, 40*, 709–714. doi[:10.1021/es052060g.](http://dx.doi.org/10.1021/es052060g)
- Chen, J. W., Peijnenburg, W. J. G. M., Quan, X., Chen, S., Martens, D., Schramm, K. W., et al. (2001). Is it possible to develop a QSPR model for direct photolysis half-lives of PAHs under irradiation of sunlight? *Environmental Pollution, 114*, 137–143. doi[:10.1016/S0269-7491\(00\)00195-0.](http://dx.doi.org/10.1016/S0269-7491(00)00195-0)
- Chen, J. Y., Taniguchi, M., Liu, G. Q., Miyaoka, K., Onodera, S., Tokunaga, T., et al. (2007). Nitrate pollution of groundwater in the Yellow River delta, China. *Hydrogeology Journal, 15*, 1605–1614. doi[:10.1007/s10040-007-0196-7.](http://dx.doi.org/10.1007/s10040-007-0196-7)
- Chiou, C. T., McGroddy, S. E., & Kile, D. E. (1998). Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. *Environmental Science & Technology, 32*, 264–269. doi[:10.1021/es970614c.](http://dx.doi.org/10.1021/es970614c)
- Dahle, S., Savinov, M. V., Matishov, G. G., Evenset, A., & Næs, K. (2003). Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara Sea shelf, Gulf of Ob and Yenisei Bay. *The Science of the Total Environment, 306*, 57–71. doi[:10.1016/](http://dx.doi.org/10.1016/S0048-9697(02)00484-9) [S0048-9697\(02\)00484-9.](http://dx.doi.org/10.1016/S0048-9697(02)00484-9)
- Duval, M. M., & Friedlander, S. K. (1981). Source resolution of polycyclic aromatic hydrocarbons in the Los Angeles atmospheres: Application of a CMB with first order decay. USEPA Report EPA-600/2-81-161, Washington DC, USA.
- Fang, H. L., Gao, H. L., & Kearney, M. (2005). Georelational analysis of soil type, soil salt content, landform, and land use in the Yellow River Delta, China. *Environmental Management, 35*, 72–83. doi[:10.1007/s00267-004-3066-2.](http://dx.doi.org/10.1007/s00267-004-3066-2)
- Fang, G. C., Wu, Y. S., Chang, C. N., & Ho, T. T. (2006). A study of polycyclic aromatic hydrocarbons concentrations and source identifications by methods of diagnostic ratio and principal component analysis at Taichung chemical Harbor near Taiwan Strait. *Chemosphere, 64*, 1233–1242. doi[:10.](http://dx.doi.org/10.1016/j.chemosphere.2005.11.031) [1016/j.chemosphere.2005.11.031.](http://dx.doi.org/10.1016/j.chemosphere.2005.11.031)
- Fernandes, M. B., Sicre, M. A., Boireau, A., & Tronczynski, J. (1997). Polyaromatic hydrocarbon

<span id="page-9-0"></span>(PAH) distributions in the Seine River and its estuary. *Marine Pollution Bulletin, 34*(11), 857–867. doi[:10.1016/S0025-326X\(97\)00063-5](http://dx.doi.org/10.1016/S0025-326X(97)00063-5)

- Gevao, B., Al-Bahloul, M., Zafar, J., Jones, K. C., & Hamilton, T. J. (2007). Polycyclic aromatic hydrocarbons in indoor air and dust in Kuwait: implications for sources and nondietary human exposure. *Archives of Environmental Contamination and Toxicology, 53*, 503–512. doi[:10.1007/s00244-006-0261-6.](http://dx.doi.org/10.1007/s00244-006-0261-6)
- Gevao, B., Jones, K. C., & Hamilton, T. J. (1998). Polycyclic aromatic hydrocarbon (PAH) deposition to and processing in a small rural lake, Cumbria UK. *The Science of the Total Environment, 215*, 231–242. doi[:10.1016/S0048-9697\(98\)00129-6.](http://dx.doi.org/10.1016/S0048-9697(98)00129-6)
- Ghosh, U., Gillette, J. S., Luthy, R. G., & Zare, R. N. (2000). Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environmental Science & Technology, 34*, 1729–1736. doi[:10.1021/es991032t.](http://dx.doi.org/10.1021/es991032t)
- Golobocanin, D. D., Skrbic, B. D., & Miljevic, N. R. (2004). Principal component analysis for soil contamination with PAHs. *Chemometrics and Intelligent Laboratory Systems, 72*, 219–223. doi[:10.1016/](http://dx.doi.org/10.1016/j.chemolab.2004.01.017) [j.chemolab.2004.01.017.](http://dx.doi.org/10.1016/j.chemolab.2004.01.017)
- Harrison, R., Smith, D. J. T., & Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science & Technology, 30*, 825–832. doi[:10.1021/es950252d.](http://dx.doi.org/10.1021/es950252d)
- IARC (1987). *IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Overall evaluation of carcinogenicity: An updating of IAPC monographs* (Volumes 1–42, Suppl. 7). International Agency for Research on Cancer, Lyon, France.
- Larsen, R. K., & Baker, J. E. (2003). Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environmental Science & Technology, 37*, 1873–1881. doi[:10.1021/es0206184.](http://dx.doi.org/10.1021/es0206184)
- Li, R. W., Li, H., Li, Y., Zhang, S. S., Qian, Z., Ma, Z. P., et al. (2001). Study of the heavy metals, nitrogen and phosphorus contaminants in the sediments of the Yellow River Delta. *Acta Sedimentologica Sinica, 19*, 622–629.
- Li, G. C., Xia, X. H., Yang, Z. F., Wang, R., & Voulvoulis, N. (2006). Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environmental Pollution, 144*, 985–993. doi[:10.1016/j.envpol.2006.01.047.](http://dx.doi.org/10.1016/j.envpol.2006.01.047)
- Liu, W. X., Chen, J. L., Lin, X. M., & Tao, S. (2006). Distribution and characteristics of organic micropollutants in surface sediments from Bohai Sea. *Environmental Pollution, 140*, 4–8. doi[:10.1016/j.envpol.2005.08.074.](http://dx.doi.org/10.1016/j.envpol.2005.08.074)
- Liu, G. Q., Zhang, G., Li, X. D., Li, J., Peng, X. Z., & Qi, S. H. (2005b). Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River Estuary, South China. *Marine Pollution Bulletin, 51*, 912–921. doi[:10.1016/j.marpolbul.2005.02.038.](http://dx.doi.org/10.1016/j.marpolbul.2005.02.038)
- Liu, X., Zhang, G., Jones, K. C., Li, X. D., Peng, X. Z., & Qi, S. H. (2005a). Compositional fractionation of polycyclic aromatic hydrocarbons (PAHs)

in mosses (*Hypnum plumaeformae* Wils.) from the northern slope of Nanling Mountains, South China. *Atmospheric Environment, 39*, 5490–5499. doi[:10.1016/j.atmosenv.2005.05.048.](http://dx.doi.org/10.1016/j.atmosenv.2005.05.048)

- Long, E. R., Macdonald, D. D., Smith, S. L., & Calder, F. D. (1995). Incidence of adverse biological effects with ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management, 19*, 81–97. doi[:10.1007/BF02472006.](http://dx.doi.org/10.1007/BF02472006)
- Luo, X. J., Chen, S. J., Mai, B. X., Yang, Q. S., Sheng, G. Y., & Fu, J. M. (2006). Polycyclic aromatic hydrocarbons in suspended particulate matter and sediments from the Pearl River Estuary and adjacent coastal areas, China. *Environmental Pollution, 139*, 9–20. doi[:10.1016/j.envpol.2005.05.001.](http://dx.doi.org/10.1016/j.envpol.2005.05.001)
- Mai, B. X., Fu, J. M., Sheng, G. Y., Kang, Y. H., Lin, Z., Zhang, G., et al. (2002). Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environmental Pollution, 117*, 457–474. doi[:10.1016/S0269-7491\(01\)00193-2.](http://dx.doi.org/10.1016/S0269-7491(01)00193-2)
- Mai, B. X., Fu, J. M., Zhang, G., Lin, Z., Min, Y. S., Sheng, G. Y., et al. (2001). Polycyclic aromatic hydrocarbons in sediments from the Pearl river and estuary, China: spatial and temporal distribution and sources. *Applied Geochemistry, 16*, 1429–1445. doi[:10.1016/S0883-2927\(01\)00050-6.](http://dx.doi.org/10.1016/S0883-2927(01)00050-6)
- Nisbet, C., & LaGoy, P. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology, 16*, 290– 300. doi[:10.1016/0273-2300\(92\)90009-X.](http://dx.doi.org/10.1016/0273-2300(92)90009-X)
- Niu, J. F., Chen, J. W., Martens, D., Henkelmann, B., Quan, X., Yang, F. L., et al. (2004). The role of UV-B on the degradation of PCDD/Fs and PAHs sorbed on surfaces of spruce (*Picea abies* (L.) Karst.) needles. *The Science of the Total Environment, 322*, 231–241. doi[:10.1016/j.scitotenv.2003.09.017.](http://dx.doi.org/10.1016/j.scitotenv.2003.09.017)
- Olajire, A. A., Altenburger, R., Kuster, E., & Brack, W. (2005). Chemical and ecotoxicological assessment of polycyclic aromatic hydrocarbons-contaminated sediments of the Niger Delta, southern Nigeria. *The Science of the Total Environment, 340*, 123–136. doi[:10.1016/j.scitotenv.2004.08.014](http://dx.doi.org/10.1016/j.scitotenv.2004.08.014)
- Ping, L. F., Luo, Y. M., Zhang, H. B., Li, Q. B., & Wu, L. H. (2007). Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. *Environmental Pollution, 147*, 358–365. doi[:10.1016/j.envpol.2006.05.027.](http://dx.doi.org/10.1016/j.envpol.2006.05.027)
- Santschi, P. H., Presley, B. J., Wade, T. L., Garcia-Romero, B., & Baskaran, M. (2001). Historical contamination of PAHs, PCBs, DDTs, and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. *Marine Environmental Research, 52*, 51–79. doi[:10.1016/S0141-1136\(00\)00260-9.](http://dx.doi.org/10.1016/S0141-1136(00)00260-9)
- Shi, Z., Tao, S., Pan, B., Liu, W. X., & Shen, W. R. (2007). Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China. *Environmental Pollution, 146*, 492–500. doi[:10.](http://dx.doi.org/10.1016/j.envpol.2006.07.009) [1016/j.envpol.2006.07.009.](http://dx.doi.org/10.1016/j.envpol.2006.07.009)
- Solomon, K., Giesy, J., & Jones, P. (2000). Probabilistic risk assessment of agrochemicals in the environ-

<span id="page-10-0"></span>ment. *Crop Protection (Guildford, Surrey), 19*, 649– 655. doi[:10.1016/S0261-2194\(00\)00086-7.](http://dx.doi.org/10.1016/S0261-2194(00)00086-7)

- Song, J. M. (2000). Transferable phosphorus in sediments of the Huanghe River estuary adjacent waters. *Marketing Science, 24*, 42–45.
- Tao, S., Cao, H. Y., Liu, W. X., Li, B. G., Cao, J., Xu, F. L., et al. (2003). Fate modeling of phenanthrene with regional variation in Tianjin, China. *Environmental Science & Technology, 37*, 2453–2459. doi[:10.1021/es021023b.](http://dx.doi.org/10.1021/es021023b)
- Tolosa, I., Mora, S. D., Sheikholeslami, M. R., Villeneuve, J. P., Bartocci, J., & Cattini, C. (2004). Aliphatic and aromatic hydrocarbons in coastal Caspian sea sediments. *Marine Pollution Bulletin, 48*, 44–60. doi[:10.1016/S0025-326X\(03\)00255-8.](http://dx.doi.org/10.1016/S0025-326X(03)00255-8)
- USEPA. (1993). *Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons*. EPA/600/R-93/089, Office of Research and Development, Washington DC, USA.
- USEPA. (2000a). *Implementation Plan for Probabilistic Ecological Assessments—Terrestrial Systems*. Technical Progress Report. <http://www.epa.gov/scipoly/sap/> (Accessed 5 April 2000).
- USEPA. (2000b). *Technical Progress Report of the Implementation Plan for Probabilistic Ecological Assessments—Aquatic Systems*. [http://www.epa.gov/](http://www.epa.gov/scipoly/sap/) [scipoly/sap/](http://www.epa.gov/scipoly/sap/) (Accessed 5 April 2000).
- Venkataraman, C., Lyons, J. M., & Friedlander, S. K. (1994). Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization.

*Environmental Science & Technology, 28*, 555–562. doi[:10.1021/es00053a005.](http://dx.doi.org/10.1021/es00053a005)

- Wang, X. L., Tao, S., Dawson, R. W., & Xu, F. L. (2002). Characterizing and comparing risks of polycyclic aromatic hydrocarbons in a Tianjin wastewaterirrigated area. *Environmental Research, 90*, 201–206. doi[:10.1016/S0013-9351\(02\)00026-9.](http://dx.doi.org/10.1016/S0013-9351(02)00026-9)
- Xu, S. Y., Gao, X. J., Liu, M., & Chen, Z. L. (2001). China's Yangtze estuary: II. Phosphorus and polycyclic aromatic hydrocarbons in tidal flat sediments. *Geomorphology, 41*, 207–217. doi[:10.1016/](http://dx.doi.org/10.1016/S0169-555X(01)00117-9) [S0169-555X\(01\)00117-9.](http://dx.doi.org/10.1016/S0169-555X(01)00117-9)
- Xu, X. G., Lin, H. P., & Fu, Z. Y. (2004). Probe into the method of regional ecological risk assessment—a case study of wetland in the Yellow River Delta in China. *Journal of Environmental Management, 70*, 253–262. doi[:10.1016/j.jenvman.2003.12.001.](http://dx.doi.org/10.1016/j.jenvman.2003.12.001)
- Yang, H. H., Lee, W. J., Chen, S. J., & Lai, S. O. (1998). PAH emission from various industrial stacks. *Journal of Hazardous Materials, 60*, 159–174. doi[:10.1016/S0304-3894\(98\)00089-2.](http://dx.doi.org/10.1016/S0304-3894(98)00089-2)
- Yuan, D. X., Yang, D. N., Wade, T. L., & Qian, Y. R. (2001). Status of persistent organic pollutants in the sediment from several estuaries in China. *Environmental Pollution, 114*, 101–111. doi[:10.1016/](http://dx.doi.org/10.1016/S0269-7491(00)00200-1) [S0269-7491\(00\)00200-1.](http://dx.doi.org/10.1016/S0269-7491(00)00200-1)
- Yue, T. X., Xu, B., & Liu, J. Y. (2004). A patch connectivity index and its change in relation to new wetland at the Yellow River Delta. *International Journal of Remote Sensing, 25*, 4617–4628. doi[:10.1080/0143116031000101549.](http://dx.doi.org/10.1080/0143116031000101549)