Characterization, ecological risk assessment and source diagnostics of polycyclic aromatic hydrocarbons in water column of the Yellow River Delta, one of the most plenty biodiversity zones in the world

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ABSTRACT

As one of the most active regions of land–ocean interaction among the large river deltas in the world, the Yellow River Delta (YRD) gains increasing concern on its ecological and environmental conditions. However, few studies on polycyclic aromatic hydrocarbons (PAHs) have been reported for this area. In this study, the distribution characteristics, probabilistic risk and possible sources of PAHs were investigated in the water column of the YRD. The PAH concentrations were found to be at relatively low or medium levels (121.3 ng L^{-1} in water and 209.1 ng g^{-1} in suspended particulate matter (SPM) on average), and the result of probability risk assessment additionally elucidated low PAH ecological risk in the YRD. The PAH composition showed that low and moderate molecular PAHs were the major species in water phase, whearas the SPM showed a different proportion of each PAH composition. An interesting result was found that low-ring PAHs and salinity in this land–ocean interaction area had a positive relationship ($R = 0.609$). For PAH source identification, both diagnostic ratios of selected PAHs and principal component analysis (PCA) with multiple linear regression (MLR) analysis were studied, suggesting mixed sources of pyrogenic and petrogenic deriving PAHs in the YRD.

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1. Introduction

As a typical ecosystem of littoral wetland in estuary, the Yellow River Delta (YRD) in China has enormous biological resources including precious and rare species. Actually, it is considered to be an important migration station, wintering habitat and breeding farm for birds in the inland of Northeast Asia and around the Pacific Ocean area [1]. Due to its environmental significance and ecological sensitivity, the YRD is vitally significant to be protected. However, as the YRD located at the end of the Yellow River, it admits the incoming water from the middle and lower reaches, where national petrochemical industry plants, mines, metallurgy factories and many other pollution sources are located [2]. In addition, the industry in the YRD developed rapidly due to the exploitation of the Shengli Oil Field; and as the largest delta in China, the YRD has become a major region for the development of agriculture and fisheries [3]. The rapidly economic development probably results in significant polycyclic aromatic hydrocarbon (PAH) pollution to aquatic environment here. Actually, oil industry, agriculture and aquaculture systems are all potential sources of PAHs, which have toxic effects on aquatic lives and show a probable carcinogenicity to human beings [4]. However, most contaminant studies on the YRD focused on distributions of nitrogen and phosphorus [5,6], few studies on PAHs were reported for this area.

PAHs are one of the most important classes of persistent organic contaminants, which are ubiquitous pollutants in the environment that are generally formed by incomplete combustion of fossil fuels or organic matter [7]. Sixteen PAH compounds have been recommended as priority pollutants by the United States Environmental Protection Agency (USEPA) [8]. PAH distributions in aquatic environments and potential human health risks have become foci of water quality research, because they can provide important information on potential impact of anthropogenic activities on aquatic environments [2]. However, recent studies on PAHs in aquatic environment of coastal areas in China have mostly concentrated on the southern sea areas [9,10] and few for the YRD has been surveyed before, although it is one of the most plenty biodiversity zones in the world and the most integrated wetland ecological system in China. Thus, studies on PAHs concentration characteristics and their ecological risk assessment in the YRD would be very informative.

The objectives of this study were to examine the PAH concentrations in water column (including the water and suspended particulate matter (SPM) phases) and to assess their potential eco-toxicological effect in the YRD. Moreover, possible PAH sources were

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identified by both diagnostic ratios and principal component analysis (PCA) with multiple linear regression (MLR) operation.

2. Materials and methods

2.1. Study area and sample collection

The Yellow River Delta, geographically spanning from 118°07′E to 119°18′E and from 36°55′N to 38°12′N, is situated on the south side of the Bohai Sea with a warm-temperate monsoon climate. Samples in this study were collected from 42 sites for surface water and 15 sites for SPM in the YRD during May–August in 2007 (Fig. 1). Water samples (all spots in Fig. 1) were collected with pre-cleaned dark glass bottles. The values of pH, dissolved oxygen (DO) and salinity of water samples were tested in situ by digital pH meter, dissolved oxygen meter and salinometer, respectively. In addition, water quality parameters such as chemical oxygen demand (COD), nitrite, nitrate and phosphate values were determined calorimetrically. Glass fibre filters (0.45 μm effective pore sizes, Beijing Shenghe Membrane Science and Technology Co., China) for separating SPM from water were baked at 450 °C for 4 h. After the SPM collection, the filters with enough SPM samples (solid spots in Fig. 1) were wrapped with aluminum foil and transported to the laboratory immediately. All sampling containers were in sequence washed with deionized water, acetone, dichloromethane and the river samples before using.

2.2. Analytical methods

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 chromatographic grade and obtained from Dikma (USA). Filtered water samples were extracted using a solid phase extraction (SPE) system from Supelco (Sigma–Aldrich Co., Bellefonte, USA), following published procedures [11]. The SPE cartridges (Supelclean LC-18) were washed with 5 mL of dichloromethane, 5 mL of methanol and 5 mL of deionized water. Two liters of water samples flowed through the treated cartridges at a controlled flow rate of 6 mL min^{-1} under vacuum. After the extraction procedure, the cartridges were eluted

with 10 mL of dichloromethane before further analysis. The SPM samples were freeze-dried until constant weights were maintained. Using combusted glass fibre filters as blanks, SPM samples were 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 4000 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 extract of water or SPM sample 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, concentrated to 1.0 mL by the rotary evaporator prior to quantitative analysis.

PAHs were analyzed by a Water column 1525 high-performance liquid chromatography (HPLC) system (Water column, USA) with Water column 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 mm × 4.6 mm, particle size 5 μm, Varian, USA) followed by a ChromSep C18 column (250 mm × 4.6 mm, particle size 5 μm, Varian, USA). The HPLC separation of the analytes was operated at a flow rate of 1.0 mL min^{-1} using a gradient elution program in which methanol–water was used as mobile phase. Owning to the relatively high environmental temperature during HPLC operations, DahA and BghiP were not individually detected. These two compounds were analyzed together as DahA/BghiP in this study.

2.3. Quality control

Quantifications of PAHs were done using external standards, with correlation coefficients for calibration curves all higher than 0.998. Before the onset of the extraction and analysis program, recovery experiments were undertaken by spiking the 16 PAHs standard solution with water and SPM samples. The six parallel experiments indicated that recoveries for the 16 PAHs were 55–95% for water and 60–105% for SPM (except Nap, 35 ± 5%), respectively. The respective relative standard deviations (RSDs) ranged from 5.2%
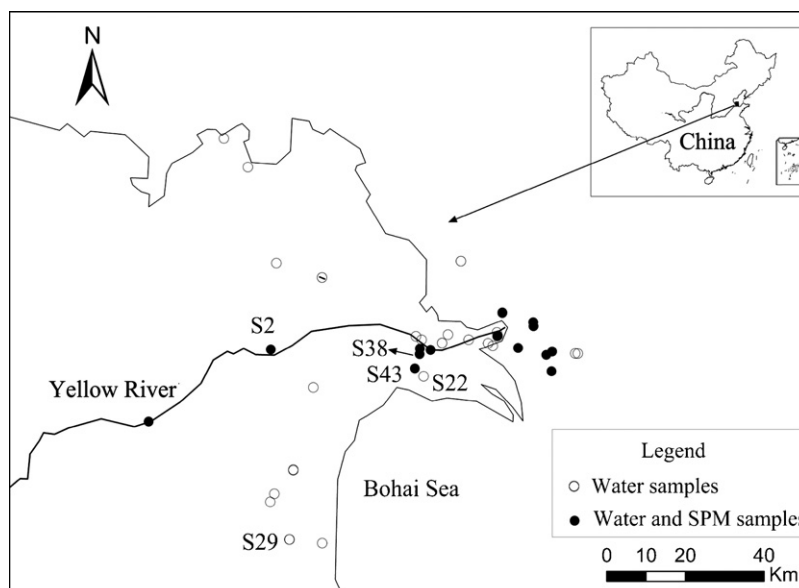

Fig. 1. Sampling sites in the Yellow River Delta.

to 15.6% for all samples. Under analytical condition, detection limits for the 16 PAHs ranged from 0.87 to 7.12 ng L^{-1} for water samples and from 0.34 to 4.05 ng g^{-1} for SPM. Method blanks operation showed no detectable amounts of PAHs contamination except for naphthalene.

3. Results and discussion

3.1. PAH distribution characteristics

3.1.1. PAH concentrations

The concentrations of the 16 PAHs in both water and SPM are depicted in Table 1. Most of the PAHs were detected except Acy in water. The average values of total PAH concentration ($\sum$PAHs) in water and SPM were 121.3 ng L^{-1} and 209.1 ng g^{-1}, respectively. The median concentrations of individual PAHs were basically lower than the corresponding average concentrations, 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.

The total PAH concentrations in aqueous phase kept constant relatively (CV = 47.4%, *n* = 42), however, those in SPM varied obviously (CV = 79.0%, *n* = 15). This was in accordance with the result of middle and lower Yellow River [2]. The highest $\sum$PAHs concentrations in water were found in sites S22 and S29 (334.6 and 289.1 ng L^{-1}, respectively), likely because they located in inhabited areas and the anthropologic pollution may act as the main PAH origin in the YRD. In contrast to aqueous phase, S38 and S43 in the marsh area had the highest concentrations of $\sum$PAHs (675.4 and 473.8 ng g^{-1}, respectively) with several times higher than that of the other SPM sampling sites. This could be attributed to the special SPM property in the marsh area. Comparing with other samples, SPM from marsh area was mainly composed of suspended plankton materials instead of the traditional sandy particles. Thus, PAHs had greater tendency to associate with solid phase matrix in the marsh area due to their strong accumulation trend on plankton materials [12]. In addition, the aqueous PAH concentrations in these sites were observed relatively low (70.2 and 64.8 ng L^{-1}, respectively), further indicating the strong sorption of PAHs onto the suspended plankton materials.

By comparing the total PAH concentrations in this study with those of some other reported estuary and offshore areas [13–16], the PAH values in the YRD were generally found to be at low or medium levels. When compared with the data of middle and lower Yellow River in China [2], $\sum$PAHs in the YRD showed lower concentrations.

3.1.2. PAH composition

For further discrimination for PAH distribution, the composition profiles of PAHs by different benzene rings were investigated. The compositional pattern of PAHs between the particle phase and aqueous phase were found to be different. The water samples were relatively depleted in high molecular weight PAHs (5–6 rings = 9.7%) and enriched in relatively low-ring PAHs (2–3 rings = 45.4%; 4 rings = 44.9%, respectively). This was attributed to the lower aqueous solubility and hydrophobic nature of the high molecular weight PAHs [2]. The high contents of lower molecular weight PAHs suggest a relatively recent local sources of PAHs entering into the river [17]. Compared with the water samples, SPM showed different proportion of each PAH composition, which was found to be 39.5% for 2–3-ring PAHs, 31.3% for 4-ring PAHs and 29.2% for 5–6-ring PAHs, respectively. Among all the SPM sites, S2 near a busy bridge showed especially higher proportion of moderate and high molecular weight PAHs (4 rings = 45.6%; 5–6 rings = 40.6%), possibly due to the diesel emission from vehicles on the bridge. For further study of possible correlation of PAHs between particle and aqueous phases, quantitative relationship analysis was carried out, and the results showed that no progressive relationship appeared among PAHs in different phases in this study (i.e. R^2 = 0.541 for 2–3 rings, R^2 = 0.053 for 4 rings, R^2 = 0.209 for 5–6 rings).

For individual PAH, it should be cautioned that BaP as a reported carcinogen was detected in 85.7% of water samples, and among them 19.0% samples exceeded the Environmental Quality Standard for Surface Water in China (2.8 ng L^{-1}, GB3838-2002). The sampling sites with high concentration of BaP were mainly situated in the river–sea juncture, the inhabited area and the stations near bridges, which was supposed to be on account of that BaP originated from the release of resuspended sediments [18], biomass combustion [19] and vehicle emission [20].

3.1.3. Correlation of PAHs with the physicochemical parameters

In this study, routine water quality parameters such as pH, DO, COD, NH$_4^-$, NO$_2^-$, NO$_3^-$ and AP were analyzed, and the salinity in water samples was also quantified. The quantitative analysis of the possible relationships were carried out among the PAHs in aqueous phase and water physicochemical parameters, and the results are presented in Table 2.

Table 1
Concentrations of PAHs in water and SPM phases from the Yellow River Delta.

PAHs	Water (ng L^{-1})				SPM (ng g^{-1})			
	Range	Mean	Mid[a]	CV[b] (%)	Range	Mean	Mid[a]	CV[b] (%)
Nap	1.9–77.2	14.8	7.6	108.7	ND ~15.9	7.5	5.4	72.2
Acy	ND	ND	ND	ND	ND ~41.5	9.1	ND	167.8
Ace	4.2–42.3	14.5	13.1	52.8	1.1–63.7	20.7	13.0	91.0
Flu	ND ~24.4	8.0	7.5	72.8	1.2–32.2	10.0	6.4	98.4
Phe	4.8–76.8	18.2	13.1	72.1	5.8–139.6	34.8	23.7	110.2
Ant	ND ~15.8	1.5	1.2	70.3	ND ~4.6	1.6	1.2	80.0
Fla	ND ~20.0	7.0	5.7	69.7	2.7–39.8	13.8	9.9	78.3
Pyr	ND ~87.7	9.0	6.0	151.8	1.6–53.3	14.2	12.2	94.2
BaA	ND ~18.2	2.7	1.2	156.8	4.3–83.5	22.5	14.4	102.0
Chr	5.3–77.4	33.4	33.9	38.2	1.9–69.8	16.4	9.9	102.8
BbF	ND ~17.8	3.5	2.1	123.0	3.6–36.3	11.7	11.1	71.0
BkF	ND ~9.9	2.0	1.4	107.4	0.7–29.0	7.8	5.7	89.7
BaP	ND ~9.7	1.9	1.3	101.3	4.5–48.6	12.0	8.3	90.2
DahA/BghiP	ND ~12.2	1.9	1.4	111.9	ND ~43.6	9.9	6.3	103.4
IcdP	ND ~14.2	2.8	2.0	95.8	4.0–67.5	16.9	11.2	93.1
$\sum$PAHs	64.8–334.6	121.3	106.3	47.4	65.6–675.4	209.1	153.4	79.0

ND: not detectable.

[a] Mid: median concentrations.

[b] CV: coefficient of variation.

Table 2
Correlation coefficients between PAH concentrations and water quality variables.

	Salinity	pH	DO	COD	Ammoniate	Nitrite	Nitrate	Phosphate
Nap	0.564[*]	−0.324	−0.040	0.257	−0.059	−0.143	−0.373	0.302
Ace	0.508[*]	−0.321	−0.037	0.168	−0.217	0.084	−0.299	0.088
Flu	0.578[*]	−0.161	0.047	0.099	−0.270	0.095	−0.263	0.178
Phe	0.449[*]	−0.075	−0.086	0.260	−0.209	0.176	−0.196	0.150
Ant	0.298	−0.273	−0.202	0.199	−0.235	0.054	−0.236	0.114
Fla	0.113	−0.360	−0.316	0.224	−0.215	−0.116	−0.403	0.201
Pyr	0.245	0.029	−0.101	0.267	−0.154	0.106	−0.184	0.046
BaA	0.059	−0.004	−0.252	0.188	−0.201	0.036	−0.120	0.164
Chr	−0.191	−0.157	−0.096	0.032	0.354	0.080	0.010	−0.169
BbF	−0.032	−0.316	−0.407	−0.003	−0.159	−0.103	−0.334	−0.011
BkF	0.031	−0.334	−0.323	0.063	−0.202	−0.080	−0.280	−0.033
BaP	0.186	−0.160	−0.293	0.067	−0.127	−0.008	−0.197	0.135
DahA/BghiP	0.276	0.056	−0.088	0.213	−0.218	0.064	−0.065	−0.039
IcdP	0.114	−0.082	−0.337	−0.014	0.017	−0.032	−0.168	−0.058
LMW	0.609[*]	−0.271	−0.055	0.265	−0.197	0.035	−0.347	0.325
MMW	0.069	−0.125	−0.198	0.225	0.052	0.083	−0.178	0.003
HMW	0.101	−0.234	−0.352	0.079	−0.189	−0.041	−0.257	−0.014
$\sum$PAHs	0.438[*]	−0.250	−0.162	0.272	−0.120	0.054	−0.322	0.200

[*] Correlation is significant in 0.01 level.

No general pattern of progressive relationship appeared between PAHs and water physicochemical parameters except salinity. As shown in Table 2, it is obvious that low-ring PAHs showed the highest positive correlation ($R = 0.609$) with salinity. As for individual PAHs, all 2–3-ring PAHs except Ant (i.e. Nap, Ace, Flu and Phe) present significant correlation with salinity, indicating that the salinity was responsible for the concentrations of low-ring PAHs.

As an active region of land–ocean interaction, the YRD area showed obvious salinity gradient, characterized by a mixture of fresh incoming water from the Yellow River and brackish seawater from the Bohai Sea. In the estuarine environment, salinity is also a factor influencing the partitioning behavior [21]. Zhou et al. [22] showed that the sorption coefficient (K_p) values are generally positively related with salinity, but no significant correlations were found between the K_p and salinity in the Humber Estuary. Moreover, some researchers studied the correlation between petroleum hydrocarbons (including PAHs) and salinity in the Alang–Sosiya ship breaking yard in India, and they showed that salinity had positive correlation with the concentrations of total petroleum hydrocarbons [23]. However, adverse conclusions revealed that PAHs presented lower aqueous concentrations in higher salinity water column [24]. Accordingly, the relationship between the concentrations of PAHs and salinities in water ambient requires further study.

3.2. Ecological risk assessment

In order to evaluate the integral PAH effects, BaP equivalency (BaP_{eq}) of PAHs are calculated based on the toxic equivalency factors (TEFs) for individual PAHs [25]. The range of BaP_{eq} in water and SPM samples were 0.00045–0.015 and 7.7–69.8, respectively. Based on BaP_{eq} of each sample, a probability risk assessment (PRA) procedure was adopted in this study to estimate PAH probabilistic ecological risk [26]. By employing Jarque–Bera method, the distribution of data for exposure concentrations and toxicological effects on sensitive species were tested, and the results indicated that all data were of log-normal distributed ($p > 0.05$). By using the means and standard deviations of exposure concentrations and toxicity data of BaP_{eq} for PAHs [27,28], the log-normal probability distribution curves for risk analysis were constructed. Fig. 2A presents the probability density curves for the exposure concentrations and toxicity data of the BaP_{eq} in water phase. The overlap area of 4.08×10^{-5} was quantified by Matlab 7.0, indicating a very low probability of toxic effect. Similarly, the probability of ecological risk in SPM phase was assessed with the probability density curves illustrated in Fig. 2B,

and the value of risk probability came to 1.13×10^{-7}. Accordingly, the potential risk of PAHs in the water column (including water and SPM phases) was rather low that adverse environmental events were supposed to rarely happen by PAH exposure in the YRD.

The joint probability curves (JPCs) which describe the probability of exceeding the concentration associated with a particular degree of effect are depicted in Fig. 3. It can be seen that the JPCs of BaP_{eq} in both water and SPM phases are close to the axes, indicating little probability of adverse effect [28,29]. From the JPC point, the probability of a particular set of exposure conditions being affected was quantified. Under current conditions, the proportion of species would be affected by 0.020% of the current observations in water
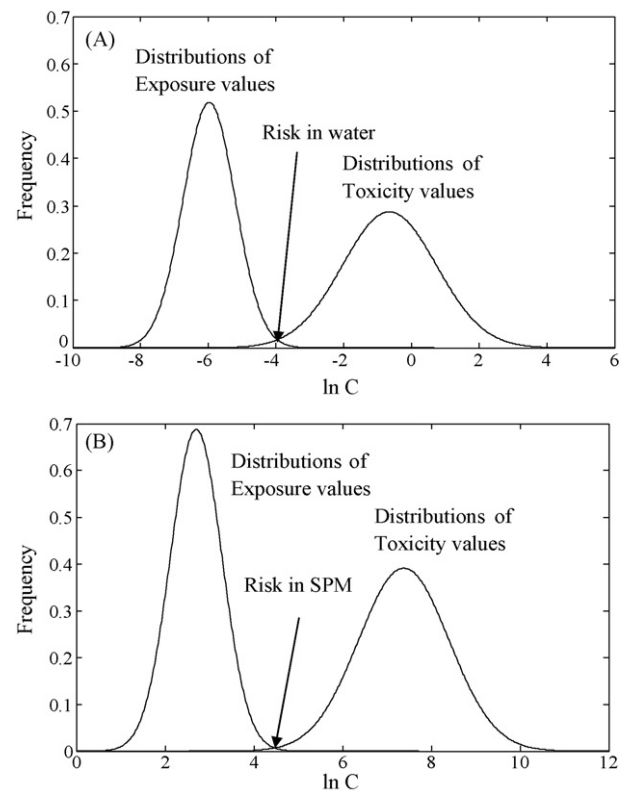

Fig. 2. Probability density curves for the exposure concentrations and toxicity data of the BaP_{eq} in (A) water and (B) SPM from the Yellow River Delta.
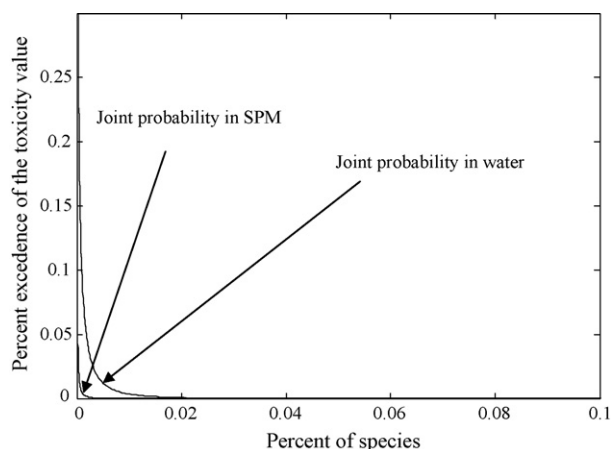
Fig. 3. Joint probability curves of the BaP_{eq} in water and SPM from the Yellow River Delta.

and 0.00034% in SPM when 5% of species will be affected. The result primarily indicated low ecological risk of PAHs in the YRD. However, as neither the probability of overlap in PRA nor the JPC point are very useful as quantitative predictors of risk [29], this result could only provide the information on relative risk of PAHs in the YRD.

3.3. Source diagnosis

3.3.1. Diagnostic ratios of PAHs

Inferring the sources of PAHs is widely considered to be very important to study the transport and fate of PAHs in environment [30]. Generally, ratios of various PAH concentrations have usually been undertaken to diagnose the possible sources of PAHs [13,31]. The ratios of PAH isomers with the same molecular weight were commonly used in PAH source analysis [31]. Among these isomer ratios, PAHs with molecular mass 178 and 202 are widely used to distinguish between combustion and petroleum sources [18]. In this study, bivariate plots of Ant/Phe against Fla/Pyr are depicted in Fig. 4 to examine the water and SPM samples, respectively.

Results from PAHs cross-plots for Ant/Phe against Fla/Pyr (Fig. 4) showed that the PAHs contamination in this study was probably from mixture sources of petroleum and combustion [31]. As oil fields spread over quite some regions in the YRD, oil-relevant origin PAHs apparently accounts for a significant proportion. On the other hand, vegetation and agricultural straw in the YRD wetland burned in the open air may have been sources of PAHs derived from the combustion of biomass. Moreover, gases from oil wells also make contributions to combustion sources of PAHs, because they get burned as soon as being generated. In addition, Li et al. [2] have revealed that in the middle and lower reaches of the Yellow River, PAHs mainly originated from coal
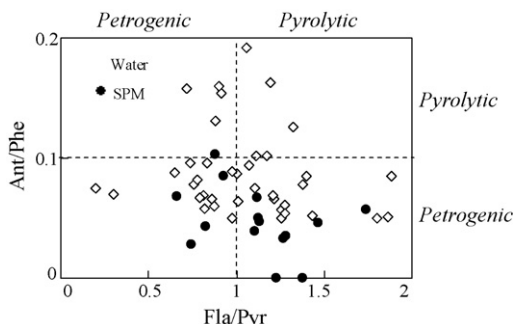

Fig. 4. PAHs cross-plots for the ratios of Fla/Pyr vs. Ant/Phe.

Table 3
Rotated component loadings of the principal components (PCs) for PAH compositions in water and SPM phases of the Yellow River Delta.

PAHs	PCs in water			PCs in SPM		
	PC1	PC2	PC3	PC1	PC2	PC3
Nap	–	–	0.83*	0.60	0.28	0.21
Acy	–	–	–	–	–	–
Ace	–	0.26	0.92*	0.45	0.83*	0.17
Flu	–	0.10	0.88*	0.46	0.85*	0.15
Phe	–	0.77*	0.56	0.36	0.84*	0.27
Ant	0.10	0.80*	0.50	0.12	0.93*	–
Fla	0.59	0.66	0.23	0.47	0.85*	–
Pyr	0.09	0.96*	0.11	0.60	0.69	–
BaA	0.54	0.76*	–	0.46	0.70*	0.32
Chr	–	0.16	0.15	0.88*	0.41	0.18
BbF	0.94*	0.25	–	0.84*	0.49	–
BkF	0.95*	0.28	–	0.91*	0.36	0.10
BaP	0.92*	0.32	–	0.94*	0.25	0.10
DahA/BghiP	0.37	0.88*	–	0.91*	0.32	–
IcdP	0.94*	0.14	–	0.93*	0.31	–
Explained variance (%)	48.0	25.1	10.7	71.7	11.0	6.8

–: PCA loading values lower than 0.1 are not presented.
* PCA loading values higher than 0.7.

burning, and this may also be a source of combustion PAHs in the YRD.

3.3.2. Principal component analysis with multiple linear regression

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. In this method, PCA was related to the information of source composition and MLR was used to quantify the source contribution [20]. The results of PCA analysis of PAH concentrations are tabulated in Table 3. Three principal components (PCs) were extracted for both water and SPM samples. The accumulative variances accounted for 83.8% and 89.5% of the total variance for water and SPM, respectively.

Each type of PAH source may provide an individual profile or signature. As depicted in Table 3, the PCs for water and SPM phases have similar loading characteristics on individual PAHs. PC1s were heavily loaded on high-ring PAHs such as BbF, BkF, BaP, IcdP, etc. According to the literature, this source appears oil combustion procedure in nature [20]. 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.

PC2s were composed of high loadings of some moderate-ring PAHs which were related to source of wood combustion [32]. 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 for water phase had high loadings on some low-ring PAHs, indicating oil exploitation in the Shengli Oil Field [13]. However, PC3 for SPM phase was heavily loaded on none of the individual PAHs. This is supposedly attributed to the relatively high water solubility of low-ring PAHs, and this result is consistent with the result of PAH compositional analysis in Section 3.1.2.

Percent contribution of different PAH sources were quantified by MLR analysis. By performing stepwise procedure, PC1 to PC3 representing oil burning, biomass combustion and oil leakage sources were regressed against the sum of PAHs. The MLR equations for water and SPM are:

$$\sum PAHs_{water} = 0.681PC1 + 0.474PC3 \quad (R^2 = 0.998) \tag{1}$$

$$\sum PAHs_{SPM} = 0.745PC1 + 0.845PC2 \quad (R^2 = 0.991) \tag{2}$$

The mean contribution of each PAH source in water and SPM phases were estimated from Eq. (1) and Eq. (2), respectively. The calculation revealed that 59.0% for oil burning and 41.0% for oil leakage contributed to the PAH source in water phase. And in SPM, 46.9% for oil burning and 53.1% for biomass combustion composed to the PAH source apportion. It can be concluded that oil burning procedure made much contribution to the PAHs in the water column of the YRD. In addition, PAHs from oil leakage were basically comprised in water phase, and biomass combustion was the main input of PAHs in SPM.

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. However, because the samples in this study were only collected in a short period, the source analysis here could just elucidate a relatively short-term contamination origin.

4. Conclusions

PAHs in water column of the Yellow River Delta in China was investigated in this study. Results demonstrated that the PAHs in the YRD (with the average concentrations of $121.3\,ng\,L^{-1}$ in water and $209.1\,ng\,g^{-1}$ in SPM) were at a relatively low or medium level by comparing with other reported studies. In addition, based on the probability risk assessment, PAHs in this study showed rarely adverse ecological effects in the YRD. The PAH compositional pattern was found varying in different phases with depleted high-ring PAHs in water. Moreover, correlation analysis between the PAHs and physicochemical parameters in water showed positive relationship ($R = 0.609$) between low-ring PAHs and salinity. For the PAH source diagnosis, both diagnostic ratios and principal component analysis with multiple linear regression were employed. They uniformly identified the complex PAH sources of oil burning, biomass combustion and petrogenic leakage in the water column of the YRD.

Acknowledgements

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