Potential source contributions and risk assessment of PAHs in sediments from the tail-reaches of the Yellow River Estuary, China: PCA model, PMF model, and mean ERM quotient analysis

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Abstract
Principal component analysis (PCA), positive matrix factorization (PMF), and the mean effects range-median quotient (MERM-Q) models were employed to determine occurrence levels, sources, and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Yellow River Estuary, China. Due to the grain size of sediments, cumulative effects, and distribution of oil fields, the total concentration of the 16 U.S. Environmental Protection Agency (US EPA) priority PAHs (T-PAHs) measured in sediments along transects in the offshore area was 119.51 ± 39.58 ng g\(^{-1}\) dry weight (dw), which is notably higher than that measured in rivers (75.00 ± 12.56 ng g\(^{-1}\) dw) and estuaries (67.94 ± 10.20 ng g\(^{-1}\) dw). PAH levels decreased seaward along all the studied transects in coastal Bohai Bay. Multivariate statistical analyses supported that PAHs in sediments were principally derived from coal and biomass combustion, oil pollution, and vehicular emissions. Based on the MERM-Q (0.0050 ± 0.0017), PAHs were at low potential of ecotoxicological contamination level. These results provide helpful information for protecting water resources and serving sustainable development in Construction of Ecological Civilization in the Yellow River Delta.

Keywords PAHs · Source apportionment · MERM-Q · Risk assessment · Spatial distribution · Yellow River Estuary

Introduction
Polycyclic aromatic hydrocarbons (PAHs) have been identified by the U.S. Environmental Protection Agency (USEPA) as priority pollutants globally (Wang et al. 2017). Because they are toxic, carcinogenic, and mutagenic, PAHs have gained considerable attention from scientists, governments, and the public (Yunker et al. 2002; Machado et al. 2014; Zanardi-Lamardo et al. 2019). The harm of PAHs mainly includes chemical carcinogenesis and phototoxicity. PAH-contaminated sediment may impact water quality and benthic organisms (Bandow et al., 2009). The damage of PAHs to plants is a kind of chronic injury, and the degree of injury is positively related to the concentration of PAHs (Chaineau et al. 1997). Human exposure to PAHs is mainly by inhalation of particulates carrying PAHs, dietary intake of contaminated food products, and direct contact with polluted soils (Davis et al. 2019). The source apportionment of PAHs in the environment has been well studied over the last 40 years (Davis et al. 2019). PAHs originated from pyrogenic (formed by combustion), petrogenic (derived from petroleum sources), and natural (biogenic or diagenetic) processes (Soclo et al. 2000; Stout et al. 2001; Kumar et al. 2017; Davis et al. 2019).

The Yellow River is an important source of water in China and one of the most sediment-laden rivers in the world. The Yellow River Delta (YRD) is an important oil industrial base. “Construction of High-efficiency Eco-economic Zone in the Yellow River Delta” and “Blue Economic Zone in Shandong Peninsula” have become national strategies in China (Dai et al. 2016). With the development of economy, coal combustion, industrial development, and exhaust emissions from
ships and vehicles, PAH pollution in the Yellow River Basin is becoming more and more serious. Therefore, it is important to study the concentration, spatial distribution, and source of PAHs in aquatic sediments, especially estuarine sediments, to evaluate the impact of sediment pollution and human activities on the ecological environment health of Yellow River. Owing to its ubiquitous distribution and toxic characteristics, PAHs have been studied in Yellow River Delta in recent years (Yang et al. 2009; Yuan et al. 2014a). PAH pollution levels have been found to be moderate in the soil and sediment, and low in the surface water and groundwater of the Yellow River Estuary (Li and Li 2017). The total concentrations of the 16 US EPA priority PAHs represent a very low pollution level, and in Yellow River Estuary, the petroleum combustion (Yuan et al., 2014a), biomass/coal combustion, natural gas combustion, and traffic emission are all possible sources of the PAHs (Yang et al. 2009; Yuan et al. 2014b). PAHs in water and sediments in the Cauca River, Colombia, have pyrogenic origin perhaps due to the effects of sugarcane burning during harvesting (Sarria-Villa et al., 2016).

To the best of our knowledge, detailed information on the spatial variability of PAHs distribution and potential ecotoxicological effect based on mean effects range-median quotient (MERM-Q) in sedimentary matter of Yellow River Estuary remain scarce, particularly reports covering Yellow River lower reaches, Yellow River estuary, and the adjacent offshore area in Bohai Sea. This study was designed to (i) analyze the regional differences in sediment PAHs from the Yellow River alone, the lower reaches, estuary, and its offshore area; (ii) quantitatively assess PAH pollution sources using principal component analysis (PCA) model; and (iii) assess potential ecotoxicological effects based on the MERM-Q. The results of this study provide valuable information on levels, sources, and potential risks of PAHs, for protecting water resources and serving the sustainable development in Construction of Ecological Civilization in the Yellow River Delta.

Material and methods

Study area and sample collection

The Yellow River is the 2nd largest river in China and the 6th largest river in the world. As the most sediment-filled big river on Earth, the Yellow River carries a huge amount of sediments to Bohai Sea every year (Yuan et al., 2014). Estuaries and coastal zones are the main areas situated between the ocean and lands. The water-sediment environment and water-salt condition of the Yellow River estuary are very complicated due to the combined influence of ocean and land hydrodynamics. Located on the YRD, Shengli Oil Field is the second biggest oil field in China. The oil exploitation activities will affect the input and deposition of organic matter in the Yellow River (Yuan et al. 2014b). In addition, the YRD has become a major region for the development of agriculture and fisheries. Rapid economic growth in the YRD raises concerns of significant of pollution and ecological environment protection.

Surface sediments (0–5 cm) were collected in April 2013 from the lower reaches of Yellow River (R1–R11), Yellow River Estuary (ES1–ES4), and its offshore area of Bohai Sea (MA1–5, MB1–4, MC1–4, and MD1–5 transects) (Fig. 1). The sediments were collected using a Van Veen style stainless steel grab sampler. The sediment sample was taken from each location three times and mixed to represent a sample from a sampling station. The weight of each sample was about 500–1000 g. The Lijin Hydrographic Station (R1) is the last hydrographic station before the Yellow River enters the Bohai Sea. R11 is the Xintan Oil Field Floating Bridge, which is regarded as the Yellow River’s entrance. The sediment samples packed in aluminum foil were transported to the laboratory within 48 h and frozen at −20 °C until analysis.

Sample extraction, separation, and GC-MS analysis

The procedure used in the present study for sample extract purification and fractionation of PAHs was modified from previous studies (Yang et al. 2009; Yuan et al. 2014a; Wang et al. 2017). Briefly, freeze-dried sediments (10 g) were washed and homogenized by a mortar and pestle. After grinding, the samples were packed with clean filter (paper was extracted) and extracted by the Soxhlet method. The sediment samples were extracted using the Soxhlet apparatus with n-hexane/dichloromethane (50/50) for 48 h. The extract was concentrated to about 1 mL on a rotating evaporator, 10 mL of n-hexane was added, and then concentrated to 1–2 mL to convert the solvent. Solvent replacement concentration was purified by adding silica gel alumina purification column. The glass chromatography column was packed with silica gel activated at 150 °C after Soxhlet extraction (100–200 mesh). The column was first eluted with n-hexane to remove aliphatic hydrocarbons and then with mixed dichloromethane and n-hexane (1:1, v/v) for PAHs.

PAHs were determined on an Agilent 7890A gas chromatography (GC) coupled to a 5975C mass selective detector (MS) equipped with a HP-5 MS capillary column (specification, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). Samples were injected in splitless mode and helium was used as the carrier gas. The injection temperature was 280 °C. The column temperature was programmed to ramp from 80 °C (held for 1 min) to 280 °C at a rate of 5 °C min⁻¹, and held at 280 °C for 12 min. On the other hand, each target PAH was quantified based on the retention time and the m/z ratio of an authentic PAH mixed standard (Sigma). Five surrogate standards (naphthalene-d8, phenanthrene-d10, dibenzothiophene-d10, fluoranthene-d10, and pyrene-d10) were added to all the samples to monitor the matrix effects. The quantification of each
individual PAH was calculated based on six-point calibration curves.

**Principal component analysis and PMF model**

In this paper, the source of PAHs in surface sediments from tail-reaches of Yellow River Estuary was analyzed by PCA to provide insight into the accuracy and quantification of source apportion. Data submitted for the analysis were arranged in matrix, where each column corresponds to one PAH component and each row represents sampling sites. Data matrices were evaluated through PCA, allowing the summarized data to be further analyzed and plotted. The statistical analysis software is SPSS 13.0.

PMF is a quantitative source analysis model based on multivariate factor analysis, which was developed by Paatero and Tapper (1994) and has been widely applied to the source analysis of PAHs in aerosols, soils, and sediments (Park et al. 2015; Xu et al. 2016). In this study, EPA PMF 5.0 model was used for PAH quantitative source analysis. The basic equation is as follows:

\[
X = GF + E \tag{1}
\]

\[
x_{ik} = \sum_{j=1}^{p} g_{ij} f_{jk} + e_{ik} \tag{2}
\]

where matrix \(X\) in Eq. (1) is approximated based on the product of the source contribution matrix \(G\) and source profile matrix \(F\), which is then added to the residual matrix \(E\). \(x_{ik}\) is the \(k\)th compound concentration measured in the \(i\)th sample, \(g_{ij}\) represents the contribution of the \(j\)th source to the \(i\)th sample, \(f_{jk}\) represents the mass fraction of the \(k\)th compound from the \(j\)th source, and \(e_{ik}\) is the residual. The goal of PMF is to minimize the object function \(Q(E)\), which is defined as the sum of the squared residues weighted by their respective uncertainties, based on Eq. (3).

\[
Q(E) = \sum_{i=1}^{n} \sum_{k=1}^{m} \left( \frac{e_{ik}}{u_{ik}} \right)^2 \tag{3}
\]

where \(u_{ik}\) is the uncertainty in the \(gth\) species for the \(ith\) sample. \(Q(E)\) in this study can be written based on Eq. (4):

\[
S_{ij} = \begin{cases} 
\frac{2 \times L_{MDL}}{\sqrt{(RSD \times x_{ik})^2 + (L_{MDL})^2}} & x_{ik} \leq L_{MDL} \\
\frac{x_{ik} > L_{MDL}} & x_{ik} > L_{MDL}
\end{cases} \tag{4}
\]

Where RSD is the relative standard deviation of compound concentration value, and \(L_{MDL}\) is the detection limit of the method.

**Quality assurance and quality control (QA and QC)**

Procedural blanks, spiked blanks, spiked matrixes, and parallel samples were performed to control data quality. As for PAHs, the recoveries ranged from 86.36 to 108.62% for all 16 target analytes. Analysis of the blanks confirmed that there was no introduced contamination or other interference over the whole experiment. The relative standard deviation was < 5%, indicating good repeatability.

**Results and discussion**

**Distribution of PAHs in surface sediments**

The variation in PAHs measured in surface sediments at the riverine, estuarine, and marine locations is shown in Fig. 2. It is clear that the total concentration of the 16 US EPA priority PAHs (T-PAHs) increased from the terminal channel diversion of the Yellow River toward the four transects (MA, MB, MC, and MD) in the marine area, which may be due to the accumulation of PAHs in the surface sediments of coastal Bohai Bay. The average T-
The PAH concentration of surface sediments from the offshore area transects was 119.51 ± 39.58 ng g\(^{-1}\) dry weight (dw), which was higher than that measured in riverine sediments in the tail-reaches (75.00 ± 12.56 ng g\(^{-1}\) dw) and estuarine sediments (67.94 ± 10.20 ng g\(^{-1}\) dw). Our results are consistent with previous studies with T-PAHs of 10.8–252 ng g\(^{-1}\) (Hui et al. 2009). In contrast, the spatial differences between river samples (downstream) and estuarine sediments are small. However, among the stations of each marine transect, stations MA1, MB1, MC1, and MD1 had the highest T-PAH concentration (Fig. 2a). These stations occur near the river mouth and are strongly influenced by anthropogenic inputs. T-PAH concentration at stations along each transect was influenced by the distance of land-based sediment transport and settlement. Sediments mainly settle at the second station of each transect where PAHs have accumulated and the highest pollutant concentrations occur. T-PAH concentrations decreased seaward into the Bohai Sea from stations MA2, MB2, MC2, and MD2.

Fig. 2 Spatial variation in sediment grain size composition of sediments (a), T-PAH concentration (b), and PAH composition based on ring size in surface sediments from the tail-end of the Yellow River, the Yellow River Estuary, and marine transects in the Bohai Sea (c). Abbreviations for PAH compounds referred to in Table 1.
The observed variation in PAHs within the estuary might be related to multiple factors such as the sediment grain size composition, PAH input rate, differential re-suspension and re-deposition or vertical mixing of sedimentary PAHs, and microbial degradation of PAHs (Boonyatumanond et al. 2006). In this study, the clay component in sediments increased from land to sea (Fig. 2a). Unlike the marine sediments, sediments from the river and estuary were mainly composed of sand and silt. No significant correlation ($R^2 = 0.48, p \leq 0.05$) was found between the median grain size (D50) and T-PAHs for studied samples. The coarse-grained sediments (silt and sand) in the river and estuary had lower levels of T-PAHs. This indicates that sediment clay content is one of the important factors restricting the accumulation and distribution of PAHs in sediments. Apart from land-source inputs from the Yellow River Delta, as well as from the drilling platform of the Gudong Oil Field in the northwest margin of the study area may also release PAHs into the sediments. Releases from the oil field may affect the composition and spatial distribution of PAHs in sediments of the Yellow River Estuary and its adjacent sea areas. As seen from Fig. 2, the concentrations of PAHs measured in the north transects (MA$_1$, MB$_1$) were higher than those in the south transects (MC$_1$, MD$_1$). However, dilution with seawater and the biodegradability (Brown and Maher 1992) and desorption of low molecular weight PAHs cause PAH concentrations to decrease gradually seaward into the Bohai Sea. Naphthalene and phenanthrene were the dominant PAH compounds (Fig. 2b) with a relative average abundance of 24.9% and 27.8%, respectively. Naphthalene has a low molecular weight and relatively fast decomposition rate, which indicates that there are continuous inputs of naphthalene-containing pollutants or new naphthalene entering sediments in the study area. The higher content of naphthalene in the sediments may come from frequent firewood and straw burning in the Yellow River Delta, as well as from the drilling platform of the Gudong Oil Field in the northwest part of the Yellow River Estuary. The T-PAHs observed in the present work (56.69–214.97 ng g$^{-1}$ dw) can be categorized as "weakly contaminated" (≤250 ng g$^{-1}$) (Socolo et al. 2000); they were similar to the sediment of the Pearl River Estuary, South China (59–330 ng g$^{-1}$ dw; Liu et al. 2005), and Amazon River Estuary, Brazil (22.2–158 ng g$^{-1}$ dw; Rodrigues et al. 2018), but were relatively lower than those in other regions in the world, such as Mersey Estuary, UK (626–3766 ng g$^{-1}$ dw; Vane et al. 2007); Curitiba, Brazil (39–2350 ng g$^{-1}$ dw; Machado et al. 2014); Yangtze River Estuary, China (84.6–620 ng g$^{-1}$ dw; Hui et al. 2009); and Jiaozhou Bay, China (16–2160 ng g$^{-1}$ dw; Wang et al. 2006).

Source apportionment

Spatial distribution patterns of PAHs

The T-PAHs were dominated by two- to three-ring PAHs followed by four-ring PAHs and thereafter by five- to six-ring PAHs (Fig. 2c). The ratio of low molecular weight PAHs (LMW PAHs, two- to three-ring) to high molecular weight PAHs (HMW PAHs, four- to six-ring) (LMW/HMW) can be used to identify PAH sources (Tam et al. 2001). An LMW/HMW ratio > 1 indicates petrogenic source while < 1 indicates a pyrolytic source. In the present study, the ratios were mostly > 1, indicating that petrogenic fractions dominate the PAH accumulation in the tail-reaches of the Yellow River. Previous studies have shown that the distribution of PAH components in the Yellow River Estuary during the dry season and flood season is similar, and that naphthalene is dominant (Wang et al. 2017). This is consistent with the high naphthalene content observed in sediments in this study. The percentage of two- to three-ring PAHs in sediments of the northern transects (MA$_1$, MB$_1$) increased gradually from the estuary toward the offshore area in the Bohai Sea. This might be because the Bohai Sea has been severely polluted by oil derived from oil exploration and exploitation activities, while the estuary is continuously scoured by water entering the sea every year resulting in relatively low oil pollution. Weakly affected by oil field exploration and exploitation, the T-PAH level in the southern transects (MC$_1$, MD$_1$) and the percentage of two- to three-ring PAHs decreased gradually from the estuary toward the offshore area in the Bohai Sea. This might be due to the dilution of seawater and the biodegradability and desorption of low molecular weight PAHs.

Source apportionment using PAH diagnostic ratios

The source of PAHs detected in the sediment can further be determined by the molecular ratios of some PAHs. The molecular tools used to identify the sources of PAHs in sediments include ratios such as Fla/(Fla + Pyr), Ant/(Ant + Phe), BaA/(BaA + Chr), etc. (Yunker et al. 2002). The Fla/(Fla + Pyr) ratio < 0.4 indicates petrogenic sourcing, and values between 0.4 and 0.5 are indicative of petroleum combustion, while values > 0.5 suggest wood, grass, and/or coal combustion (Yunker et al. 2002). An overwhelming grass, wood, and coal combustion signature was identified as a PAH pollution source of marine regions (Fig. 3a). The ratio < 0.4 and between 0.4 and 0.5 for riverine samples provide insight to mixed sourcing of petroleum and petroleum combustion (Fig. 2). The Ant/(Ant+Phe) ratio distinguishes between petrogenic and combustion sources, as values < 0.1 indicate petrogenic and those > 0.1 indicate combustion (Yunker et al. 2002). It can be confirmed that PAHs in sediments mainly come from combustion process (Fig. 3a). The BaA/(BaA +
Chr) ratio provides insight to petrogenic and combustion (pyrogenic) sources and includes a range for mixed sourcing. Values < 0.2 indicate petrogenic sourcing, and values between 0.2 and 0.35 indicate mixed sourcing, while values > 0.40 are indicative of combustion sources. Except the two sites of MB, all other samples present a value that indicates wood, grass, and/or coal combustion (Fig. 3b).

**PCA model analysis**

As can be seen from Fig. 3a, for the study area of offshore profiles, the number of samples falling in the burning area of grass, wood, and coal is slightly more than that of petroleum products. The ratio method usually involves only two kinds of PAH monomer compounds. Thus, the PCA analysis was performed to further understand the sources of PAHs in the next section. High loading variables are indicated with bold numbers in Table 1. As shown in Table 1 and Fig. 4a,b, PC1 of the riverine and estuarine area is 66.92%, and the positive loads of PAHs are higher. PC1 was heavily loaded (exceeding 0.89) with Phe, Ant, Fla, Pyr, BaA, Chr, BkF, BaP, IcdP, and BghiP. Coal combustion emissions are enriched in Flu and Phe, and Phe and Ant can be used as markers of biomass burning (Harrison et al., 1996). In addition, BaA, BaP, and BghiP are typical markers of petroleum combustion, and oil burning emissions are enriched in Flu and Chr (Larsen and Baker 2003). Therefore, PC1 was identified as a mixed source of oil combustion, biomass burning source, and coal combustion emission. PC2 (18.11% of the total variance) showed high loadings of Nap and Acy, which were related to sources of crude oil pollution. PC3 (18.11% of the total variance) had high loadings of Nap, which is a marker of crude oil pollution. PC2 (19.36% of the total variance) showed high a loading of Nap, which is a marker of crude oil pollution. PC3 (9.66% of the total variance) had high loadings of BbF and BkF, indicating diesel combustion. Based on PCA analysis, the
PAH contributions of the major sources for the lower reaches of the Yellow River and the estuary area were quantified as 66.92% from oil, coal, and biomass combustion; 18.11% from oil pollution; and 6.24% from diesel combustion. The PAH contributions of the major sources for the offshore area were quantified as 52.31% from oil, coal, and biomass combustion; 19.36% from oil pollution; and 9.66% from diesel combustion.

Table 1  Factor loadings for principal components for sediment from tail-reaches of Yellow River Estuary

| No. | PAH compounds          | Abbreviation | Riverine and estuarine area | Marine area |
|-----|------------------------|--------------|-----------------------------|-------------|
|     |                        |              | PC1 | PC2 | PC3 |  PC1 | PC2 | PC3 |
| 1   | Naphthalene            | Nap          | 0.23 | 0.93 | 0.15 | 0.38 | 0.66 | -0.28 |
| 2   | Acenaphthylene         | Acy          | 0.40 | 0.86 | -0.18 | 0.83 | 0.39 | -0.13 |
| 3   | Acenaphthene           | Ace          | 0.32 | 0.73 | 0.21 | 0.71 | 0.59 | -0.01 |
| 4   | Fluorene               | Flu          | 0.68 | 0.58 | -0.13 | 0.79 | 0.55 | -0.18 |
| 5   | Phenanthrene           | Phe          | 0.95 | 0.16 | -0.13 | 0.81 | 0.41 | -0.14 |
| 6   | Anthracene             | Ant          | 0.89 | 0.29 | -0.10 | 0.86 | 0.36 | -0.13 |
| 7   | Fluoranthene           | Fla          | 0.98 | -0.13 | 0.03 | 0.87 | -0.16 | -0.01 |
| 8   | Pyrene                 | Pyr          | 0.93 | -0.19 | 0.25 | 0.61 | -0.52 | -0.11 |
| 9   | Benzo[a]anthracene     | BaA          | 0.96 | -0.17 | -0.10 | 0.63 | -0.52 | 0.02 |
| 10  | Chrysene               | Chr          | 0.97 | -0.19 | 0.16 | 0.75 | -0.50 | -0.07 |
| 11  | Benzo[b]fluoranthene   | BbF          | 0.61 | -0.12 | 0.69 | 0.49 | 0.19 | 0.81 |
| 12  | Benzo[k]fluoranthene   | BkF          | 0.91 | -0.19 | -0.17 | 0.60 | 0.24 | 0.72 |
| 13  | Benzo[a]pyrene         | BaP          | 0.97 | -0.17 | 0.13 | 0.59 | -0.54 | 0.20 |
| 14  | Indeno[1,2,3-c,d]pyrene| IcdP         | 0.96 | -0.16 | -0.13 | 0.80 | -0.39 | -0.22 |
| 15  | Dibenzo[a,h]anthracene | DabA        | 0.74 | -0.25 | -0.47 | 0.72 | -0.32 | -0.29 |
| 16  | Benzo(g,h,i)perylene   | BghiP        | 0.97 | -0.19 | 0.03 | 0.90 | -0.32 | 0.14 |

Explained variance (%)  66.92 18.11 6.24 52.31 19.36 9.66

PAH contributions of the major sources for the off-shore area were quantified as 52.31% from oil, coal, and biomass combustion; 19.36% from oil pollution; and 9.66% from diesel combustion.
PMF model analysis

After inputting the sample concentration value and the uncertainty value, the factor number between 3 and 7 in turn was adjusted. The Robust mode was used for 20 times of each adjustment iteration, and the best factor number was selected according to the concentration degree of residual error between $-3.0$ and $3.0$. $Q_{\text{Robust}}$ values $(252)$ close to the $Q_{\text{theoretical}}$ value $(265)$ suggest that the calculated result is reasonable. As shown in Table 2, factor 1 included relatively higher Phe, Ant, Pyr, and Chr levels in the riverine and estuarine locations, indicating coal combustion and traffic exhaust. Factor 2 was dominated by Nap and Phe, which are associated with crude oil pollution. Factor 3 had high loadings of Nap, Phe, Flu, and Fla, indicating crude oil pollution and coal combustion emission. For the marine area, factor 1 had high loadings of Nap, Phe, Flu, and Fla, which is a marker of crude oil pollution and coal combustion emission. Factor 2 was dominated by Phe, which is identified as a coal combustion emission. Factor 3 was mainly linked to coal combustion and traffic exhaust because it was enriched in Nap, Phe, Flu, Fla, and BkF.

| Species | Riverine and estuarine area | Marine area |
|---------|-----------------------------|-------------|
|         | Factor 1 | Factor 2 | Factor 3 | Factor 1 | Factor 2 | Factor 3 |
| Nap     | 0.00     | 3.91     | 20.66    | 16.04    | 0.66     | 5.51      |
| Acy     | 0.01     | 0.52     | 3.48     | 2.76     | 0.02     | 0.98      |
| Ace     | 0.00     | 0.47     | 2.61     | 1.93     | 0.00     | 0.75      |
| Flu     | 0.00     | 0.94     | 7.62     | 7.18     | 0.55     | 2.45      |
| Phe     | 0.19     | 1.34     | 13.82    | 19.30    | 7.29     | 6.71      |
| Ant     | 0.08     | 0.12     | 1.88     | 2.32     | 0.71     | 0.81      |
| Fla     | 0.00     | 0.00     | 1.86     | 5.30     | 1.70     | 2.80      |
| Pyr     | 0.11     | 0.34     | 2.11     | 2.40     | 0.12     | 0.83      |
| BaA     | 0.00     | 0.00     | 0.00     | 0.03     | 0.12     | 0.03      |
| Chr     | 0.12     | 0.05     | 0.03     | 0.48     | 1.34     | 1.32      |
| BBF     | 0.13     | 0.00     | 0.01     | 0.01     | 0.09     | 1.34      |
| BkF     | 0.00     | 0.00     | 0.00     | 0.02     | 0.30     | 2.87      |
| BaP     | 0.00     | 0.10     | 0.00     | 0.06     | 0.00     | 0.19      |
| IcdP    | 0.00     | 0.00     | 0.00     | 0.05     | 0.47     | 0.01      |
| DahA    | 0.00     | 0.00     | 0.00     | 0.02     | 0.16     | 0.00      |
| BghiP   | 0.06     | 0.00     | 0.00     | 0.12     | 0.41     | 0.05      |

Risk assessments

Previous studies have suggested that PAH concentrations in Yellow River Estuary, China, are below the effects range-median (ERM) and probable effects level (PEL) values (Wang et al. 2017). However, sediments often act as a sink for many pollutants where synergistic or antagonistic effects may be observed among pollutants. Therefore, the combined toxicity assessment of multiple pollutants in sediments might be higher than the toxicity of individual chemicals. The mean ERM quotient (MERM-Q) method has been used to analyze the ecological hazard of multiple toxic chemicals (McCready et al. 2006). In this paper, MERM-Q was used to evaluate the ecological risk of 15 PAHs (there is no ERM value for IcdP) in surface sediments of the lower reaches, estuary, and offshore areas of the Yellow River (Fig. 5). Quotients were calculated as follows:

$$\text{MERM-Q} = \frac{\sum (C_i / ERM_i)}{n}$$

where $C_i$ is the concentration of compound i in sediment, $ERM_i$ is the ERM for compound i, and $n$ is the number of compounds. The MERM-Q values can be categorized into low (<0.1), medium-low (0.11–0.5), medium-high (0.51–1.5), and high (>1.5) contamination (Long et al. 1995). As can be seen from Fig. 5, the MERM-Q value of all stations (0.0050 ± 0.0017) was far lower than 0.1, suggesting that ecological risk from PAHs in the surface sediments of the Yellow River Estuary is low.
sediments of all stations is unlikely. This corresponds to the lower PAH contaminant levels in the surface sediments of the study area. Affected by oil exploitation, the risk for the northern transects in the offshore area is higher than that in the southern transects. Consistent with the concentration of aromatic hydrocarbons, the ecological risk in the offshore area is slightly higher than that in the lower reaches of the Yellow River.

**Conclusion**

The average concentration of 16 US EPA priority PAHs (T-PAHs) in surface sediments from transects in the offshore area was 119.51 ± 39.58 ng g$^{-1}$ dw, which is higher than that measured in the riverine sediments of the lower reaches (75.00 ± 12.56 ng g$^{-1}$ dw) and estuarine sediments (67.94 ± 10.20 ng g$^{-1}$ dw). This spatial distribution may be due to the sediment grain size composition, cumulative effects, and distribution of oil fields. T-PAH concentrations in sediments generally decreased seaward along all of the studied transects in the coastal area of Bohai Bay. The percentage of two- and three-ring PAHs in sediments from the northern transects increased gradually from the estuary toward the offshore area in the Bohai Sea, possibly because the Bohai Sea is severely polluted with oil from exploration/exploitation activities, while the estuary is continuously scoured by water entering the sea every year and thus is less polluted by oil. Understanding the specific sources contributing PAHs to sediments is of importance for environmental management. Therefore, the identification of PAH sources can help assess PAH risks and control pollution in the YRD. The PAHs in surface sediments were principally derived from coal and biomass combustion, petroleum pollution, and vehicular emissions. The toxic assessment suggested that based on the PAH levels, there was low potential for ecotoxicological effects as indicated by the MERM-Q (0.0050 ± 0.0017). The ecological risk of PAHs along the northern transects was higher than that of PAHs along the southern transects, and the risk in the offshore area was slightly higher than that in the lower reaches of the Yellow River. Analyzing the ecological risk of PAHs in surface sediments from the YRD is of great significance for protecting human health and security.

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