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Source apportionment and ecological risk assessment of PAHs in surface sediments from the Liaodong Bay, northern China

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Abstract

The sources and ecological risk from sixteen polycyclic aromatic hydrocarbons in surface sediment in the Liaodong Bay were investigated from 2014 to 2015. The total concentrations of PAHs ranged from 88.5 to 347.1 ng/g, and the high value occurred in the central region of the Liaodong Bay. Cluster analysis identified two site clusters representing the coastal region affected by land-based pollution and the central region of the Liaodong Bay. Principal component analysis-multiple linear regression and diagnostic ratios suggested that PAHs contaminants originated from a mixture of combustion and petroleum sources, and the major was combustion sources. Based on sediment quality guideline, naphthalene, acenaphthylene, acenaphthene, phenanthrene and dibenz[*a*,*h*]anthracene may occasionally cause adverse biological effects in some stations. The toxic equivalent concentrations of carcinogenic PAHs indicated low carcinogenic risk for the Liaodong Bay. The ecological risk and toxic pollution levels of PAHs were higher in the central region than in the coastal region along the Liaodong Bay.

Key words: polycyclic aromatic hydrocarbons, Liaodong Bay, source apportionment, ecological risk assessment, sediment

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous persistent organic pollutants that are widely distributed in various environments. Some PAHs can bring adverse health effects to humans, including carcinogenicity, teratogenicity and mutagenicity (Douben, 2003). Sixteen PAHs have been identified as the priority pollutants due to their toxicity to mammals and aquatic organisms by the US Environmental Protection Agency (US EPA) (Keith and Telliard, 1979). PAHs are generated from natural sources and anthropogenic inputs (Darılmaz et al., 2013); PAHs in the natural environment are mainly derived from anthropogenic inputs, such as incomplete combustion of fossil fuels, leakage of crude oil and petroleum products, industrial manufacturing and vehicular petroleum (Li et al., 2015). Natural sources such as forest fires, volcanic eruptions and biosynthesis activities play a minor role in PAH accumulation compared with anthropogenic inputs (Lima et al., 2005; Parinos et al., 2013; Yunker et al., 2002). In the marine environment, PAHs can be easily deposited and fixed in marine sediments. Marine sediment is an important reservoir of environmental pollutants. PAHs in marine sediments will have a long-term adverse effect on benthic organisms (Christensen et al., 1997; Liu et al., 2012), and can also be transported and bio-accumulated through the food chain at various trophic levels leading to long-term changes in the biota (Fernandes et al., 1997). The PAHs pollution to the environment is likely to pose a threat to human health (Zhang et al., 2016a). Thus most studies have focused on the distribution, source apportionment and ecological risk assessment of PAHs in the marine environment.

The Liaodong Bay, a high-latitude location and one of the largest bays in China, is located in the north of the Bohai Sea, connected to the Yellow Sea through the Bohai Strait. As one of the most important spawning and breeding grounds for many economically important marine organisms, the Liaodong Bay has many biological resources, including valuable and rare species (Zhang et al., 2016b, 2013). However, marine ecosystem environment of the Liaodong Bay has been affected by many pollution hazards, including PAHs. The poor seawater exchange and the accelerated industrialization and urbanization of the cities around the Liaodong Bay would inevitably result in a considerable contamination of pollutants in aquatic environment of the bay (Ma et al., 2014). PAHs pollution is introduced into the bay by

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riverine runoff, small fishing vessels, aquiculture, industry, and municipal sewage treatment plants, the oil and gas fields, and the accidents of oil spill. In the study area, there are plenty of the oil and gas fields, such as the Lvda Oilfield, Suizhong 36-1 Oilfield, Jinzhou 9-3 Oilfield and Liaohe Oilfield. Moreover, the coast of the Liaodong Bay is the home to the Jinzhou Harbor, Panjin Harbor, Yingkou Harbor and Qinhuangdao Harbor. Meanwhile, the study area is an important oil and gas production base in China, and plays an important role in the offshore oil exploration and marine transportation of China. The main rivers flowing into the Liaodong Bay are the Daliaohe River, Liaohe River, Dalinghe River, Xiaolinghe River, Liuguhe River and Luanhe River, and carry large amounts of pollutants into the bay. Due to the strong anthropogenic influence and various contamination sources of PAHs, especially the accidents of oil spill (Penglai 19-3 oil spill accidents and Jinzhou 9-3 oil spill accidents), marine transportation and fishing operation, the Liaodong Bay is under a tremendous environmental pollution stress. Marine sediment in the Liaodong Bay is a reservoir of PAHs from various contamination sources, with two main input pathways for the sedimentary PAHs. One is the PAHs from seawater transferred into the sediment, and the other is the particulate-bound PAHs deposited into the sediment. The PAHs in seawater from the Liaodong Bay are mainly derived from the air-water exchange, riverine runoff, wastewater from anthropogenic activities and the oil and gas fields, as well as the accidents of oil spill. The particulate-bound PAHs are mainly derived from the dry deposition of particle-phase PAHs in air, the suspended particulates brought from the rivers (Liaohe River, Daliaohe River, Dalinghe River, Xiaolinghe River), and the particulate-bound PAHs in seawater.

In the present study, thirty-six surface sediments from the Liaodong Bay were collected with focusing on PAHs, and the possible sources and ecological risk of sedimentary PAHs were explored. Principal component analysis-multivariate linear regression (PCA-MLR) and diagnostic ratios were used to analyze the apportion sources of PAHs, and potential ecological effects were also assessed by sediment quality guidelines (SQGs) and toxic equivalent concentrations. The study could provide a valuable reference for PAH pollution control and management in the Liaodong Bay.

2 Materials and methods

2.1 *Sample collection*

Thirty-six sampling sites were investigated from the Liaodong Bay during four separate marine surveys between 2014 and 2015, as shown in Fig. 1. The sampling sites were set in coast and offshore petroleum exploration area of the Liaodong Bay. Sediment was collected using stainless grab sampler. Approximately the top 5 cm of sediments was removed carefully with a stainless steel spoon, mixed well and stored in pre-cleaned aluminum containers and preserved in –20°C. After being transported to the laboratory, samples were homogenized and freeze-dried, the samples were ground using an agate mortar and sieved through an 80 mesh sieve.

2.2 *Sample extraction and chemical analysis*

Approximately 15 g of homogenized sediment samples were weighted and mixed with 1 g diatomaceous earth. PAHs in dry sediment were extracted with a mixture of dichloromethane and hexane (v:v=1:1) by an Accelerated Solvent Extractor (ASE 350, ThermoFisher Scientific Co. Ltd., USA). A total of 100 ng of the surrogate standards (naphthalene-*d8*, acenaphthylene-*d10*, phenanthrene-*d10*, chrysene-*d12*, and perylene-*d12*, J&K Chemicals Co. Ltd.) was added prior to extraction. After extraction, the sample extract was concentrated to 2 mL by a rotary evaporator, and approximately 2.0 g of activated copper powder was added into the concentrated extract for desulphurization by shocking. A glass column was filled with 4 g of silica gel, 6 g of neutral aluminum oxide, and 1 g of anhydrous sodium sulfate, and was precleaned with hexane. The concentrated extract was passed through the column, and eluted with a 1:1 mixture of dichloromethane and hexane. The eluting solution containing PAHs was collected and concentrated to 1 mL with hexane, and then concentrated to 0.5 mL under nitrogen. The final sample was spiked with internal standards prior to instrumental analysis.

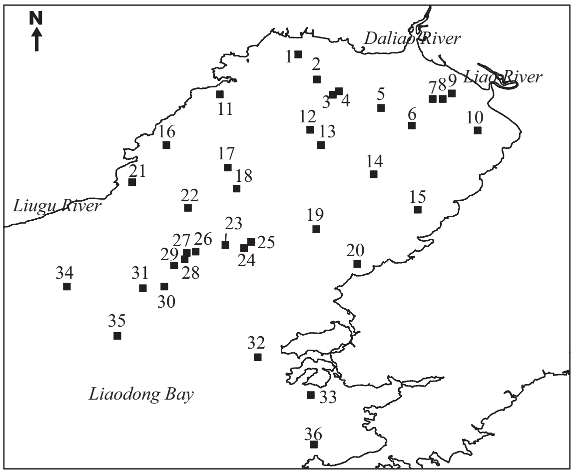

Fig. 1. Sediment sampling sites in the Liaodong Bay.

The PAHs were detected using gas chromatography-mass spectrometer (GC-MS) (6890N/5975C, Agilent Technologies INC, USA) with a DB-5MS capillary column (30 m×0.25 mm diameter, 0.25 μm film thickness). Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min, 1 μL concentrated sample extract was injected in the splitless mode. The mass selective detector (MSD) was run in selected ion monitoring mode (SIM) for optimum sensitivity. The electron impact ion source (EI) with electron energy of 70 eV was used. The GC column temperature initially at 50°C, increased at a rate of 4°C/min to 220°C and held 3 min, and then increased at a rate of 10°C/min to 300°C and held 9 min. The sixteen priority quantified PAHs compounds were naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Acp), anthracene (An), phenanthrene (Phe), fluorene (Fl), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*a*]pyrene (BaP), benz[*b*]fluoranthene (BbF), benz[*k*]fluoranthene (BkF), dibenz[*a*, *h*]anthracene (DbA), indeno[1, 2, 3-*cd*]pyrene (InP), and benzo[*ghi*]perylene (BgP).

2.3 *Quality assurance and quality control*

Strict quality controls were operated to ensure the correct identification and accurate quantification of the PAH compounds. Method blanks, spiked blanks and sample duplicates were analyzed as quality control measures. One method blank sample was analyzed in each batch of ten samples to decide the contamination, and the results in blanks were below or close to detection limits. In addition, surrogate standards (naphthalene-*d8*, acenaphthylene-*d10*, phenanthrene-*d10*, chrysene-*d12*, and perylene-*d12*) were added to all samples to monitor procedural performance and matrix effect, and the average recoveries varied from 40% to 97%. PAHs results were quantified using the internal calibration method, and corrected by the internal standards and surrogate recoveries. All equipments were rinsed with dichloromethane before experiment. The detection limits of the analytical method were calculated as three times of standard deviation (n=7) in low concentration samples and ranged from 0.1 ng/g to 0.3 ng/g for sixteen PAH compounds.

2.4 *Toxicity and ecological risk assessment*

Two sets of SQG, the effect range low (ERL)/effect range median (ERM) and the threshold effect level (TEL)/probable effect level (PEL), were applied to assess the ecological risk of individual PAHs (Long et al., 1995; Macdonald et al., 1996). ERL/ERM and TEL/PEL values were based on a compilation of large toxicity data bases for marine organisms and widely used for sediment quality assessments in aquatic environments. The adverse biological effects of PAHs concentrations were expected: rarely (<ERL/TEL), occasionally (⩾ERL/TEL and <ERM/PEL), and frequently (⩾ERM/PEL).

BaP toxic equivalency factors (TEFs) were commonly used to assess the carcinogenic toxicity caused by exposure to multiple PAHs in the sediments, and applied to estimate the benzo[a] pyrene equivalue (BaP_{eq}) concentrations (Tsai et al., 2004; Wang et al., 2011). The BaP_{eq} concentrations were calculated by multiplying the individual PAHs concentration by its TEF. The carcinogenic potency of PAHs could be evaluated by the sum of BaP_{eq} of individual PAHs.

2.5 *Data analysis*

SPSS 18.0 Software (SPSS Inc., Chicago, IL, USA) was applied to data statistical analyses of cluster analysis and principal component analysis-multivariate linear regression (PCA-MLR), and all of the variables used in statistical analyses were standardized by standard deviation, the equation was: (analysis concentration-mean concentration)/standard deviation. Cluster analysis was operated on the basis of Euclidean distance correlation coefficients using Ward's merging criterion. PCA factor scores and normalized total PAH concentration were used as independent and dependent variables of MLR, respectively. The regression was operated by a stepwise method, and the relative contributions from various sources were calculated by standardize regression coefficients. Origin 8.0 was used to plot the photographs of the ratios using to identify the possible PAH sources.

3 Results and discussion

3.1 *The spatial distribution and composition patterns of PAHs*

3.1.1 *The level and spatial distribution of PAHs*

Sixteen PAHs were investigated in thirty-six surface sediment samples from the Liaodong Bay. The measured total concentrations of PAHs (∑PAHs) in surface sediments ranged from 88.5 to 347.1 ng/g with an average of 202.1 ng/g (Table 1). The highest concentration was at Site 24 (347.1 ng/g) followed by Site 7 (339.1

Table 1. Comparison of ∑PAH concentrations in surface sediment samples collected from different locations

Location	N	∑PAH/ng·g^{-1}	Pollution levels	Reference
Laizhou Bay, China	16	97.2–204.8	low to moderate	Hu et al. (2011a)
Zhanjiang Bay, China	16	41.96–933.90	low to moderate	Huang et al. (2012)
Leizhou Bay, China	16	21.72–319.61	low to moderate	Huang et al. (2012)
Liaodong Bay, China	16	144.5–291.7	moderate	Hu et al. (2011b)
Haikou Bay, China	14	420.2–2 539.1	moderate to high	Li et al. (2015)
Northern Liaodong Bay, China	16	192.0–624.4	moderate	Zhang et al. (2016c)
Intertidal zone of Bohai Bay, China	16	37.2–206.6	low to moderate	Qian et al. (2016)
Bohai Bay, China	16	140.6–300.7	moderate	Hu et al. (2010)
Bohai Sea, China	16	97.2–300.7	low to moderate	Hu et al. (2013)
Yellow Sea, China	16	148.28–907.47	moderate	Liu et al. (2009)
Zhoushan Archipelago, China	16	3.67–31.30	low	Wang et al. (2015)
Xiangshan Harbor, China	16	11.58–481.44	low to moderate	Wang et al. (2015)
Daliaohe Estuary, China	16	276.26–1 606.89	moderate to high	Men et al. (2009)
Guanhe Estuary, China	21	90–218	low to moderate	He et al. (2014)
Huanghe Estuary, China	16	111.3–204.8	low to moderate	Hu et al. (2014)
Bahía Blanca Estuary, Argentina	17	19.7–30 054.5	low to very high	Oliva et al. (2015)
Western sea coast, South Korea	16	69.8–1 175.2	low to high	Cho et al. (2009)
Mediterranean Sea, Egypt	16	3.51–14 100	low to very high	Barakat et al. (2011)
Northern continental shelf, Spain	13	37–34 085	low to very high	Viñas et al. (2010)
Arcachon Bay, France	16	32–4 120	low to high	Baumard et al. (1998a)
Niger Delta, Nigeria	28	65–331	low to moderate	Ekpo et al. (2012)
San Francisco Bay, USA	16	120.0–9 560.0	moderate to very high	Nilsen et al. (2015)
Lenga Estuary, Chile	16	290.0–6 118.0	moderate to very high	Pozo et al. (2011)
Daliaohe River system	16	suspended particulates: 317.5–238 518.7 sediment: 61.9–840.5	high to very high low to moderate	Guo et al. (2007)
Liaohe River system	16	suspended particulates: 410–76 480 soil: 285–8 347 sediment: 27.8–1 479	high to very high high to very high low to high	Hu et al. (2016) Song et al. (2008) Yang (2003)
North coastal area of the Bohai Sea	16	surface soil: 66.3–920.4	low to moderate	Jiao et al. (2013)
This study	16	88.5–347.1	low to moderate	

Note: N is number of PAH compounds analyzed in each study and ∑PAHs the measured total concentrations of 16 PAHs.

ng/g), Site 28 (336.7 ng/g) and Site 30 (336.7 ng/g), while the lowest concentration was at Site 16 (88.5 ng/g). There were obvious differences on individual PAH concentrations among all sediments. Nap had the highest concentrations of (42.8±16.2) ng/g, followed by Phe ((36.4±23.0) ng/g) and Flu ((25.8±19.9) ng/g). BaP, which was considered to be one of the most hazardous PAHs compounds, was found in all samples and ranged from 0.6 to 5.9 ng/g with an average of (2.8±1.6) ng/g. The sequence of mean value of the sixteen PAHs congeners was Nap>Phe>Flu> Pyr>Chr>BbF>Fl> BkF>BaA>Acp>InP>BgP>An>BaP>Ace>DbA.

A comparison of the total PAH concentrations in surface sediments from different coastal regions worldwide and its adjacent seas were given in Table 1 and Fig. 2. The pollution level of sediment evaluated by PAH concentrations could be classified into four categories (Baumard et al., 1998b): low, 0–100 ng/g; moderate, 100–1 000 ng/g; high, 1 000–5 000 ng/g; very high, >5 000 ng/g. The PAHs pollution level in the Liaodong Bay was low to moderate. Comparing with other coastal and estuarine areas around the world, average concentration of the total PAHs in this study was slightly higher than those in the Laizhou Bay (Hu et al., 2011a), Liaodong Bay (Hu et al., 2011a), intertidal zone of the Bohai Bay (Qian et al., 2016), Bohai Bay (Hu et al., 2010), Bohai Sea (Hu et al., 2013), Guanhe Estuary (He et al., 2014) and Huanghe Estuary (Hu et al., 2014), but lower than those in the Haikou Bay (Li et al., 2015), Yellow Sea (Liu et al., 2009), Daliaohe Estuary (Men et al., 2009), Bahía Blance Estuary (Oliva et al., 2015), Mediterranean Sea (Barakat et al., 2011), Northern continental shelf (Spain) (Viñas et al., 2010) and Arcachon Bay (Baumard et al., 1998a). Obviously, the comparison indicated that PAHs pollution in the Liaodong Bay was still at a relatively low level, though more attention should be paid to prevent it from further pollution. Such comparison based on historical data was subjective and might cause inaccuracies because of variances in the number and type of PAHs, the number and location of surface sediment samples and the analytical methods. The status of PAH pollution in this work was compared with those in the various environmental matrixes from the land-based inputs of the Liaodong Bay, such as suspended particulates, sediments and soils of the nearby region. The PAHs levels of sediments in the Liaodong Bay were lower than those in suspended particulates and sediments of the Liaohe River and Daliaohe River system (Guo et al., 2007; Song et al., 2008; Yang, 2003), and were slightly lower than those in the north coastal area of the Bohai Sea (Jiao et al., 2013). Therefore, the land-based inputs, such as riverine runoff of the Daliaohe River and Liaohe River, might be the PAHs pollution sources of sediments from the Liaodong Bay.

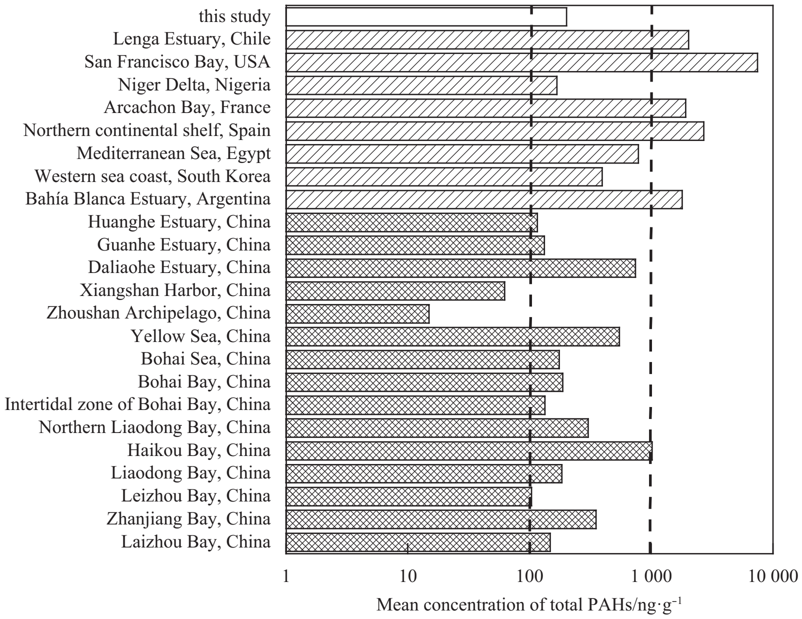

Fig. 2. Mean concentrations of total PAHs in surface sediments from different regions worldwide.

3.1.2 *The regional differences of PAHs level according to cluster analysis*

The dendrogram of the Q-mode cluster analysis on the concentrations of individual PAH compounds divided thirty-six sample sites into two clusters (Fig. 3). The first cluster represented the coastal region along the Liaodong Bay, and was affected by land-based pollution and oil platforms. Cluster 2 represented the central region of Liaodong Bay, and the offshore oil exploration area (Fig. 4). The mean values and ranges of the individual and total PAH concentrations in every cluster are listed in Table 2. The PAHs concentrations (133.7 ng/g) in Cluster 1 were lower than Cluster 2 (309.4 ng/g). For Cluster 1, Nap had the highest concentrations of (38.4±13.1) ng/g, followed by Phe ((25.2±13.9) ng/g) and Flu ((12.0±4.72) ng/g). For Cluster 2, Phe was the most dominant PAH compounds ((53.9±23.8) ng/g) among sixteen PAHs, and followed by Nap ((49.7±18.5) ng/g) and Flu ((47.4±14.3) ng/g). Based on the PAH concentrations, the higher pollution sites are mainly located in the central region of the Liaodong Bay (Cluster 2) which is the offshore oil exploration area, with many oil and gas fields, such as the Lvda Oilfield, Suizhong 36-1 Oilfield, and Jinzhou 25-1 Oilfield. The oil-containing wastewater from offshore oil exploration might bring PAHs into the sediment, and cause the high occurrence of PAHs abundance in the central region. Meanwhile, the surface sediment types of the central region were predominated by sandy silt, slit and silty clay, the grain-sizes of sediment were much finer in the central region than in the coastal region of the Liaodong Bay (Xu, 2012). The PAHs concentrations were higher in fine grain-

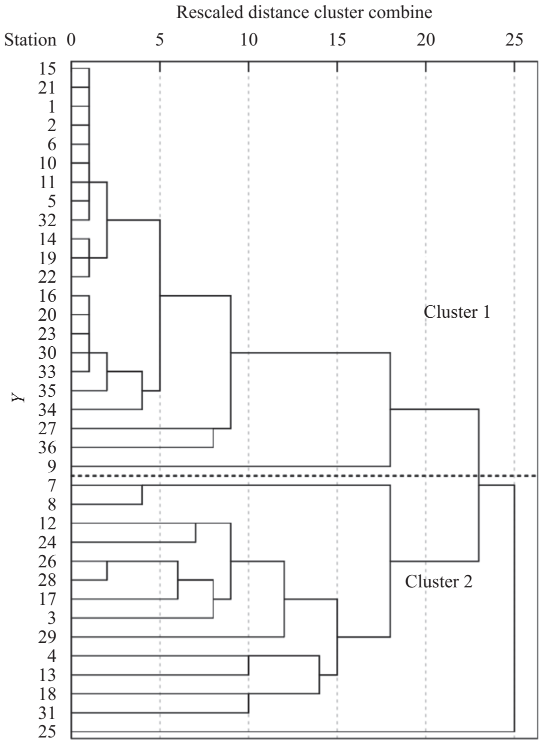

Fig. 3. Hierarchical clustering of sample sites based on 16 individual PAH concentrations.

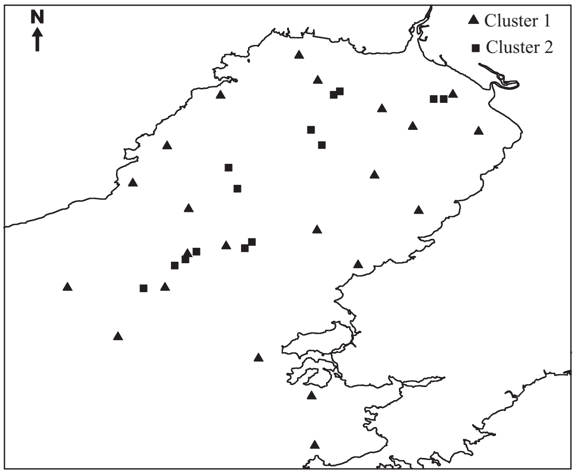

Fig. 4. Spatial distribution of each cluster on the basis of Euclidean distance correlation coefficients using Ward's merging criterion.

size sediments (Feng et al., 2007). Therefore, the sediment types may cause the high occurrence of PAHs abundance in the central region.

3.1.3 *The composition patterns of PAHs*

The composition patterns of PAHs by the number of aromatic rings in surface sediments from the Liaodong Bay were shown in Fig. 5 and Fig. 6. For Cluster 1, 2-ring and 3-ring PAHs were predominant in the Liaodong Bay, followed by 4-ring and 5-ring PAHs, and the relative abundance of 6-ring PAHs was lowest. 2-ring and 3-ring accounted for 30.5% and 29.9% of total 16 PAHs on average, respectively. The relative abundance of 4-ring PAHs was highest in Cluster 2, followed by 3-ring and 2-ring PAHs. The composition patterns of PAHs in Cluster 2 were not consistent with Cluster 1 and total sites. However, the composition patterns of PAHs in the Liaodong Bay showed no significant difference between low molecular weight (LMW, 2–3-ring) PAHs concentrations (Cluster 1 60.4%, Cluster 2 42.6%, total sites 53.0%) and high molecular weight (HMW, 4–6-ring) PAHs concentrations (Cluster 1 39.6%, Cluster 2 57.4%, total sites 47.0%) for Cluster 1, Cluster 2

Table 2. PAH concentrations in 36 surface sediments of the Liaodong Bay

Compounds		ERL$^{1)}$ /ng·g^{-1}	ERM$^{1)}$ /ng·g^{-1}	TEL$^{1)}$ /ng·g^{-1}	PEL$^{1)}$ /ng·g^{-1}	TEF$^{2)}$	Cluster 1		Cluster 2	
							Range/ng·g^{-1}	Mean±SD/ng·g^{-1}	Range/ng·g^{-1}	Mean±SD/ng·g^{-1}
2-ring	Nap	160	2 100	34.60	391	0.001	14.2–62.9	38.4±13.1	22.9–80.7	49.7±18.5
3-ring	Ace	44	640	5.87	128	0.001	0.79–4.47	1.61±0.77	1.48–9.22	4.28±2.40
	Acp	16	500	6.71	88.9	0.001	0.75–23.9	3.74±4.85	2.04–13.5	4.19±2.98
	Fl	19	540	21.20	144	0.001	4.75–15.7	7.61±2.61	8.5–19.6	12.7±3.3
	Phe	240	1 500	86.70	544	0.001	12.1–71.6	25.2±13.9	24.4–93.2	53.9±23.8
	An	853	1 100	46.90	245	0.01	0.99–5.91	2.13±1.07	2.35–8.90	5.46±1.79
4-ring	Flu	600	5 100	113	1 494	0.001	5.62–21.2	12.0±4.72	20.2–67.6	47.4±14.3
	Pyr	665	2 600	153	1 398	0.001	6.21–39.4	11.5±6.96	18.6–72.2	43.8±15.6
	BaA	261	1 600	74.80	693	0.1	1.13–5.46	2.74±1.30	2.99–11.6	8.58±2.20
	Chr	384	2 800	108	846	0.01	3.26–26.3	9.10±5.47	2.38–73.6	34.5±23.3
5-ring	BbF	320	1 800			0.1	3.15–13.7	7.46±3.10	5.68–26.5	16.5±5.00
	BkF	280	1 620			0.1	1.83–8.69	4.58±2.11	1.43–18.9	7.69±4.88
	BaP	430	1 600	88.80	763	1	0.64–4.16	2.07±1.19	1.04–5.94	3.86±1.68
	DbA	63.40	260	6.22	135	1	0.06–1.85	0.71±0.44	0.97–10.4	4.27±2.70
6-ring	InP					0.1	0.36–9.74	2.63±2.34	0.54–26.7	7.04±7.03
	BgP	552	3 160			0.01	0.29–9.05	2.28±1.90	2.22–8.55	5.44±1.82
CPAH$_7$							12.1–61.5	29.3±13.1	51.3–116.5	82.5±21.7
∑PAHs		4 022	44 792				88.5–237.3	133.7±42.3	254.3–347.1	309.4±29.9

Note: ERL represents effect range-low, ERM effect range-median, TEL threshold effect level, PEL probable effect level, TEF BaP toxic equivalency factor, CPAH$_7$ seven potentially carcinogenic PAHs, ∑PAHs the measured total concentrations of 16 PAHs, and SD standard deviation.$^{1)}$ The guideline data sources are from the works in the references (Long et al., 1995; Macdonald et al., 1996). $^{2)}$ The data are from the work in the reference (Wang et al., 2011).

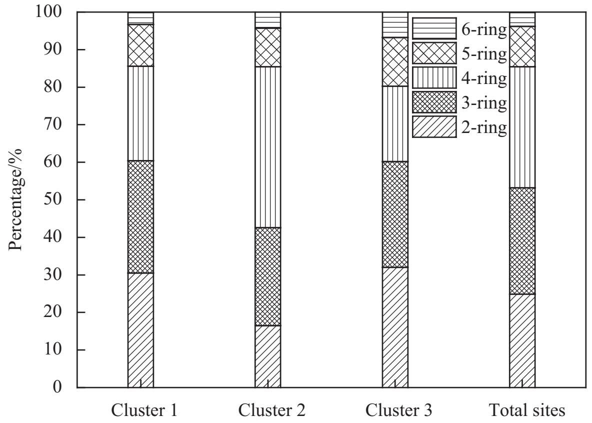

Fig. 5. Percentage of 2-, 3-, 4-, 5-, and 6-rings to the 16 PAHs in sediments from the Liaodong Bay.

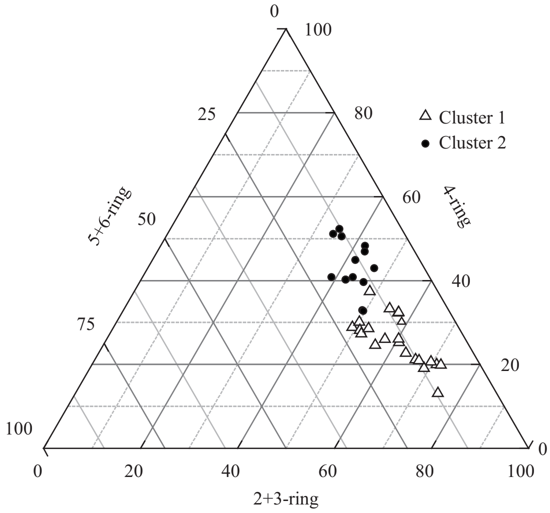

Fig. 6. Percentage distribution of 2- and 3-, 4-, 5- and 6-rings to the 16 PAHs for each cluster sample sites in the sediments from the Liaodong Bay.

and total sites. The different composition patterns of PAHs indicated that there were different PAH sources between Cluster 1 and Cluster 2.

3.2 *The source identification of PAHs*

3.2.1 *PCA-MLR for the PAH source identification*

Principal component analysis (PCA) is an effective method for studying the complex characteristics of the polluting sources. The four factors accounted for 81.19% of the total variance (Table 3). Principal component 1 (PC1), accounting for 51.14% of the total variance, was heavily loaded by Ace, Fl, An, and BaA (>0.7), and had moderate loading of Pyr, Flu, BbF and BgP. This source appears to have a coal/wood combustion origin. Higher relative abundances of Pyr, BaA, Fl, and An suggested the source of coal combustion (Harrison et al., 1996; Zuo et al., 2007) while Ace and Flu are typical indicators for wood combustion (Guo et al., 2003). In China, coal is the most important energy source and widely used for industrial and domestic purpose, especially in north China where coal is used for home heating in winter. Thus, it is reasonable to assign PC1 to biomass combustion (coal/wood combustion). Principal component 2 (PC2) was responsible for 12.63% of the total variance. This factor was predominately weighted by BbF, BkF, BaA, Flu, and Phe (>0.7), with a moderate loading of Pyr. Flu and Phe were identified as typical tracers of coal combustion (Harrison et al., 1996; Masclet et al., 1986; Simcik et al., 1999), BbF and Pyr are typical indictors for petroleum combustion, and the higher level of BkF indicates diesel combustion (Larsen III and Baker, 2003; Venkataraman et al., 1994). This source appears to have a mixed source of biomass and petroleum combustion. Principal component 3 (PC3) explained 10.47% of the total variance, with a high loading of Chr, DbA, BaP and InP (>0.7) and a moderate loading of BgP. Chr, DbA and InP are identified as markers for PAH compounds emitted from combustion of fossil fuels, and BgP is a typical tracer for vehicle use (Harrison et al., 1996; Larsen III and Baker, 2003). InP had been used as a tracer for gas and diesel engine and gasoline vehicle (Larsen III and Baker, 2003) and gasoline vehicle soot (Boonyatumanond et al., 2007). The Liaodong Bay is under a tremendous environmental pollution stress. Exhaust from marine transportation and fishing operation play an important role in the PAH pollution. Therefore, PC3 represents traffic-related pollution. Principal component 4 (PC4) explained 6.96% of the total variance. This factor was predominately weighted by Nap and Acp which were designated as typical indicator of volatilization or spill of petroleum-related products (Dobbins et al., 2006; Larsen III and Baker, 2003; Ye et al., 2006; Yunker et al., 2002). It could be due to ship breaking activities and anthropogenic activities such as oil spillages during exploitation processes and the waterway transportation industry. Based on such results, PC4 were selected to reflect a petrogenic origin.

In summary, the results obtained from PCA revealed that petrogenic, biomass combustion, traffic-related pollution, and a mixed source of biomass and petroleum combustion were main sources of PAHs in surface sediments from the Liaodong Bay.

PCA-MLR was an effective method to apportion PAHs sources in atmosphere, sediments and soils. Percentage contribution of different PAH sources were qualified by multivariate linear regression analysis. PC1, PC2, PC3 and PC4 were regressed against the standardized normal deviation of the total PAH concentrations at 95% confidence level. The multivariate

Table 3. Rotated component matrix of PCA

Compounds	PC1	PC2	PC3	PC4	Compounds	PC1	PC2	PC3	PC4
Nap	0.480	−0.118	0.175	0.710	BaA	0.635	0.701	0.250	0.013
Ace	0.903	0.119	0.152	0.260	Chr	0.292	0.080	0.840	−0.117
Acp	−0.055	0.083	0.033	0.860	BbF	0.550	0.768	0.114	0.155
Fl	0.830	0.289	0.296	−0.098	BkF	0.076	0.864	−0.109	0.084
Phe	0.143	0.709	0.368	−0.226	BaP	0.154	0.186	0.793	0.229
An	0.817	0.447	0.201	0.079	DbA	0.007	0.508	0.763	0.075
Flu	0.525	0.716	0.283	0.036	InP	0.199	−0.093	0.750	0.065
Pyr	0.585	0.698	0.180	−0.035	BgP	0.544	0.325	0.493	0.031

linear regression equation was as follows: Z=0.564PC1+0.616PC2+0.508PC3+0.107PC4 (adjusted r^2=0.962), the P value for the regression coefficients were less than 0.05. Based on the multivariate linear regression analysis, a mixed source of biomass and petroleum combustion was the most significant contributor (34.3%), followed by biomass combustion (31.4%), traffic-related pollution (28.3%) and petrogenic sources (6.0%).

Based on the PCA and PCA-MLR, the results revealed that PAHs in surface sediments from the Liaodong Bay were from complex mixed sources, combustion sources were probably the main contributors, as well as petrogentic existence.

3.2.2 *The regional differences of PAHs potential sources according to isomer ratios*

Identifying the possible sources of PAHs is critical in understanding the fate of PAHs in the environment. PAH diagnostic ratios are proportions of “kinetic” PAH isomers versus their “thermodynamic” isomers, and have been developed to indentify the possible sources of PAHs (Yunker et al., 2002). The ratios of BaA/(BaA+Chr), Flu/(Flu+Pyr) and InP/(InP+BgP) were used to identify the sources of PAHs in sediment, and the source interpretations for PAH diagnostic ratios were shown in Fig. 7. A large portion of the Flu/(Flu+Pyr) ratios varied between 0.1 and 0.5. Samples from Cluster 2 had the Flu/(Flu+Pyr) ratios less than 0.4, indicating the predominance of the petrogenic sources. For Cluster 1, most of the samples had the Flu/(Flu+Pyr) ratios between 0.3 and 0.5, which means most likely the petroleum combustion and petrogenic source were the contributors to PAHs. In general, the ratios of BaA/(BaA+Chr) and InP/(InP+BgP) varied between 0 and 0.9. For Cluster 1, most of samples had the BaA/(BaA+Chr) ratios between 0.2 and 0.35, which means the mixed sources of petrogenic and pyrolytic origins were predominant, and 18.2% of the samples had the BaA/(BaA+Chr) ratios less than 0.2, which was indicative of petrogenic sources. In Cluster 2, 42.8% of the samples had the BaA/(BaA+Chr) ratios less than 0.2, which was indicative of petrogenic sources, 21.4% of the samples had the BaA/(BaA+Chr) ratios between 0.3 and 0.35, which was indicative of petrogenic and pyrolytic sources, 35.7% of the samples had the BaA/(BaA+Chr) ratios greater than 0.35, which means that pyrolytic sources were from PAHs. In Cluster 2, the InP/(InP+BgP) ratios varied between 0 and 0.9, which was indicative of a mixture of the coal/wood combustion, petroleum combustion and petroginic sources, 7% of the samples had the InP/(InP+BgP) ratios less than 0.2, which was indicative of petrogenic sources. Samples from Cluster 1 had InP/(InP+BgP) ratios greater than 0.2, which was indicative of petroleum combustion and coal/wood combustion sources.

Overall, the PAH diagnostic ratios indicated different PAH sources in each cluster. Clusters 1 and 2 were impacted by a mixture of petrogenic and pyrolytic sources, PAHs in the central region of Liaodong Bay (Cluster 2) were predominant with prolytic and petrogenic sources, while the major PAH source in the coastal region of Liaodong Bay (Cluster 1) was prolytic sources. The contribution of PAHs from petrogenic sources was higher in the central region of Liaodong Bay (Cluster 2) than in the coastal region of Liaodong Bay (Cluster 1).

The correlation between BaA/(BaA+Chr), InP/(InP+BgP) and Flu/(Flu+Pyr) were poor (R^2<0.11) in sediment samples. The results of correlation analysis implied the uncertainty of isomer ratios analyses. Results may differ by use of different isomer ratios. Therefore, the pollution sources had not been identified by simple isomer diagnostic ratios yet. A factor (PP) was used to further distinguish PAHs between combustion sources and petroleum sources (Zhu et al., 2005).

$$PP_i = (Ratio - M)/M, \tag{1}$$

$$PP = \sum PP_i, \tag{2}$$

where M is the critical value, $M_{(\mathrm{BaA/(BaA+Chr)})}$=0.2, $M_{(\mathrm{InP/(InP+BgP)})}$=0.2, $M_{(\mathrm{Flu/(Flu+Pyr)})}$=0.4; in the present study, ratios of BaA/(BaA+Chr), InP/(InP+BgP) and Flu/(Flu+Pyr) were considered with PP and is calculated below:

$$PP = [\mathrm{BaA}/(\mathrm{BaA}+\mathrm{Chr}) - 0.2]/0.2 + [\mathrm{InP}/(\mathrm{InP}+\mathrm{BgP}) - 0.2]/0.2 + [\mathrm{Flu}/(\mathrm{Flu}+\mathrm{Pyr}) - 0.4]/0.4, \tag{3}$$

where PP>0, major source of PAHs was combustion source; while PP<0, major source of PAHs was petroleum source.

In the Liaodong Bay, PP value of all samples ranged from –1.14 to 3.18 with a mean of 1.79 (Fig. 8). For Cluster 1, the PP value ranged from –0.07 to 2.71 with a mean of 1.80. The values of PP in Cluster 2 ranged from –1.14 to 3.18 with a mean of 1.76. The value

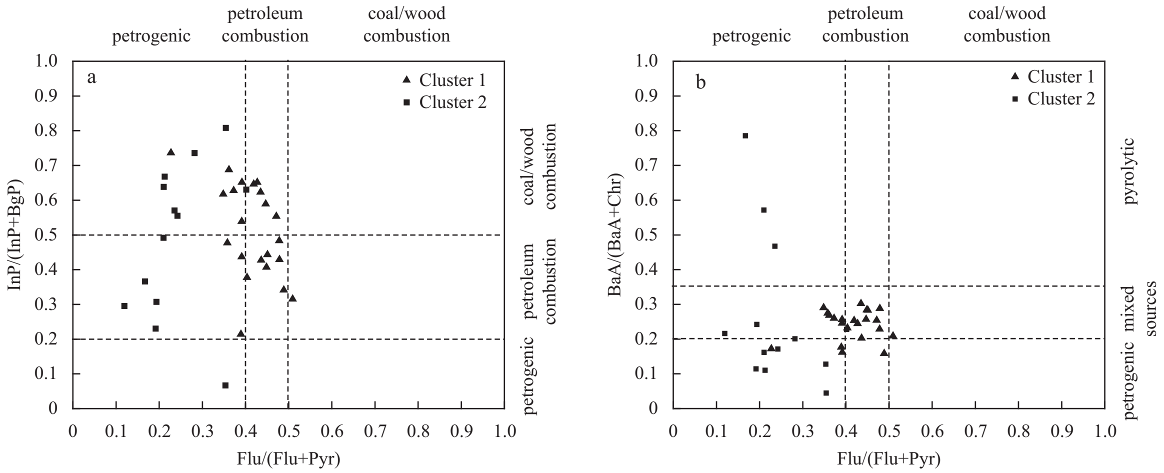

Fig. 7. PAH cross-correlations for the ratios of each cluster sample sites InP/(InP+BgP) vs. Flu/(Flu+Pyr) (a) and BaA/(BaA+Chr) vs. Flu/(Flu+Pyr) (b).

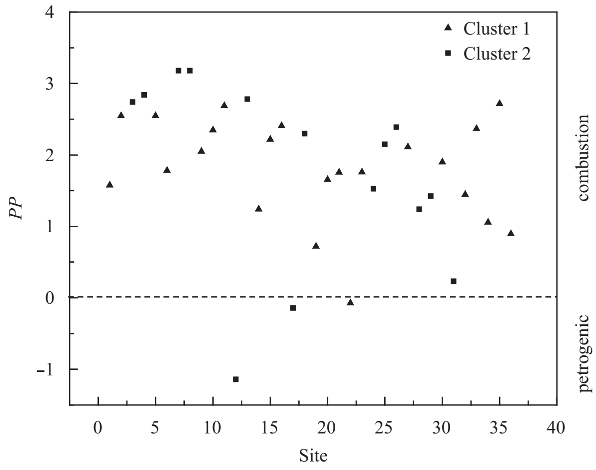

Fig. 8. The *PP* value of each cluster sampling sites in sediments from the Liaodong Bay.

of *PP* in Cluster 1 was slightly higher than in Cluster 2. The contribution of petroleum sources was higher in Cluster 2 than in Cluster 1. While the values in Sites 12 (Cluster 2), 17 (Cluster 2) and 22 (Cluster 1) were lower than 0, which showed PAHs mainly originated from the petroleum sources. The *PP* values in most of samples site were higher than 0, indicating the contamination sources of combustions. Based on the *PP* indices, the results suggest that combustion sources would be the main source, the contribution of PAHs petrogenic sources was slightly higher in the central region of Liaodong Bay (Cluster 2) than in the coastal region of Liaodong Bay (Cluster 1). By comparison, the PAH ratios and the PCA-MLR both showed consistent PAH sources. The central region of Liaodong Bay is the offshore oil exploration area where the oil exploration activities might be the petrogenic sources of the central region.

3.3 *Toxicity and ecological risk assessment*

3.3.1 *Ecological risk assessment of PAHs*

According to SQGs, ERL/ERM and TEL/PEL values were both applied to assess the ecological toxicity of individual PAHs in sediments in this study. The ERL/ERM and TEL/PEL values were presented in Table 2. For Clusters 1 and 2, the concentrations of all PAHs were below ERL, indicating that rare adverse biological effects could occur in the Liaodong Bay according to ERL/ERM. But based on TEL/PEL, the results were different. For Cluster 1, the concentrations of Nap and Acp were in the intermediate range (⩾TEL and <PEL). For Nap, concentrations at 72.3% of the stations exceeded TEL levels, indicating that occasionally adverse biological effects were likely to occur at 72.3% of all stations for Cluster 1. Acp at Site 9 was in the intermediate range, it would cause occasional adverse biological effects at this station. For Cluster 2, the concentrations of Nap, Ace, Acp, Phe and DbA were between TEL and PEL. For Nap, concentrations at 71.4% of the stations for Cluster 2 were in the intermediate range, the results suggested that Nap might be occasionally associated with adverse biological effects at 71.4% of the stations. Concentration of Ace exceeded TEL only at Sites 14 and 17, suggesting that adverse biological effects might occasionally occur at these stations. Phe concentration was in the intermediate range only at Sites 7 and 29, indicating that occasionally adverse biological effects were likely to occur at these two stations. For DbA, concentrations exceeded ERL at Sites 24, 25 and 29, indicating that occasionally adverse biological effects were likely to occur.

In conclusion, SQG assessment for individual PAHs revealed that Nap and Ace might cause occasional adverse biological effects at the stations in the coastal region of Liaodong Bay (Cluster 1), and Nap, Ace, Acp, Phe and DbA might cause occasional adverse biological effects at these stations in the central region of Liaodong Bay (Cluster 2). Acp, Phe and DbA might cause higher ecological risk in the central region than in the coastal region of Liaodong Bay. Acp and Phe are 3-ring PAHs, 2-ring and 3-ring PAHs are the main components of the wastewater from offshore oil exploration, and account for 93% of the total PAHs concentration (Rong, 2011). Therefore, the oil exploration activities might cause the ecological risk of the central region. Occasional adverse biological effects were likely to occur for Nap, Ace, Acp, Phe and DbA in surface sediment from the Liaodong Bay. The ecological risk of the central region of Liaodong Bay was higher than the coastal region of Liaodong Bay.

3.3.2 *Toxicity assessment of PAHs*

The BaP_{eq} concentrations of total PAHs ranged from 2.13 ng/g to 8.19 ng/g, with a mean value of 4.52 ng/g for Cluster 1, and ranged from 7.25 ng/g to 20.4 ng/g, with an average value of 12.1 ng/g for Cluster 2. The results revealed that the toxicity of PAHs in the central region of Liaodong Bay was higher than the coastal region along the Liaodong Bay. For Clusters 1 and 2, the mean BaP_{eq} concentration of BaP, BbF, DbA, BkF, BaA and InP was higher than other individual PAHs. The seven potentially carcinogenic PAHs ($CPAH_7$), including BaA, Chr, BbF, BkF, BaP, DbA and InP, were commonly used for the toxicity assessment of sediments. The BaP_{eq} concentration of $CPAH_7$ ranged from 2.02 ng/g to 8.00 ng/g, with a mean value of 4.38 ng/g for Cluster 1, and ranged from 6.91 ng/g to 20.1 ng/g, with a mean value of 11.8 ng/g for Cluster 2. For Clusters 1 and 2, the BaP_{eq} concentration trend of CPAHs was consistent with total PAHs. The BaP_{eq} concentrations of CPAHs accounted for more than 95% of total PAHs, and were the main contributors to carcinogenic potencies of the Liaodong Bay sediments. In comparison, the BaP_{eq} concentrations of $CPAH_7$ in sediments of the Liaodong Bay were lower than those of other areas reported in previous studies, such as the Meiliang Bay in China (94–856 ng/g) (Qiao et al., 2006), the Kaohsiung Harbor in Taiwan, China (3.9–1 970 ng/g) (Chen et al., 2013). The low BaP_{eq} concentrations indicated potentially low carcinogenicity. The contribution of CPAHs decreased in the order as follow: BaP (2.07 ng/g)>BbF (0.75 ng/g)>DbA (0.71 ng/g)>BkF (0.46 ng/g)>BaA (0.27 ng/g)>InP (0.03 ng/g)>Chr (0.09 ng/g) (Cluster 1) and DbA (4.27 ng/g)>BaP (3.86 ng/g)>BbF (1.65 ng/g)>BaA (0.86 ng/g)>BkF (0.77 ng/g)>InP (0.07 ng/g)>Chr (0.35 ng/g) (Cluster 2).

4 Conclusions

Sixteen PAHs were quantitatively analyzed in thirty-six surface sediments of the Liaodong Bay. The concentrations of sediments from the Liaodong Bay were lower than those in other areas worldwide. The higher pollution sites are mainly located in the central region of Liaodong Bay and the offshore oil exploration area. A combination of cluster analysis, PCA-MLR and diagnostic ratios was used to identify the sources of PAHs in surface sediment from the Liaodong Bay. PAH contaminations in the Liaodong Bay were caused by mixed sources and the majority was combustion sources, potential contributions from petroleum sources were not excluded. The surface sediments of the Liaodong Bay posed a slight potential threat to organisms living there, and would occasionally cause negative ecological effects according to the ecological risk assessment. The results indicated that surface sediments in the Liaodong Bay had low ecological risk with low toxic pollution, and the ecological risk and toxic pollution levels in the central region of Liaodong Bay and the offshore oil exploration area were higher than the coastal region along the Liaodong Bay.

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