Distributions and sources of petroleum, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in surface sediments from Bohai Bay and its adjacent river, China

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ABSTRACT

Surface sediment samples from Bohai Bay and its adjacent river, China, were analyzed for aliphatic hydrocarbon, PAHs and biomarkers in order to determine the distribution, composition and source of organic matter in a coastal environment. Results suggested that the input of organic matter from anthropogenic activities has a more significant influence on its distribution than that from natural processes. Petroleum contamination, mainly from offshore oil exploration and discharge of pollutants from rivers, was the main source of n-alkanes. PAHs were mostly of pyrogenic origin; while some sites in Yellow River Estuary were derived mainly from the petrogenic sources. The toxic assessment suggested that the PAHs in surface sediments will not cause immediately adverse biological effects in sediments from Bohai Bay and its adjacent river, China.

Estuaries and coastal zones are the main channels between the lands and the oceans, which can trap significant quantities of natural and anthropogenic organic matter (OM) under the interactions of a series of physical, chemical and biological processes (Thornton and McManus, 1994; Liu et al., 2012). Land-derived OM can be transported into the marine systems by river discharge and atmospheric deposition. Bohai Bay is a large, semi-enclosed shallow water basin located along the western region of Bohai Sea in the northeastern part of China. Over the last decade, rapid economic development and urbanization have significantly impacted on its environments. These changes, in turn, have the potential to alter the nature and content of OM of marine deposits in Bohai Bay.

Hydrocarbons are abundant components of organic material in coastal zones, and one of the major classes of organic compounds. Among the organic contaminants, aliphatic and polycyclic aromatic hydrocarbons (PAHs) have received much attention due to their ubiquitous distribution in marine sediments (e.g. Sultan and Sameer, 1997; Zanardi et al., 1999; Wang et al., 2006; Liu et al., 2009; Yang et al., 2009; Commendatore et al., 2012; Kanzari et al., 2014). There are several reports on the environmental

aspects of Bohai: seawater (Hu et al., 2005), sediment (Ma et al., 2001; Hu et al., 2009) and biota (Zhou et al., 2007). However, detailed information on petroleum and aliphatic hydrocarbon distribution in this region remains scarcely documented, especially covering both the marine and riverine regions. Here, the levels of aliphatic hydrocarbon (total and linear alkanes), PAHs and petroleum biomarker (terpanes and steranes) were measured in surface sediments of coastal Bohai Bay to determine the distribution, composition, source and the factors controlling their distribution and accumulation. A systematic survey on inputs of petroleum pollutant from main continental rivers flowing into Bohai Bay was also conducted.

Sediments used in this study were collected from 40 sites of coastal Bohai Bay in April 2012. The sampling stations were arranged along the major rivers (*Luanhe River*, *Douhe River*, *Yongdingxinhe River*, *Ziyaxinhe River* and *Yellow River*) of this area extending from the land to the sea and formed five transects (TA, TB, TC, TD and TE) (Fig. 1). The surface sediments from the marine region were collected using a Van Veen style stainless steel grab sampler, and the surface sediments from rivers were collected using a plastic spatula. The top 0–5 cm sediment was collected at each sampling site. After collection, the samples were homogenized and placed into sterile polyethylene bags, sealed and frozen at −20 °C in the dark until further analysis.

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Sediment samples were first dried at 60 °C and separated with a 125-μm sieve to remove large particles and debris. The dried sediment samples were then ground into powder with a mortar and pestle. For total lipid extraction, about 100 g dry sediment sample was Soxhlet-extracted with chloroform for a period of 72 h. Elemental sulfur was removed from the extracts using activated copper. The extracts were fractionated by column chromatography on alumina over silica gel. Saturated hydrocarbons, aromatic hydrocarbons and non-hydrocarbons were obtained by successively eluting with *n*-hexane, toluene and chloroform/methanol (98:2), respectively. The aliphatic and aromatic fractions were concentrated again on a rotary evaporator, transferred to a vial, and then the volume was adjusted to 1 mL exactly using a stream of filtered N_2 gas. An aliquot of 1 ml of each extract was subjected to gas chromatography–mass spectrometry (GC–MS) analysis.

The aliphatic hydrocarbon were analyzed on Hewlett–Packard 6890 gas chromatograph interfaced with a Hewlett–Packard 5973 mass detector made by Agilent (USA). The samples were analyzed using a fused silica capillary column (30 m × 0.20 mm × 0.25 μm film thickness) with helium as carrier gas. The temperature was programmed from 80 °C to 290 °C at 4 °C/min and held at the final temperature for 30 min. The injector temperature and transfer line temperature were 250 °C and 180 °C, respectively. The mass spectrometer was operated at an electron energy of 70 eV with an ion source temperature of 250 °C.

The concentration of *n*-alkanes was determined by using authentic standards of *n*-alkanes (C_{16}, C_{20}, C_{24}, C_{28}, and C_{32}). Individual *n*-alkanes were identified based on the retention times and mass spectra of target compounds against the authentic standards. The terpanes and steranes were detected in their key mass chromatograms (*m/z* 191, 217) based on the relative retention times and by comparing their mass spectra with published data. The standard deviation of the calculations of the peak areas was better than 0.5%. Individual PAHs were quantified based on the retention time and *m/z* ratio of an authentic PAHs mixed standard (Sigma), and concentrations of each PAHs were calibrated based on the standard calibration curve. For quality assurance and quality control, the method blanks (solvent) and spiked matrixes (standards spiked into soil) were analyzed. None of the target compounds was detected. Seven surrogate standards (naphthalene-d8, acenaphthylene-d8, phenanthrene-d10, fluoranthene-d10, pyrene-d10,

benzo(a)pyrene-d12 and benzo(g,h,i)perylened12) were added to all samples to monitor matrix effects. The average recoveries of surrogate standards varied from 81.6% to 92%. In addition, the detection limit ranged from 0.15 to 0.7 ng/g dry weight (dw).

The sample granulometry was analyzed on fresh sediments using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of the following three groups of grain sizes were determined: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand).

A high abundance of aliphatic hydrocarbons in sediments is a potential source of pollution. The levels of $\sum n$-C_{12-34} concentrations concentration of the studied sediments is 994.62 ± 537.63 ng g^{-1} dry weight (Fig. 2), which were relatively lower or moderate compared to those of worldwide locations reported to be chronically contaminated by oil, such as 500–8120 ng g^{-1} in Jiaozhou Bay (Wang et al., 2006), 160–1880 ng g^{-1} in Yangtze River Estuary (Bouloubassi et al., 2001), 100–14,560 ng g^{-1} in highly contaminated sediments from Santos, Brazil (Medeiros and Caruso Bíego, 2004). Furthermore, the concentrations of *n*-alkane from North region are higher than those of South region (Fig. 2). Sediment granularity in intertidal zone showed the obvious difference of "fine in north" (dominated by clayey-silt) and "coarse in south" (dominated by sandy) (Fig. 3), which illustrated the different sedimentary dynamics in two areas, and it also explained the spatial difference of TOC and *n*-alkane concentration. The four tributaries, Suyun River, Yongding River, Duliujian River and Ziya River, produce a marked effect on discharge of flood for the Haihe River in summer. Based on the fact that the rivers flow through the main areas with high density of population in North China, hence, receiving plenty of sewage from cities was inevitable. Except Luanhe River and Yellow River, the total *n*-alkane concentrations of riverine sediment are much higher than that of offshore area, which suggested the fugitive petroleum contamination from sewage discharge from the Dohe River, Yongdingxinhe River and Ziyaxinhe River. In addition, the total *n*-alkane concentrations decrease seaward along all the studied transects (Fig. 2). This explanation is also consistent with the seaward decrease in autogenous organic carbon (Gao et al., 2012).

n-Alkanes in the sediment profiles showed two model (Fig. 4). The first model (Type A) range from *n*-C_{12} to *n*-C_{34}, with *n*-C_{29} or *n*-C_{31} as maximum, and a significant odd carbon number
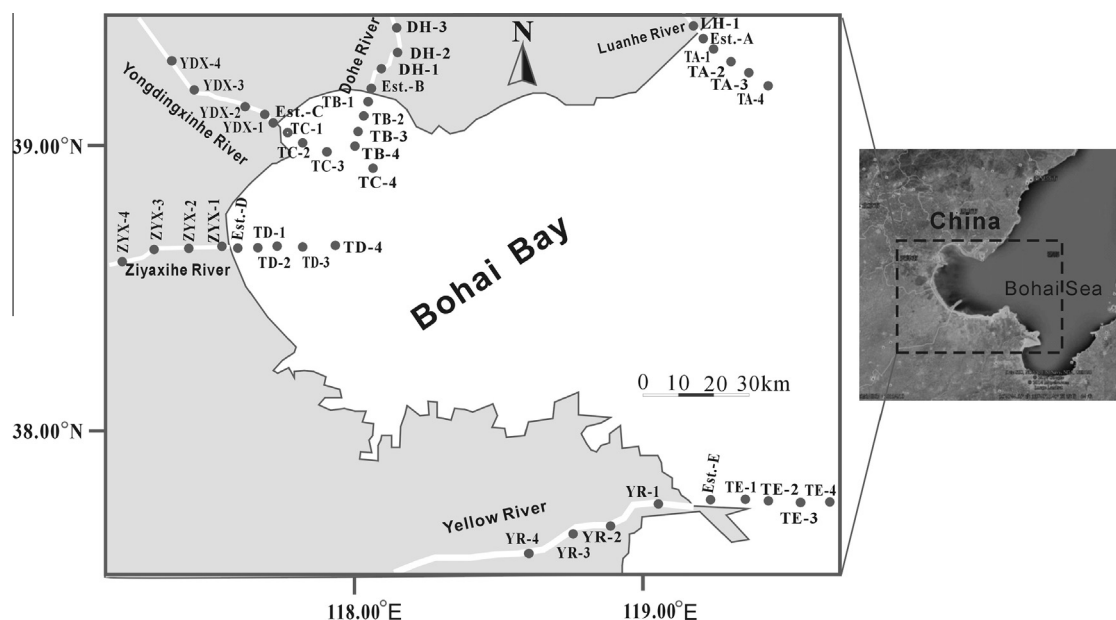

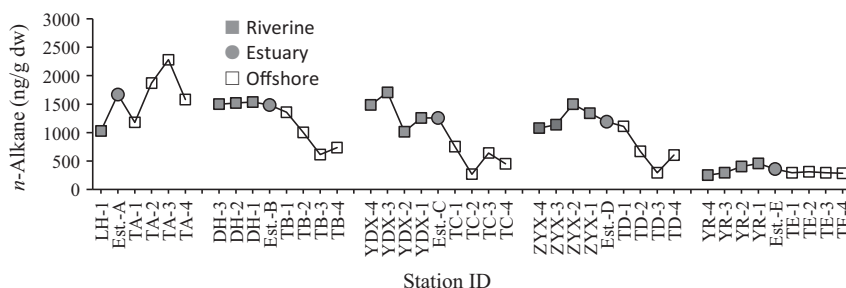**Fig. 1.** Location of sampling sites in coastal Bohai Bay.

Fig. 2. GC–MS chromatograms of the aliphatic hydrocarbons in the typical surface sediment sample (site YDXH-4 and site YR-4). (Pr = pristane, Ph = phytane, UCM = unresolved complex mixture.)
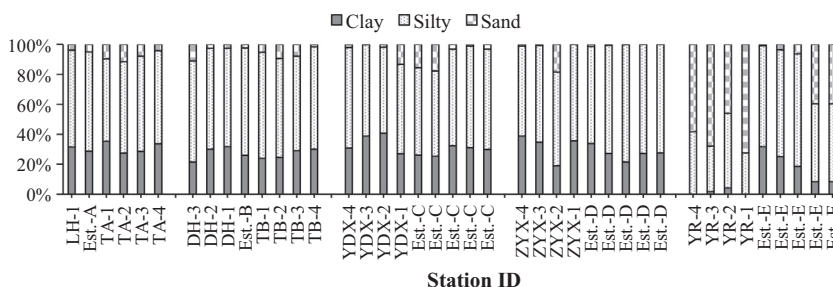

Fig. 3. Spatial variations of total n-alkanes (ng g^{-1} dw) in surface sediments of coastal Bohai Bay. (Est.-A: the estuary of Luanhe River; Est.-B: the estuary of Dohe River; Est.-C: the estuary of Yongdingxinhe River; Est.-D: the estuary of Ziyaxinhe River; Est.-E: the estuary of Yellow River.)

predominance. The second mode (Type B) for n-alkane ranging from n-C$_{12}$ to n-C$_{34}$, with a maximum at C$_{15}$–C$_{19}$ and a minor odd/even predominance, was probably caused by both a microbial hydrocarbon contribution and a slight higher plant wax contribution. Except Yellow River and its coastal marine environment, most other samples are all belong to Type A.

The Low Molecular Weight to High Molecular Weight ratio (LMW/HMW), and the Carbon Preference Index (CPI), have frequently been used as source indicators of n-alkanes in marine sediments (Prahl et al., 1994; Doskey, 2001; Hu et al., 2009). The LMW/HMW ratios of the samples are all <1 for most samples (Fig. 5). We expect that the presence of heavier oil or more degraded crude oil, along with the preferential degradation of light hydrocarbons, would give the observed low ratios of LMW/HMW (<1) as suggested by Commendatore et al. (2000). Contamination from natural hydrocarbon seepage as observed in many coastal environments could also influence the values of LMW/HMW and CPI of n-alkanes in sediments depending on the degradation stage of injected oil. On the whole, aliphatic hydrocarbons in 24 out of 40 sediment samples analyzed in the present study were characterized with an obvious odd–even carbon preference, with CPI$_{24-34}$

greater than 1 (1.07–2.97) but lower than 3. On the other hand, CPI$_{24-34}$ in the remaining samples (mainly in Yellow River) contained no obvious odd–even carbon number preference with CPI$_{24-34}$ around 1, suggested an increasing input of anthropogenic hydrocarbons as well as the mixture of marine bacterial inputs (Harji et al., 2008; Pearson and Eglinton, 2000). CPI$_{24-34}$ values in surface sediments from riverine sampling sites are apparently lower than that from the marine region (Fig. 6). It reflected that the input of organic matter from anthropogenic activities has a more significant influence on its spatial distribution than from natural processes.

The terrigenous/aquatic ratio (TAR) can evaluate the importance of terrigenous inputs versus aquatic inputs (Mille et al., 2007). The ratio is very high for all stations and confirms the significance of terrestrial inputs in coastal zone area of Bohai Bay (Fig. 7). High TAR values could also be caused by the preferential preservation of terrestrial hydrocarbons over planktonic ones in marine environment. There is a net seaward decrease in TAR in marine sediments. A straightforward explanation for this trend is a progressive seaward decrease in the proportions of terrigenous organic matter relative to marine autogenous organic matter. This explanation is also consistent with the seaward decrease in CPI. However, such a distribution pattern is not very distinct in the marine region of coastal Bohai Bay in this study, which may be due to that the hydrodynamic condition and flat sea-floor of this area make organic matter from different sources well mixed.

The occurrence of unresolved complex mixture (UCM) may be reflective of petroleum contamination and/or chronically degraded complex mixture of hydrocarbons (Gough and Rowland, 1990; Frysinger et al., 2003; Tolosa et al., 2004; Mille et al., 2007). The low values for UCM/Σn-alkane (<10) ratios of this study indicate a pollution diluted by natural input (Silva et al., 2012). In this study, UCM/Σn-alkane ratio values ranged from 1.05 to 3.42, showing an important biodegradation of petroleum related input. Other indicators of petroleum contamination are isoprenoids, such as pristane and phytane (Volkman et al., 1992). Except for sites YR-2, YR-1 and Estuary-E (Fig. 8), other samples were characterized
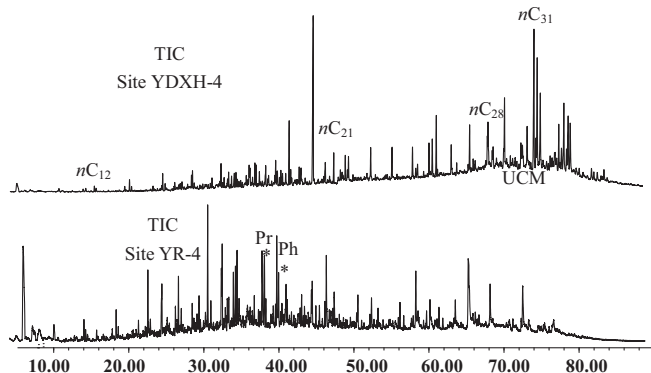

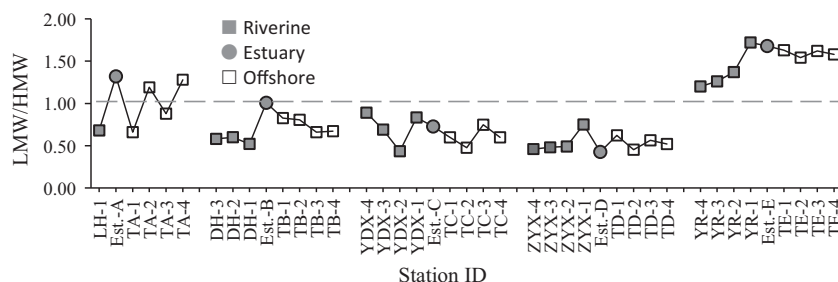**Fig. 4.** Diagram showing the sediment classification and deposition patterns.

Fig. 5. Spatial variations of LMW/HMW ratios in surface sediments of coastal Bohai Bay. (LMW/HMW: [Sum of Low Molecular Weight (nC_{12} to nC_{21})]/[Sum of High Molecular Weight (nC_{22} to nC_{34})] n-alkanes ratio.)
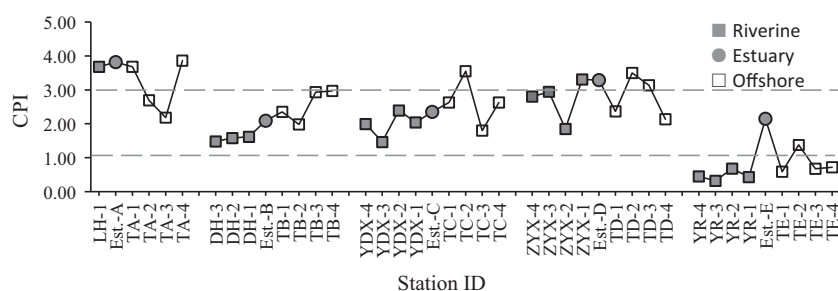

Fig. 6. Spatial variations of CPI ratios in surface sediments of coastal Bohai Bay. (CPI: Carbon Preference Index calculated as $0.5 * [(C_{23} + C_{25} + C_{27} + C_{29} + C_{31})/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{23} + C_{25} + C_{27} + C_{29} + C_{31})/(C_{22} + C_{24} + C_{26} + C_{28} + C_{30})]$.)
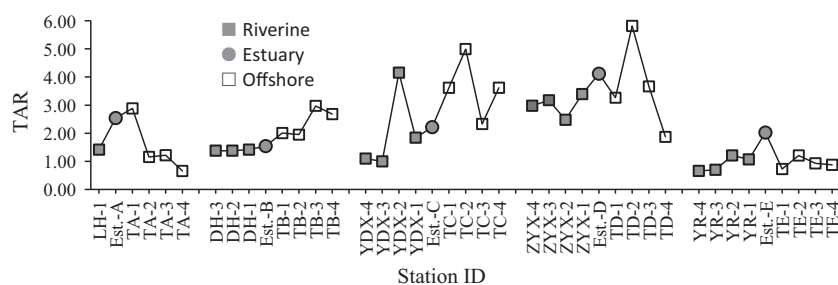

Fig. 7. Spatial variations of TAR ratios in surface sediments of coastal Bohai Bay. (TAR: terrigenous/aquatic ratio calculated as $(nC_{27} + nC_{29} + nC_{31})/(nC_{15} + nC_{17} + nC_{19})$.)

with low Pr/Ph values (0.77 ± 0.16), suggesting predominant petrogenic sources rather than biogenic (zooplanktons and/or marine animals). For recent sediments, the ratios Pr/n-C$_{17}$ and Ph/n-C$_{18}$ lower than 1 indicate a relatively recent oil input, while values higher than 1 of these indices coupled with high concentrations of hydrocarbons suggest the presence of degraded oil products (Mille et al., 2007; Commendatore et al., 2012). For most stations, low ratio values of Pr/n-C$_{17}$ and Ph/n-C$_{18}$ were found which confirms a recent pollution of oil inputs (Fig. 8).

The presence of oil is also confirmed by the identification of the hopane and sterane series. The hopanes distribution is characterized by the predominance of C$_{30}$ 17α (H), 21β(H)-hopane with a smooth decrease in the abundance of C$_{31-35}$ homohopanes in these series. Gammacerane, a nonhopanoid C$_{30}$ triterpane, was also present in the samples (Fig. 9). This compound is a biomarker commonly found in most Chinese crude oil geologically derived from lacustrine sources (Philp and Fan, 1987). Similar hopane distributions were reported for the petroleum samples from the Shengli
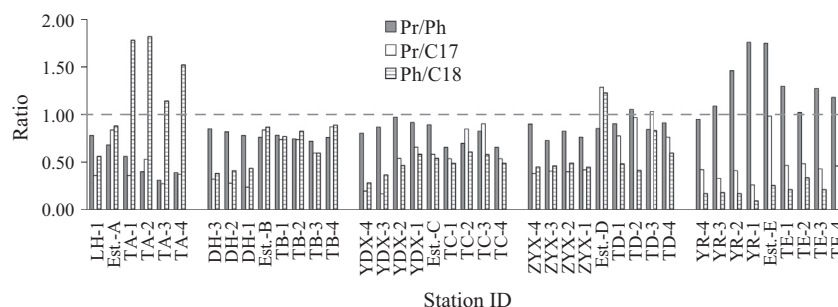

Fig. 8. Spatial variations of Pr/Ph, Pr/n-C$_{17}$ and Ph/n-C$_{18}$ ratios in surface sediments of coastal Bohai Bay.
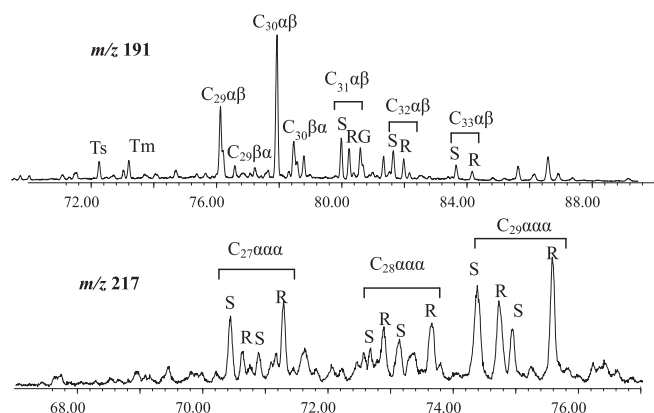
Fig. 9. Mass fragmentogram of $m/z = 191$ (hopanes) and $m/z = 217$ (steranes) from sediment in site YDX-4. (For hopane, α, β = 17α(H), 21β(H)-hopanes; β, α = 17β(H), 21α(H)-hopanes; R and S = C-22 R and S configuration; G = Gammacerane; Ts = 18α(H)-22,29, 30-trisnorhopane; Tm = 17α(H)-22, 29, 30-trisnorhopane. For steranes, $\alpha\alpha\alpha$ = 5α(H), 14α(H), 17α(H)-steranes; $\alpha\beta\beta$ = 5α(H), 14β(H), 17β(H)-steranes; R and S = C-20 R and S configuration.)

Fig. 11. Spatial variations of 16 PAHs (ng g^{-1} dw) in surface sediments of coastal Bohai Bay.

Oilfield (Pang et al., 2003) and the surface sediments in the Yellow River Estuary (Bigot et al., 1989; Wang et al., 2011). The steranes were detected in all samples analyzed and comprised mainly the 5α, 14β, 17β and minor 5α, 14α, 17α configurations, both occurring as 20S and 20R epimers (Fig. 9). The relative abundances of three regular sterane series are in an order of $C_{29} > C_{27} > C_{28}$, suggesting the oil contaminate the sediments derived from mixed terrigenous and algal–bacterial organic matter with higher plant as dominanties formed under a weakly reducing. The values of the ratio 22S/22S + 22R epimers of $\alpha\beta C_{31}$ homohopanes vary in a narrow range 0.55–0.60, close to the value of 0.6 for equilibrium of oil full maturity (Peters et al., 2005), suggesting petroleum-related hydrocarbon contamination in sediments (Fig. 10a). Maturity indicators based on steranes such as $C_{29}\alpha\alpha\alpha S/(S + R)$ ratio (0.5 at equilibrium; Peters et al., 2005) also show only minor variations among the analyzed samples (0.41–0.57) (Fig. 10b) and have the high maturity level. Therefore the occurrence of mature hopanes and steranes in Bohai Bay sediments clearly confirms the input of a fossil fuel contamination.
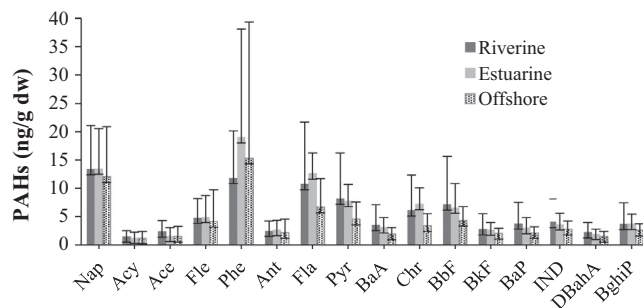
Bohai has many offshore oilfields. In particular, the Chengdao offshore oilfield, a part of the land-based Shengli Oilfield (the second largest one in China) is in the north of the Yellow River Estuary (YRE). Thus, detecting petroleum-based contaminants in this area should be no surprise. In the coastal areas of the Bohai Bay near Tianjin Harbor, UCM concentrations were also high, suggesting the fugitive petroleum contamination from shipping activities and sewage discharge from the Haihe River.

As a large group of persistent organic pollutants, PAHs can undergo long-range transport and exist for a long time in the environment. Due to their carcinogenicity, mutagenicity, and toxicity, 16 US EPA priority PAHs (16 PAHs) are included in the list of priority pollutants of US EPA. The total concentrations of $\Sigma16$ PAHs in samples ranged from 24.62 to 280.60 ng/g dry weight with a mean concentration of 79.27 ± 52.40 ng/g. Compared with the other area in the world (Tolosa et al., 1996; Yuan et al., 2014), the PAH contamination was lower than those reported from Pearl River Delta (China; 217–2680 ng g^{-1}), Yangtze River Estuary (China; 90.14–502.12 ng g^{-1}), South Carolina marsh (USA; 69–37,000 ng g^{-1}) and Mediterranean coast (Egypt; 3.5–14,100 ng g^{-1}), but higher than the Chongming wetlands (China; 38.7–136.2 ng g^{-1}). The highest concentrations of ΣPAHs were found in sites from YDX4, YDX-3, YDX-2, YDX-1, Est.-E, TE-1, TE-2, TE-3, TE-4, in the Yongdingxinhe River and the offshore area near Yellow River. These sites were also characterized with high concentration of
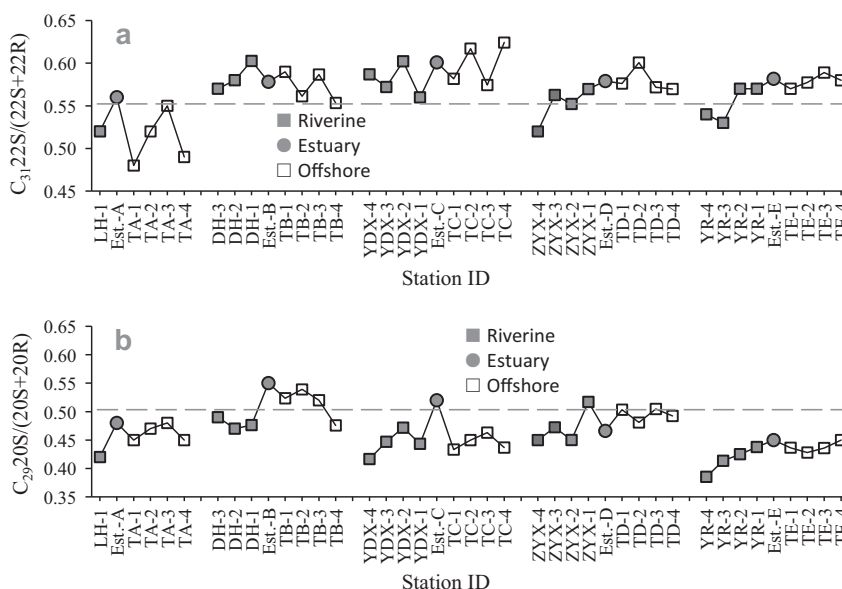

Fig. 10. Spatial variations of C_{31}22S/(22S + 22R) and C_{29}20S/(20S + 20R) ratios in surface sediments of coastal Bohai Bay.
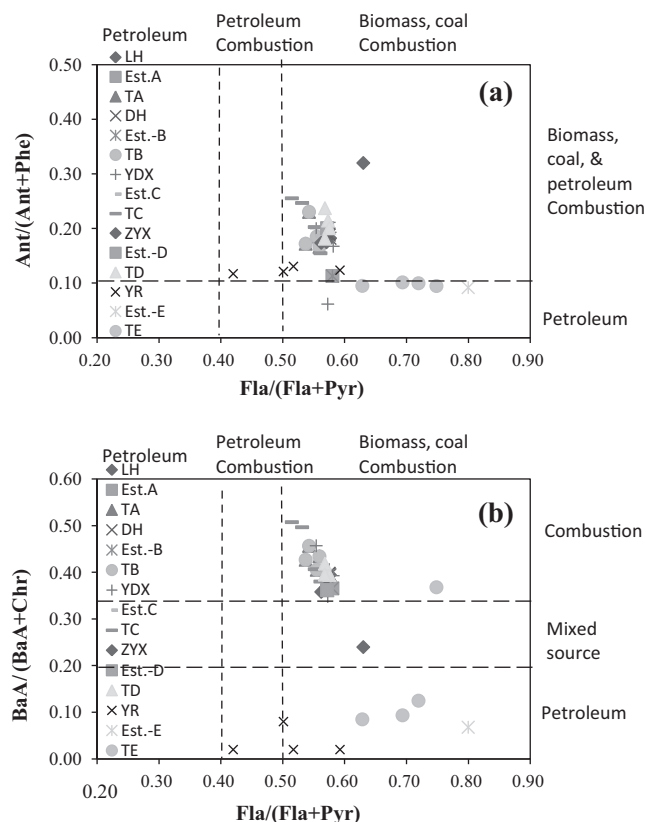
Fig. 12. Diagnostic PAHs ratios of (a) Ant/(Ant/Ant + Phe) versus Fla/(Fla + Pyr) and (b) BaA(BaA + Chry) versus Fla/(Fla + Pyr).

2002; Yang et al., 2009). In summary, it can be seen that the samples for YR, Est.-E, TE and DH exhibited more evidence of petroleum derived pollution (Fig. 12), while other samples may be derived primarily from biomass and coal combustion. Except pyrolytic input as a major source, petrogenic may be also a source for PAHs may be due to Shengli Oilfield and other oilfield drilling platforms in Bohai Bay.

Sediment quality guidelines (SQGs) are an important tool for the assessment of contamination in marine and estuarine sediments (Long et al., 1995; Quiroz et al., 2010). Two sets of SQGs, including (a) the ERL/ERM and (b) the TEL/PEL values, were applied in this study to assess the ecological toxicity of individual PAHs concentrations in sediments (Fig. 11; Table 1). In the three ranges of chemical concentrations, adverse biological effects were expected rarely (<ERL/TEL), occasionally (≥ERL/TEL and <ERM/PEL), and frequently (≥ERM/PEL) (Long et al., 1995; Qiao et al., 2006). It showed that concentrations of all PAHs were below their respective ERL and PEL values in all stations by the comparison of pollutants levels with SQGs. It may be concluded that PAHs will not cause immediately adverse biological effects in sediments from Bohai Bay and its adjacent river, China.

The anthropogenic activities have a significant influence on the geochemistry of organic matter in riverine sediments besides natural processes; the spatial distributions of LMW/HMW, CPI and TAR in marine sediments are mainly controlled by the mixing inputs of terrigenous and marine components. The ubiquitous presence of UCM, composition patterns of hopanes and steranes, and Pr/n-C_{17}, Ph/n-C_{18} ratios indicated that the petroleum contamination in Bohai Bay was mainly from the offshore oilfields and sewage discharges from the surrounding rivers. PAHs isomeric ratios indicated that the PAHs in sediments were mostly of pyrogenic origin; while various sites in Yellow River Estuary were derived mainly from the petrogenic sources. PAHs will not cause immediately adverse biological effects in sediments from Bohai Bay and its adjacent river, China.

Acknowledgements

the low rings PAHs. The industrial wastewater from Yongdingxinhe River and oil spill from Shengli Oilfield may contribute to this. The spatial distributions of PAHs in surficial sediments from the coastal Bohai are broadly similar with their average values being lower in offshore sediments than in riverine ones and estuarine (Fig. 11).

PAHs are introduced into environmental compartments both from natural (organic matter diagenesis, plant synthesis, forest and prairie fires, volcanoes, etc.) and anthropogenic processes (fossil fuel burning, incomplete combustion of organic matter, petroleum, incineration, etc.). Diagnostic ratios of PAHs, such as Ant/(Ant + Phy), BaA/(BaA + Chry) and Flu/(Flu + Pyr) have been developed to identify the possible sources of PAHs (Yunker et al.,

Table 1
Toxicity guidelines of PAHs compounds for sediment matrices (ng g^{-1}) and maximum concentrations in the surface sediments.

PAHs	Guideline				This study					
					Max			Ave		
	ERL	ERM	TEL	PEL	Riverine	Estuary	Offshore	Riverine	Estuary	Offshore
Nap	160	2100	34.6	391	27.79	25.38	34.35	13.38	13.44	12.03
Ace	16	500	6.71	88.9	3.38	2.97	4.03	1.49	1.23	1.17
Acy	44	640	5.87	128	6.90	4.17	5.95	2.37	1.57	1.46
Flu	19	540	21.2	144	10.27	11.60	19.24	4.77	4.92	4.15
Phe	240	1500	86.7	544	35.25	53.08	90.82	11.83	19.00	15.30
Ant	85.3	1100	46.9	245	8.34	5.37	9.53	2.47	2.65	2.15
Fla	600	5100	113	1494	43.62	17.03	23.73	10.75	12.59	6.66
Pyr	665	2600	153	1398	32.54	11.32	14.02	8.16	7.77	4.52
BaA	261	1600	74.8	693	13.29	5.00	4.35	3.51	3.12	1.87
Chr	384	2800	108	846	24.89	11.31	9.87	6.12	7.21	3.37
Bap	430	1600	88.8	763	15.11	5.04	4.28	3.77	2.97	2.13
DahA	63.4	260	6.22	135	4.81	2.92	2.43	2.25	1.91	1.47

ERL: effects range-low; ERM: effects range-median; TELs: threshold effects levels; PELs: probable effects levels; Ave: Average concentration; Max: maximum concentration.

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