Sources and distribution of aliphatic and polycyclic aromatic hydrocarbons in Yellow River Delta Nature Reserve, China

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ABSTRACT

Sediment samples collected from the Core Area, Experimental Area and Buffer Area of Yellow River Delta National Nature Reserve (YRDNNR), China, were analyzed by GC–MS in order to determine the degree of hydrocarbon contamination, and identify the sources of aliphatic hydrocarbons and PAHs. The total petroleum hydrocarbon contents of sediments were relatively low or moderate compared to world-wide locations reported to be chronically contaminated by oil. On the whole, the degree of petroleum contamination in the Core Area and Buffer Area in YRDNNR is weaker than that of the Experimental Area. The potential ecosystem risk assessment indicated that PAHs will not cause immediate adverse biological effects in the YRDNNR. Besides oil-related hydrocarbon inputs in this region, aliphatic hydrocarbon analysis showed the presence of hydrocarbons of terrestrial origin at some sampling sites, characterized by high CPI values. Based on PAH ratios and principal component analysis, pyrolytic input may be a major source of PAHs in YRDNNR sediment, while petrogenic inputs were more apparent at some sites in the Experimental Area due to oil exploration in the Shengli Oilfield.

1. Introduction

Organic pollution of aquatic environments is of great concern. Among the organic contaminants, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) have received much attention due to their ubiquitous distribution in marine sediments (Witt, 1995; Tolosa et al., 1996; Wang et al., 2006; Zhang et al., 2007; Hu et al., 2009). More importantly, concern has focused on the mutagenic and genotoxic potential of PAHs in the environment, and their carcinogenic effects on natural ecosystems (Long et al., 1995; Benlahcen et al., 1997; Zhang et al., 2004a,b; Hu et al., 2009). This is especially true for many coastal regions where high anthropogenic influence and various contamination sources exist.

Yellow River Delta National Nature Reserve (YRDNNR, 118°33′–119°20′E longitude, 37°35′–38°12′N latitude), was established in 1992 for the protection of a newly born wetland ecosystem. It has a total area of 153,000 ha, of which 79,000 ha the Core Area,

11,000 ha is the Buffer Area, and an area of 6.3 ha is the Experimental Area. However, Shengli Oilfield, the second largest oilfield in China, is located here, which threatens the ecosystem of YRDNNR due to oil well blowouts, leaks and spills from underground tanks, pipelines and illegal disposal. Because of its environmental significance, ecological sensitivity and development potential, the unique environmental conditions in YRDNNR have received great attention. However, most studies of contamination in the Yellow River Delta (YRD) have focused on the distributions of contaminant metals, N and P (Song, 2000; Li et al., 2001; Chen et al., 2007; Hui et al., 2009). A few studies on hydrocarbon pollutants have been undertaken (Luo et al., 2005; Hui et al., 2009) but rarely on aliphatic hydrocarbons, which have toxic effects on aquatic organisms and are probably carcinogenic to humans.

This paper represents the first extensive study of the spatial distribution and sources of aliphatic hydrocarbons and PAHs in the sediments from YRDNNR. The main purposes of this research were to assess the level of petroleum contamination in sediments due to the oil production platforms and drilling activities in the studied area, and to find out the source of aliphatic hydrocarbons and PAHs using n-alkane profiles, PAH compositions and petroleum biomarkers.

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2. Materials and methods

2.1. Study area and sampling

Seventeen surface sediment samples throughout the YRDNNR were collected in June 2009. The sampling sites in the Experimental Area, Buffer Area and Core Area of YRDNNR, are shown in Fig. 1. The samples were collected from the top 0–20 cm using a Dutch auger and bulked to form composite samples for analysis. At sites S1, S2 and S6, samples were collected in a traverse from the oil-well at 0.1, 20, 100 m, respectively, in order to determine the horizontal distribution of pollutants at different distances from the oil-well base. Bulked (600–1000 g) composite surface soil samples from each sampling point were put in a sterile polyethylene bag, flame-sealed and transported to the laboratory for gas chromatography–mass spectroscopy (GC–MS) analysis.

2.2. Extraction and fractionation

Sediment samples were first dried at 60 °C and sieved at 125 μm 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 samples were Soxhlet-extracted with chloroform for a period of 72 h. Elemental S was removed from the extracts using activated Cu. 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 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 GC–MS analysis.

2.3. Instrumental analysis

The saturated and aromatic hydrocarbons were determined by Agilent HP 6890 gas chromatograph interfaced with HP 5973 mass-selective detector (MSD). A fused silica capillary column (30 m × 0.25 mm) coated with HP-5MS (film thickness 0.25 μm) was used with He as carrier gas. The temperature was programmed from 80 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.

Individual n-alkanes were identified based on the retention time of the authentic standards (nC$_{10-40}$, Sigma), and concentrations of each n-alkane were calculated based on the standard calibration curve of each corresponding standard compound. Individual PAHs were quantified based on the retention time and m/z ratio of an authentic PAHs mixed standard (Sigma), and concentrations of each PAH were calibrated based on the standard calibration curve.

For quality assurance and quality control, method blanks (solvent) and spiked matrixes (standards spiked into soil) were analyzed. None of the target compounds was detected. The recovery and relative standard deviation for n-C$_{13}$–n-C$_{18}$ were in the range of 68.8–85% and 4.2–19.3%, respectively, and those for n-C$_{19}$–n-C$_{36}$ were in the range of 87.5–96.2% and 2.8–12.4%, respectively. The detection limits of the method range from 3.1 and 12.4 ng/g. All concentrations are expressed on a soil dry weight basis. For PAHs, 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).

3. Results and discussion

3.1. Assessment of petroleum contamination

The levels of total petroleum hydrocarbons (TPH) in sediments were relatively low or moderate. It has been reported that the free hydrocarbon content of the sediment of the YRD ranged from 10 to 440 μg g^{-1} (Li et al., 2001). The concentrations of hydrocarbon in the samples are shown in Table 1. The highest concentration of
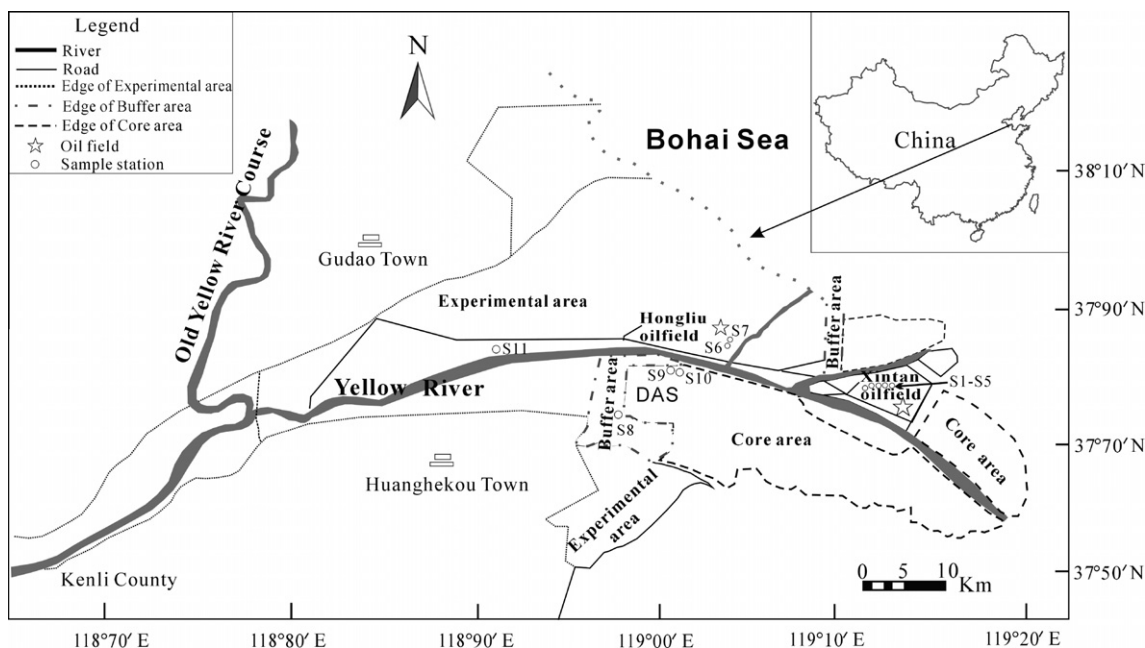

Fig. 1. Study areas and sampling locations in the YRDNNR.

Table 1
Total petroleum hydrocarbon, aliphatic hydrocarbon and PAH concentrations ($\mu g\,g^{-1}$ dry wt) with different distances from oil well in surface sediment of S1-S11 sites.

Site no.	Station		TPH			Aliphatic hydrocarbon	PAHs
	Distance from oil well (m)		0.1	20	100	0	0
S1	Experimental Area	Xintan Oilfield	1780	360	210	55.22	18.55
S2			4850	720	240	81.15	27.10
S3			114.0	n	n	38.40	7.70
S4			651.16	n	n	32.86	10.14
S5			49.89	n	n	36.38	7.19
S6		Hongliu Oilfield	240	180	100	38.65	6.82
S7			182.9	n	n	35.73	3.59
S8	Buffer Area		77.72	n	n	37.92	5.64
S9	Core Area	DAS	170	n	n	40.20	5.79
S10			134.3	n	n	38.03	3.96
S11	Experimental Area		100	n	n	22.10	8.43

n: Data not available; TPH include hexane, benzene, toluene, xylene, naphthalene, fluorene, and other constituents of gasoline, jet fuels, mineral oils, and other petroleum products.

TPH was found at the oilfield, which could be a consequence of illegal discharge of petroleum wastewater or crude oils. For example, the highest value for the sludge samples appears at sites of S1 and S2, where a small-scale oil spill accident had occurred. Compared with this, the lowest values were found at site S11 in the Experimental Area, S8 in the Buffer Area, and S9 and S10 in the Core Area, ranging from 77.72 to 170 $\mu g\,g^{-1}$. On the whole, the TPH concentration in the Experimental Area and Buffer area were much lower than that of Experimental Area. Moreover, TPH content shows a significant decline outward from the center of the oil-wells (Table 1). Generally speaking, total hydrocarbon concentrations >500 $\mu g\,g^{-1}$ are indicative of significant pollution, values <10 $\mu g\,g^{-1}$ are considered to denote unpolluted sediments (Volkman et al., 1992). Except for the sludge sample that was significantly contaminated, the levels of TPH concentration in YRDNNR were relatively lower or moderate compared to those of worldwide locations reported to be chronically contaminated by oil, such as 0.05–779 $\mu g\,g^{-1}$ in the Gulf of Oman (Tolosa et al., 2005), 60–646 $\mu g\,g^{-1}$ in highly contaminated sediments from Hong Kong's Victoria Harbor (Hong et al., 1995) and 11–6900 $\mu g\,g^{-1}$ along the oil-impacted coastline of Saudi Arabia after the Gulf War (Readman et al., 1996).

The concentrations of aliphatic hydrocarbons (22.1–81.15 $\mu g\,g^{-1}$ dw) measured in the surface sediments of YRDNNR are in the low to medium range when compared with many other contaminated coastal sediments (Table 1). For example, Commendatore et al. (2000) reported aliphatic hydrocarbon concentrations as high as 1305 $\mu g\,g^{-1}$ in petroleum polluted coastal sediments of Patagonia, Argentina. Concentrations of a total of 16 PAHs in the surface sediments studied were relatively low in comparison with many other aquatic systems in China (Ma et al., 2001; Wu et al., 2003; Zhang et al., 2004b; Qiao et al., 2006).

3.2. Aliphatic hydrocarbons

The n-alkanes from sediment could have originated from anthropogenic or natural sources. Generally, the n-alkane fraction isolated from the sediment extracts showed the presence of a homologous series of n-alkanes extending from C_{12} to C_{35}. Typically, abundance of C_{27}, C_{29} and C_{31} with odd-carbon number predominance is an indicator of terrestrial plants, whereas a dominance of the n-alkanes in the range C_{18}–C_{24} without odd-carbon number predominance, suggests an oil input (Sultan and Sameer, 1997). In this study, n-alkanes, representing two distinct sources, are evident on the basis of their distribution pattern in the samples collected. As can be seen in Fig. 2a, the GC profile shows a dominance of n-alkanes in the range C_{11}–C_{19} and has very prominent humps indicating the unresolved complex mixture (UCM) of petroleum-origin hydrocarbons. This profile is very similar to that extracted from the crude oil in this region and as a result is characteristic of petroleum input. Samples S1, S2, S4 and S6 are included the group of predominant petroleum input. In contrast, other samples have both petroleum and terrestrial plant inputs showing a predominance of odd-carbon-number n-alkanes in the range C_{25}–C_{31} and the presence of UCM (Fig. 2b).

UCMs are mainly composed of branched alkanes, cycloalkanes and aromatics and are one of the indicators of petrogenic inputs (Volkman et al., 1992; Frysinger et al., 2003). UCMs with different shapes and range were observed in most studied samples, suggesting a petroleum input to the sediment in the YRDNNR area. The presence of a major UCM derived from petroleum residues was further confirmed by the presence of the molecular markers described below. The degree of petroleum contamination can be expressed as the ratio of the unresolved to resolved hydrocarbon compounds (U/R). Values of U/R vary from 1.12 to 11.75, which confirm widespread traces of a petroleum origin in all studied areas.
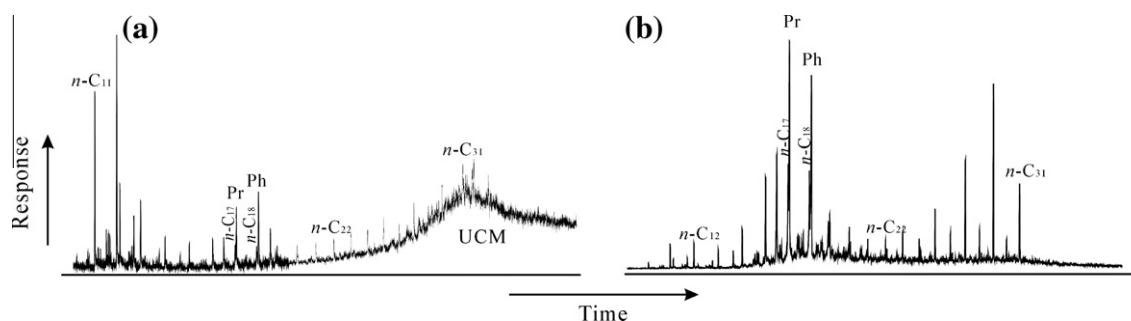

Fig. 2. Aliphatic hydrocarbon profile of a typical sediment sample at site S4 (a) and S8 (b).

Table 2
Characteristics of aliphatic hydrocarbons in surface sediments from the YRDNNR.

Site No.	Pr/Ph	CPI_1	CPI_2	L/H	Ts/Ts + Tm	$C_{31}22S/(22S + 22R)$	γ/C_{30}hopane	C_{27}/C_{29}	$C_{29}20S/(20S + 20R)$	U/R
S1	0.52	0.85	2.25	1.50	0.44	0.58	0.22	0.78	0.42	5.65
S2	0.53	0.78	2.98	1.45	0.40	0.58	0.20	0.85	0.44	10.42
S3	0.51	0.82	2.31	1.60	0.46	0.59	0.21	0.92	0.38	3.45
S4	0.62	0.91	1.29	1.51	0.55	0.59	0.24	0.76	0.53	11.75
S5	0.52	0.78	3.87	1.71	0.41	0.58	0.16	0.86	0.46	4.35
S6	0.61	1.05	1.08	1.11	0.55	0.60	0.12	0.97	0.54	7.57
S7	0.79	0.84	3.78	0.60	0.48	0.58	0.12	1.06	0.39	3.18
S8	0.58	0.67	2.58	0.66	0.44	0.58	0.07	0.70	0.48	5.37
S9	0.73	1.01	3.90	0.60	0.43	0.55	0.07	0.78	0.46	4.40
S10	0.64	0.84	2.13	0.87	0.38	0.60	0.06	0.98	0.48	4.24
S11	0.80	1.03	2.94	0.45	0.44	0.42	0.05	0.85	0.38	1.12

γ: Gammacerane; Ts: 18α-22,29,30-trisnorhopane; Tm: 17α-22,29,30-trisnorhopane; CPI_1: carbon preference index calculated between n-C_{15} and n-C_{23}; CPI_2: carbon preference index calculated between n-C_{23} and n-C_{31}; L/H: ratio of low molecular weight hydrocarbon (n-C_{12}–n-C_{21}) to high molecular weight hydrocarbon (n-C_{22}–n-C_{34}); $C_{31}22S/(22S + 22R)$: 22S(22S + 22R) for C_{31}-17α,21β(H)-homohopane; $C_{29}20S/(20S + 20R)$: ratios of 20S/(20S + 20R) for C_{29}-5α(H),14α(H),17α(H)-steranes; C_{27}/C_{29}: ratio of C_{27} regular steranes to C_{29} regular steranes.

Carbon preference index (CPI) and low/high molecular weight hydrocarbon ratio (L/H) have frequently been used as source indicators of n-alkanes in sediments. The n-alkanes from epicuticular waxes of higher plants show a pronounced odd-carbon number predominance, while fossil fuel and microbial hydrocarbons exhibit CPI ~ 1 (Pearson and Eglinton, 2000; Zhang et al., 2004a). It has been reported that L/H ratios less than 1 usually represent n-alkanes produced by higher plants, marine animals and sedimentary bacteria, while close to 1 suggests n-alkanes that are mainly from petroleum and plankton sources (Gearing et al., 1976), and >2 often indicates the presence of fresh oil in sediments (Commendatore et al., 2000). Petrogenic n-alkanes (CPI_1) values ranged from 0.78 to 1.03, with a median value of 0.88, typical of a petroleum origin. Except for S4 and S6, higher plant wax n-alkanes (CPI_2) values varied between 2.13 and 3.87 with a median of 2.97, suggesting leaf epicuticular waxes as the predominant source for this n-alkane range in most samples. In addition, CPI_1 and CPI_2 of S4 and S6 samples are all close to 1, which is typical of a petroleum origin. Similar results were observed for the L/H. The L/H ratios are all >1 for the samples (S1-S6) from the Experimental Area with oilfields. On the

other hand, the L/H ratios are in the range of 0.45–0.87 for samples from the Core Area and Buffer Area, indicating that vascular plant sources played a very important role.

The two isoprenoids, pristine (Pr) and phytane (Ph), common indicators for petroleum pollution, were present in most sediment extracts. In uncontaminated sediments, the Pr/Ph ratio is typically between 3 and 5 (Steinhauer and Boehm, 1992). The ratio of Pr/Ph was low (0.51–0.80) for the studied samples (Table 2), again indicating a petroleum contribution to the sediments.

3.3. Petroleum biomarkers

Examples of the petroleum biomarker distribution patterns are shown in Fig. 3. Hopanes comprised a series of 17α(H), 21β(H)-compounds, maximizing at the C_{30} homologue, and less prominent 17β(H), 21α(H)-hopanes. Extended hopanes ($C \geqslant 31$) were also present as pairs of the C-22 diastereoisomers (22R, 22S) with a 22S/22S + 22R ratio of about 0.6, which also typifies petrogenic material. Gammacerane, a non-hopanoid C_{30} triterpane, was also present in the analyzed sediments due to most Chinese crude oils
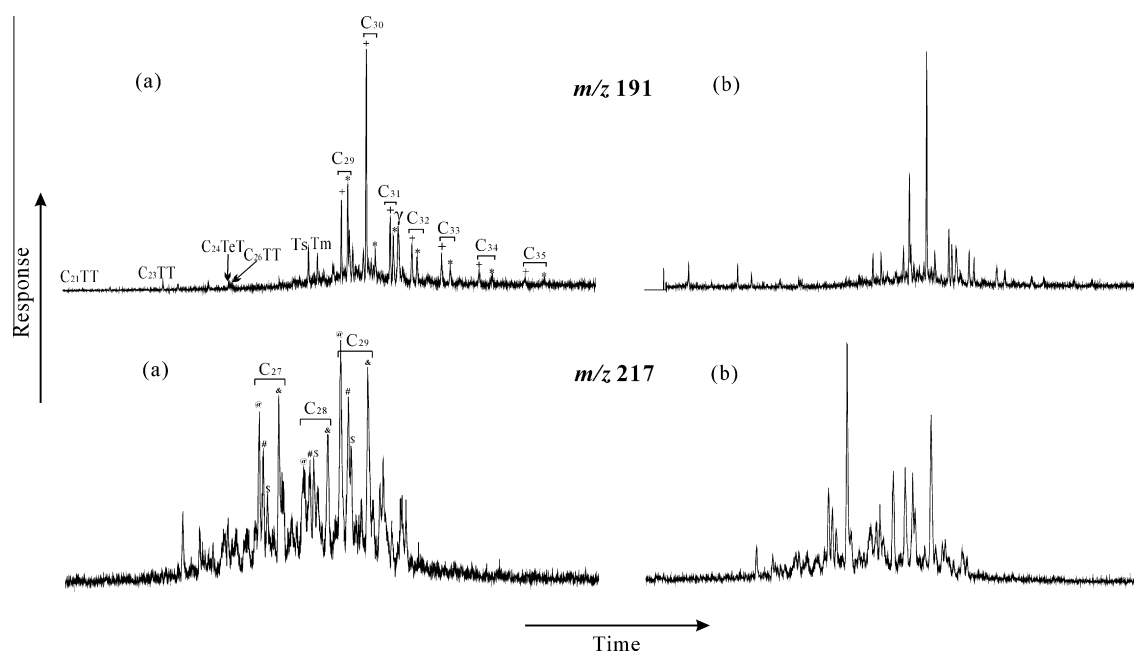

Fig. 3. Representative m/z 191 and m/z 217 mass fragmentograms showing distribution of terpanes and steranes from sediment at site S4 (a) a and S8 (b) TT: tricyclic terpanes; TeT: Tertacyclic terpanes; Ts: 18α(H)22,29,30-tris-norhopanes; Tm: 17α(H)22,29,30-tris-norhopanes; +: 17α(H),21β(H)-hopanes; *: 17β(H),21α(H)-hopanes; γ: Gammacerane; @: $\alpha\alpha\alpha$cholestane(22S); #: $\alpha\beta\beta$cholestane(22R); $: $\alpha\beta\beta$cholestane(22S); &: $\alpha\alpha\alpha$cholestane(22R).

Table 3
Toxicity guidelines of PAH compounds for sediment matrices (ng g⁻¹) and maximum concentrations in the surface sediments from YRDNNR (Long et al., 1995; Liu et al., 2009a,b; Quiroz et al., 2010).

PAHs	Guideline				YRDNNR	
	ER-L	ER-M	TEL	PEL	Ave	Max
Nap	160	2100	34.6	391	202	380
Ace	16	500	6.71	88.9	26	59
Acy	44	640	5.87	128	7	23
Flu	19	540	21.2	144	49	138
Phe	240	1500	86.7	544	218	533
Ant	85.3	1100	46.9	245	28	49
Fla	600	5100	113	1494	80	201
Pyr	665	2600	153	1398	84	3.14
BaA	261	1600	74.8	693	21	0.72
Chr	384	2800	108	846	80	3.27
BbF	NA	NA	NA	NA	39	1.15
BkF	NA	NA	NA	NA	4	15
BaP	430	1600	88.8	763	1	3
IND	NA	NA	NA	NA	24	77
DBahA	63.4	260	6.22	135	24	8
Bghip	NA	NA	NA	NA	2	304

ERL: effects range-low; ERM: effects range-median; TELs: threshold effects level; PELs: probable effects level; Ave: average concentration; Max: maximum concentration; NA: not available.

being derived geologically from lacustrine sources (Philp and Fan, 1987; Fu and Sheng, 1989). Based on the data, the relative content of gammacerane from the seriously contamination part of the Experimental Area are higher than those of the Buffer and Core Areas. As shown in Fig. 3, in addition to the hopanes, a series of tricyclic hopanes were also observed, including a homologous series, and the trisnorhopanes (Ts and Tm). In all analyzed samples, the ratio $Ts/(Ts + Tm)$ vary in the range of 0.38–0.55, which confirms the presence of mature petroleum in the sediments.

Steranes present in fossil fuels are also useful biomarker indicators for petroleum pollution. Steranes were detected in all analyzed samples and comprised mainly the $5\alpha,14\beta,17\beta$ and minor $5\alpha,14\alpha,17\alpha$ configurations, both occurring as 20S and 20R epimers. The relative abundances of three regular sterane series are in an order of $C_{29} > C_{27} > C_{28}$, suggesting that a lacustrine sourced crude oil from China has contaminated the sediments (Sheng et al., 1993). Maturity-indicators based on steranes such as $C_{29}\alpha\alpha\alpha S/(S + R)$ ratio (0.5 at equilibrium) show only minor variations among the analyzed samples (0.38–0.54) and have a high maturity level. Such sterane signatures also confirm the presence of mature petroleum in the sediments.

3.4. Polycyclic aromatic hydrocarbons

3.4.1. Ecological risk assessment of PAHs

PAHs are ubiquitously distributed in diverse environmental matrices such as soil and sediment, and deserve increasing attention due to their high stability, low solubility and toxic, carcinogenic and mutagenic effects. Sediment quality guidelines (SQGs,) are an important tool for the assessment of contamination in marine and estuarine sediments (Long et al., 1995, 2006; Qiao et al., 2006; Quiroz et al., 2010). In this study, two sets of SQGs, including: (a) the ERL/ERM and (b) the TEL/PEL values, were applied to assess the ecological toxicity of individual PAH concentrations in sediments (Table 3). In the three ranges of chemical concentrations, adverse biological effects are expected rarely (<ERL/TEL), occasionally (≥ERL/TEL and < ERM/PEL), and frequently (≥ERM/PEL) (Long et al., 1995; Liu et al., 2009a). The assessments showed that concentrations of all PAHs were below their respective ERL and PEL values in all stations from the comparison of pollutants levels with SQGs. Naphthalene, acenaphthene, fluorane and phen-

anthrene concentrations were in the intermediate range (≥ERL/TEL and <ERM/PEL) at stations S1, S2 and S4, indicating that occasionally adverse biological effects are likely to occur for such compounds at these stations, and in the other stations, their concentrations were below ERLs/TELs. It may be concluded that PAHs will not cause adverse biological effects in the YRDNNR sedimentary environment at present.

3.4.2. PAH source identification

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.). PAH isomer ratios, such as anthracene/anthracene + phenanthrene (Ant/(Ant + Phy)), benzo(a)anthracene/benzo(a)anthracene + chrysene (BaA/(BaA + Chry)) and fluoranthene/fluoranthene + pyrene (Flu/(Flu + Pyr)), methylphenanthrene/phenanthrene (MP/P) have been used as distinct chemical tracers to infer possible sources of PAHs (Budzinski et al., 1997; Yunker et al., 2002; Zhang et al., 2004b; Yang et al., 2009). Based on the PAH isomer pair ratio measurements compiled by Yunker et al. (2002): Flu/(Flu + Pyr) < 0.4 implies petroleum, 0.4–0.5 implies petroleum combustion, and >0.5 implies combustion of coal and biomass; Ant/(Ant + Phe) ratio <0.10 are seen in petroleum input or diagenetic sources, whereas values >0.1 are characteristic of combustion processes; and BaA/(Chry + BaA) ratio <0.20 indicates petroleum, 0.20–0.35 petroleum and combustion, and >0.35 combustion. Furthermore, MP/P ratios higher than 1 are seen for petroleum input
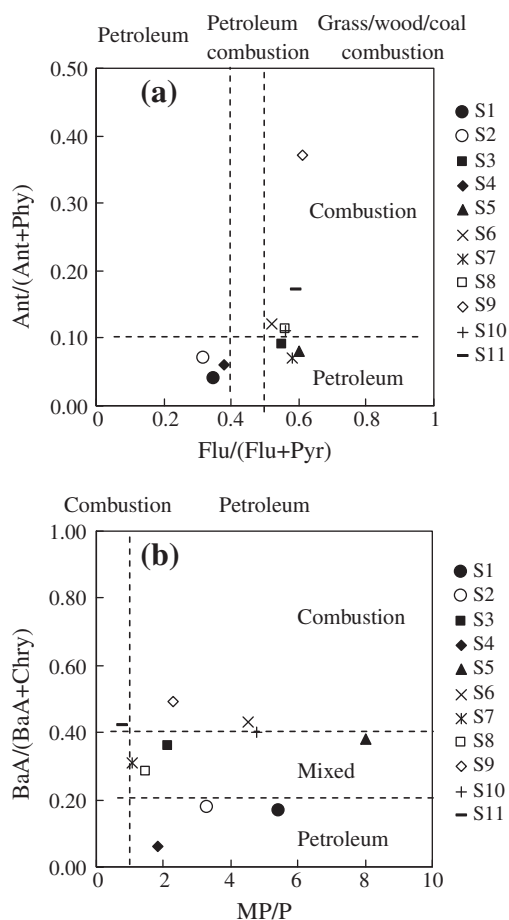
Fig. 4. Plots of PAH isomer pair ratios for source identification: (a) Ant/(Ant + Phy) versus Flu/(Flu + Pyr), (b) BaA/(BaA + Chry) versus MP/P.

Table 4
Rotated component loadings of three principal components (PCs) for PAH compositions in the sediments of the YRDNNR.

	PC1	PC2	PC3
Nap	0.43	**0.75**	–
Ace	0.31	**0.79**	0.42
Acy	–	0.72	–
Fle	**0.73**	0.58	0.28
Phe	**0.78**	0.55	0.20
Ant	0.03	0.12	0.64
Fla	**0.93**	–	0.18
Pyr	**0.94**	0.27	0.15
BaA	**0.92**	0.04	0.18
Chr	**0.86**	0.17	–
BbF	**0.95**	0.24	–
BkF	**0.91**	0.04	0.06
BaP	–	0.29	0.07
IND	0.63	–	0.54
DBahA	0.70	0.24	0.05
BghiP	**0.94**	–	0.30
Variance (%)	54.14	17.38	10.60
Cumulative (%)	54.14	71.52	82.12

Note: Only loading values with moduli large than 0.1 are presented and those higher than 0.7 are in bold.

or diagenetic sources, whereas values lower than 1 are characteristic of combustion processes (Yang et al., 2009).

For each sediment sample PAH isomer pair ratios, Ant/(Ant + Phy) and BaA/(BaA + Chry) were plotted against Flu/(Flu + Pyr) to show how PAHs are distributed relative to their possible sources (Fig. 4). It can be seen that S1, S2 and S4 exhibited evidence of petroleum derived pollution, while other samples may be derived primarily from biomass and coal combustion. Moreover, the BaA/(BaA + Chry) > 0.2 and MP/P > 1 show that PAHs from samples S3, S5, S6, S7, S8, S9, S10 and S11) have mainly originated from combustion, while petroleum-derived pollution cannot be ignored. As well as pyrolytic input as a major source, petrogenic input may be also a source for PAHs because Shengli Oilfield is near YRDNNR where oil exploration and refineries could contribute PAHs.

In order to enhance the accuracy of source identification and quantitatively apportion the contribution percentage of each PAH source, principal component analysis (PCA) was applied to analyze the data set. Details can be found in Yang et al. (2009) and Liu et al. (2009b). As shown in Table 4, PC1 explained a total variance of 54.14% of the data. The factor was heavily loaded on Flu, Phe, Pyr, BaA, Chr, BbF, BkF, DBahA, and BghiP, which were identified as being from incomplete combustion and pyrolysis of fuel. The second factor (PC2) is responsible for 17.38% of the total variance. This factor had high loadings on Nap and Ace, which are reported to be dominant as tracers for pollution by spilled oils. This is supposedly attributed to the oil exploitation in the Shengli Oilfield located in the YRDNNR. However, PC3, responsible for 10.60% of the total variance, was heavily loaded on none of the individual PAHs and represented an unknown source. The PCA showed concordant results with the diagnostic ratios of PAHs which indicated mixed sources of pyrogenic- and petrogenic-deriving PAHs in the YRDNNR.

4. Conclusions

TPH ranged from 49.89 to 1780 $\mu g\,g^{-1}$ with a mean value of 798.82 $\mu g\,g^{-1}$, indicating low or medium levels compared with values reported for other deltas. Concentrations of PAHs for samples varied from 3.59 to 27.10 $\mu g\,g^{-1}$ dry wt and at moderately lower levels, which will not cause any immediate adverse biological effects. The distribution patterns of *n*-alkanes show a strong UCM with a small predominance of odd over even numbered *n*-alkanes in most samples revealing a petroleum-related source. On the whole, the degree of contamination in the Core Area and Buffer Area is weaker than that of the Experimental Area. In addition to oil-related hydrocarbon inputs in this region, aliphatic hydrocarbon analysis also showed the presence of hydrocarbons of terrestrial origin at some sampling sites, characterized by high CPI_2 and lower L/H values. Both hopanes and steranes provided convincing evidence that oil-derived hydrocarbons are widespread in the sediments of the study area. For the PAH source diagnosis, both diagnostic ratios and principal component analysis were employed. Source analysis showed that PAHs are derived primarily from combustion of fossil fuels/petroleum (gasoline, crude oil, and coal) and biomass (wood and grasses), with minor amounts of PAHs derived from direct petroleum input. Pyrolytic input appears be a major source of PAHs in YRDNNR sediment, and petrogenic sources are also apparent for PAHs, from oil well blowouts, spills and illegal disposal in the Shengli Oilfield.

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