ORIGINAL ARTICLE

Chemical characteristics and pollution sources of petroleum hydrocarbons and PAHs in sediments from the Beiluohe River, Northern China

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Abstract To determine the degree of hydrocarbon contamination and the contribution of local petroleum industries to contaminant loadings in sediments from the Beiluohe River, China, 12 surface sediment samples were collected for geochemical analysis in 2005. Sediment samples were extracted by organic solvents, separated by silica gel column chromatography and the profiles of *n*-alkanes, biomarkers and polycyclic aromatic hydrocarbons (PAHs) in sediments were analyzed by gas chromatography with flame ionization detector and gas chromatography/mass spectroscopy. Concentrations of total hydrocarbons in the sediments varied from 12.1 to 3,761.5 μg g^{-1} dry wt, indicating that most sediments in Beiluohe River was only slightly to moderately contaminated by hydrocarbons. Concentrations of PAHs for six samples (sum of 16 isomers) varied from 17.7 to 407.7 ng g^{-1} dry wt and at present low levels of PAHs did not cause adverse biological effects in Beiluohe River sedimentary environment. PAH compositions, *n*-alkanes and biomarker profiles all suggested that there were different sources of contaminations in studied areas. *n*-Alkanes reflect two distinct sources: a fossil *n*-alkane series from crude oil at sites S40, S43, S87 and plantwax *n*-alkanes at sites S39 and S45. Judged by their PAH ratios, the sediments at site S15 were pyrolytic, sediments at S17

and S43 were petrogenic, and sediments at S39, S40 and S64 had a mixture source of pyrolytic and petrogenic.

Introduction

Hydrocarbons as important components of organic input have received much attention because most of them are toxic, mutagenic and carcinogenic. In aquatic environment, due to their low water solubility and hydrophobic properties, hydrocarbons are commonly found to be transported to the sediments. Hydrocarbon in sediments reflects the relative contributions from multiple sources: biogenic, diagenetic, petrogenic and pyrogenic (Yunker et al. 1993; Hostettler et al. 1999). Thus, the chemical characteristics and distribution of hydrocarbons in the environment can vary greatly from one area to another. A number of indicators such as hydrocarbon concentrations, *n*-alkane profiles, polycyclic aromatic hydrocarbon (PAH) composition and petroleum biomarkers have been proposed to estimate the pollution level and find out the pollution sources (Volkman et al. 1992; Witt 1995).

River Beiluohe, the second-order tributary of the Yellow River, is located in northern Shaanxi Province, geographically belonging to the Loess Plateau. It has a total length of 680.3 km with a catchment basin of 26,905 km^2. In Yan'an areas, the Beiluohe River flow throughout six counties including Zhidan, Wuqi, Ganquan, Fuxian, Luochuan and Huangling, which have large oil and gas reserves. Oil production

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and transportation are among the most important economic activities in these regions. However, these activities have generated large quantities of toxic waste, runoff and oil spills to the Beiluohe River. Moreover, located in the arid region of China, the Beiluohe River is of fundamental importance for agricultural activities and water supply for human consumption. However, due to a long history of wastewater drainage and platform runoff from nearby petroleum industries, many locations in Beiluohe River waters are no longer considered fit for their designated beneficial uses. Pollution has threatened the economic development and human health in this region (Mu 1994; Lin et al. 2005). However, to date, information regarding the local pollution level and its effects is very limited. Especially, reliable data on concentrations and origin of petroleum hydrocarbon in the river sediments is scarce. As a result, an integrated geochemical, hydrochemical and ecological survey of the Beiluohe River Basin, was implemented by the local government during the period October 2005–April 2006.

In this paper, we report the analysis of 12 sediment samples obtained from the Beiluohe River for petroleum hydrocarbons and selected PAHs. Our objectives were to assess the level of contamination in river sediments by petroleum hydrocarbons due to the oil production platforms and drilling activities undertaken in the study area, and to find out the source of hydrocarbon pollution using n-alkane profiles, PAH composition and petroleum biomarkers.

Materials and methods

Study area and sampling

Figure 1 shows the studied site—the Beiluohe River, which is located between 35°24′, 37°15′ North latitude and 107°40′, 110°17′ East longitude. To determine the hydrocarbon contamination, a total of 12 surface sediment samples throughout the Beiluohe River and its tributary were collected in October 2005 and they were extracted and detected by gas chromatography with flame ionization detector (GC/FID). Among these 12 samples, we selected 6 samples for gas chromatography/mass spectroscopy (GC/MS) detection and 6 samples for PAHs analysis. The sample localization is shown in Fig. 1. Sediments were obtained at a depth 0–10 cm utilizing a stainless-steel grab and placed in pre-cleaned brown glass jars and frozen immediately until laboratory analysis.

Extraction and fractionation

In the laboratory, about 100 g dry sediment samples were Xoxhlet-extracted with chloroform for a period of 72 h. Elemental sulfur was removed from the extracts using activated copper. The extract was fractionated into aliphatic and aromatic hydrocarbons by adsorption liquid chromatography using a column of alumina and silica-gel, and gradient solvents as eluent: ligarine and ligarine/dichloromethane (3:9, v/v) or aliphatic and aromatic fractions, respectively. The

Fig. 1 Study areas and sampling location in the Beiluohe River, northern Shaanxi
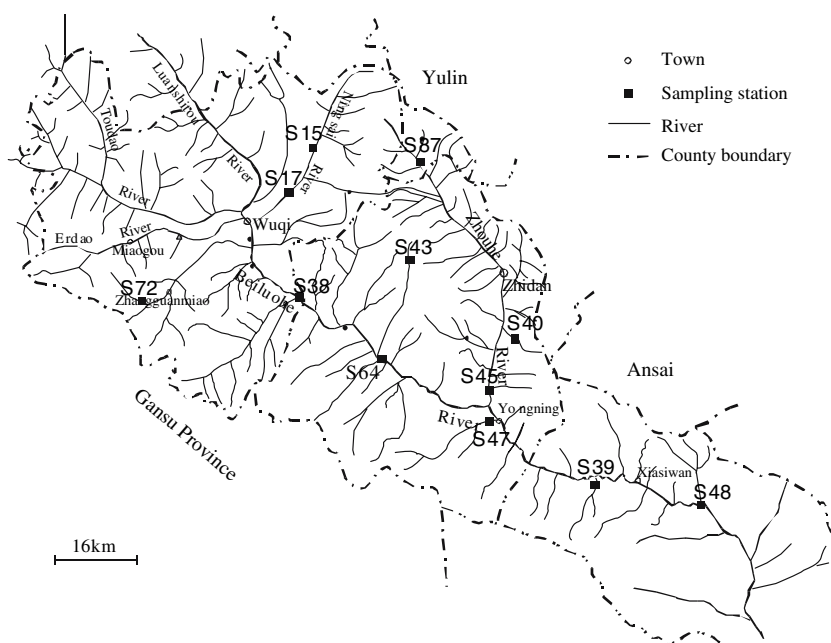
aliphatic and aromatic fractions were concentrated again on a rotary evaporator, transferred to a vial, and then the volume was adjusted to 1 ml exactly using a stream of filtered N_2 gas. An aliquot of 1 μl of each extract was subjected to GC/FID and GC/MS analysis.

Instrumental analysis

Normal and isoprenoid alkanes analyses were conducted on a Hewlett-Packard (HP) 6890 II GC-FID. The samples were analyzed using a fused silica capillary column (30 m × 0.32 mm, 0.25 μm film thickness) with helium as carrier gas. The GC conditions were: injector 290°C, oven temperature program: 40°C for 1 min; 6°C min^{-1} to 290°C. Petroleum biomarkers were analyzed by GC/MS (HP 6890 II GC coupled to a Platform II mass spectrometer). The capillary column used was coated with DB-5 (30 m × 0.32 mm, 0.25 μm film thickness) with helium as carrier gas. The GC conditions were the same as described earlier. The MS operating conditions were: electron energy 70 eV, scanned from 50 to 600 amu. The samples were analyzed in the splitless mode. The 16 PAHs in the concentrated and purified extracts were quantified with a gas chromatograph (HP-6890 model) with a mass spectrometer (HP-5975 MSD). A capillary GC column (30 m × 0.25 mm, 0.25 μm) was used. The GC oven temperature program was: 60°C for 2 min, then 3°C min^{-1} to 290°C, held constant for 25 min. The PAHs were determined by selected ion monitoring (SIM). SIM acquisition was carried out by comparison of the base peak of each PAH.

Results and discussion

Concentrations of total petroleum hydrocarbons

Concentrations of total hydrocarbons ranged between 12.1 and 3,761.5 μg g^{-1} dry sediment, with an average of 1,886.8 μg g^{-1} dry wt (Table 1). Petroleum hydrocarbon concentrations in sediments are typically a few μg g^{-1} in unpolluted coastal areas and from 50 to >1,000 μg g^{-1} in contaminated areas (Clark and Macleod Jr 1977). Insufficient documentation exists for total hydrocarbon contents of Beiluohe sediments. Results obtained from the present studies show that total hydrocarbon concentrations in the uncontaminated sediments of Beiluohe Basin range between 6.4 and 15.6 μg g^{-1}. These low total hydrocarbon concentrations may be regarded as the natural background levels in the Beiluohe area. As a result, total hydrocarbon concentrations <15 μg g^{-1} are considered to denote unpolluted sediments, whereas values >200 μg g^{-1} are generally indicative of significant pollution.

The highest TPH concentration was found at Station S87, which was ascribed to the effect of the direct discharge water from the production platform. The lowest values found for stations S15 and S48 ranging from 7.9 to 14.4 μg g^{-1}, were typical of uncontaminated sediments because of less petroleum activities in the neighborhood. Station S72 was very special for its low hydrocarbon concentration although it was located near the many production platforms. Stations such as S17, S39 and S43, had medium concentration ranging from 57.5 to 147.3 μg g^{-1}, which might be a consequence of illegal discharge of petroleum wastewater from refinery factories or platforms. The station S64, situated near the garbage dumps of Danba, also presenting a medium TPH concentration, might result from anthropogenic activities. Other stations S38, S40, S45 and S47, presented a slight pollution with TPH concentration ranging from 16.4 to 40.1 μg g^{-1}. In addition, the stations located in the tributary due to limited water circulation presented a higher value than those in the mainstream. Except the sample from S87 that was significantly contaminated, the levels of TPH concentration in Beiluohe were relatively low compared to those at worldwide industrial locations. The studied area, geographically located in the Loess

Table 1 Concentrations (μg g^{-1} dry wt) and characteristics of petroleum aliphatic hydrocarbons in surface sediments from the Beiluohe River

Site no.	Station	Total hydrocarbons	Aliphatic hydrocarbons	Pr/Ph	CPI
S15	Wugucheng	7.9	2.6	–	–
S17	Zoumatai	88.1	48	1.01	1.03
S38	Loufangping	30.7	18.2	1.21	1.08
S39	Chaigou	92.2	66.7	0.93	1.72
S40	Kangjiagou	41.1	24.3	0.77	1.08
S43	Huoshaozui	147.3	118.4	1.04	1.00
S45	Yangcheng	16.4	10.9	0.73	1.48
S47	Shawan	37.4	25.3	1.04	1.11
S48	Shimenzi	14.4	9.6	1.03	1.20
S64	Danba	57.5	48.2	1.11	1.17
S72	Chouguanzi	12.1	5.2	1.32	1.02
S87	Hongliu	3,761.5	2,275.2	1.05	1.02

CPI indicates carbon predominance index calculated between n-C_{17} and n-C_{31} (adapted from Bray and Evans 1961), *Pr/Ph* indicates ratio of pristane to phytane

Plateau, easily experienced erosion of soil materials resulting in larger inputs of sediments to rivers and the river was relatively shallow in depth so it had not accumulated most pollutants in sediments. As a result, we suggest that higher inputs of sediments in Beiluohe could contribute to the lower TPH concentrations in Beiluohe sediments.

Aliphatic hydrocarbons

The *n*-alkane found in sediment could be originated from anthropogenic or natural sources in aquatic environment. *n*-Alkanes GC profiles and some indicators such as ratio of odd/even carbon numbers, pristane/phytane ratio and the presence of the unresolved complex mixture (UCM) can be used to distinguish the two origins.

Generally, the aliphatic hydrocarbon fraction isolated from the sediment extracts showed the presence of a homologous series of *n*-alkanes extending from C_{15} to C_{34}. Typically, abundance of C_{27}, C_{29} and C_{31} with odd carbon predominance is an indicator of terrestrial plant, whereas a dominance of the *n*-alkanes in the range C_{18}–C_{24} without odd carbon predominance, suggests relatively 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_{19}–C_{22} and has very prominent humps indicating the 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 inputs. Stations S17, S40, S43 and S87 can be ranged in the group of predominant petroleum input. In contrast, stations S39, S45 and S64 had both petroleum and terrestrial plant inputs showing a predominance of odd on even numbered *n*-alkanes in the range C_{25}–C_{31} and the presence of UCM (Fig. 2b).

The carbon predominance indices (CPI), which represent the ratios between the odd and the even carbon-homologues were around 1 at stations S17, S43, S38, S40 and S87. These CPI values and the FID/GC profiles suggest oil contribution to these sediments. Higher values of CPI were found for stations S39, S45 and S64 and a strong dominance of odd-numbered linear alkanes in the range C_{25}–C_{31} could be noted, which was typical of the origin of higher plants. As a result, besides petrogenic contribution, there is also a significant terrestrial plant input at stations S39, S45 and S64. In spite of low hydrocarbon concentration, the FID/GC fingerprints and geo-

chemical indices indicated the trace of oil contamination at station S72.

Another useful indicator of the origin of the hydrocarbons is the ratio of isoprenoids, pristane and phytane. In uncontaminated sediments, the ratio Pr/Ph is typically between 3 and 5 (Steinhauer and Boehm 1992). However, ratio of pristane to phytane was relatively low (0.73–1.32) in all samples in this study, indicating petroleum contribution to sediments.

Petroleum markers

Six samples (S38, S40, S43, S47, S64 and S72) were selected to identify the hopane and sterane series detected in GC/MS analysis by monitoring *m/z* 191 and 217, respectively. Hopanes (Fig. 3) comprised a series of $17\alpha(H),21\beta(H)$-compounds, maximizing at the C_{30} homologue, and less prominent $17\beta(H),21\alpha(H)$-hopanes. Such isomeric configurations are thermodynamically stable and occur in crude oils and mature rocks (Perters and Moildovan 1993). They are derived from the diagenic interconversion of the $17\beta(H),21\beta(H)$ homologues of bacterial origin. Extended hopanes ($C \geq 31$) 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 (Mackenzie 1984). Gammacerane, a non-hopanoid C_{30} triterpane, was also present in the analyzed sediments. This compound is a biomarker common to most Chinese crude oils derived geologically from lascustrine sources (Fu and Sheng 1989). As shown in Fig. 3, in addition to the hopanes, a series of tricyclic hopanes were also observed, including a homologous series of tricyclic hopanes and the trisnorhopanes (Ts and Tm). In all analyzed samples, the ratio Ts/(Ts + Tm) vary in the range 0.44–0.71, which confirms the presence of mature petroleum in sediments.

The steranes were detected in all samples analyzed 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 (Fig. 4). The configuration of steranes reflects an origin from crude oil and mature rocks (Perters and Moildovan 1993). The relative abundances of three regular sterane series are in an order of $C_{29} > C_{27} > C_{28}$, suggesting a lacustrine sourced crude oil from China that contaminate the sediments (Sheng et al. 1993). Maturity-indicators based on steranes such as $C_{29}\alpha\alpha\alpha S/(S + R)$ ration (0.5 at equilibrium) show only minor variations among the analyzed samples (0.51–0.67) and have the high maturity level. And as a result, it is likely that the petroleum-derived hydrocarbons are introduced into the river through illegal dumping of petroleum waste.

Fig. 2 a The aliphatic
hydrocarbon profile of a
typical sediment sample
at site S40. The dominance
of C_{21} without odd carbon
predominance suggests oil
input. **b** The aliphatic
hydrocarbon profile of a
typical sediment sample at
site S39. The dominance of
long chain *n*-alkanes (C_{27}, C_{29}
and C_{31}) suggests high plant
input
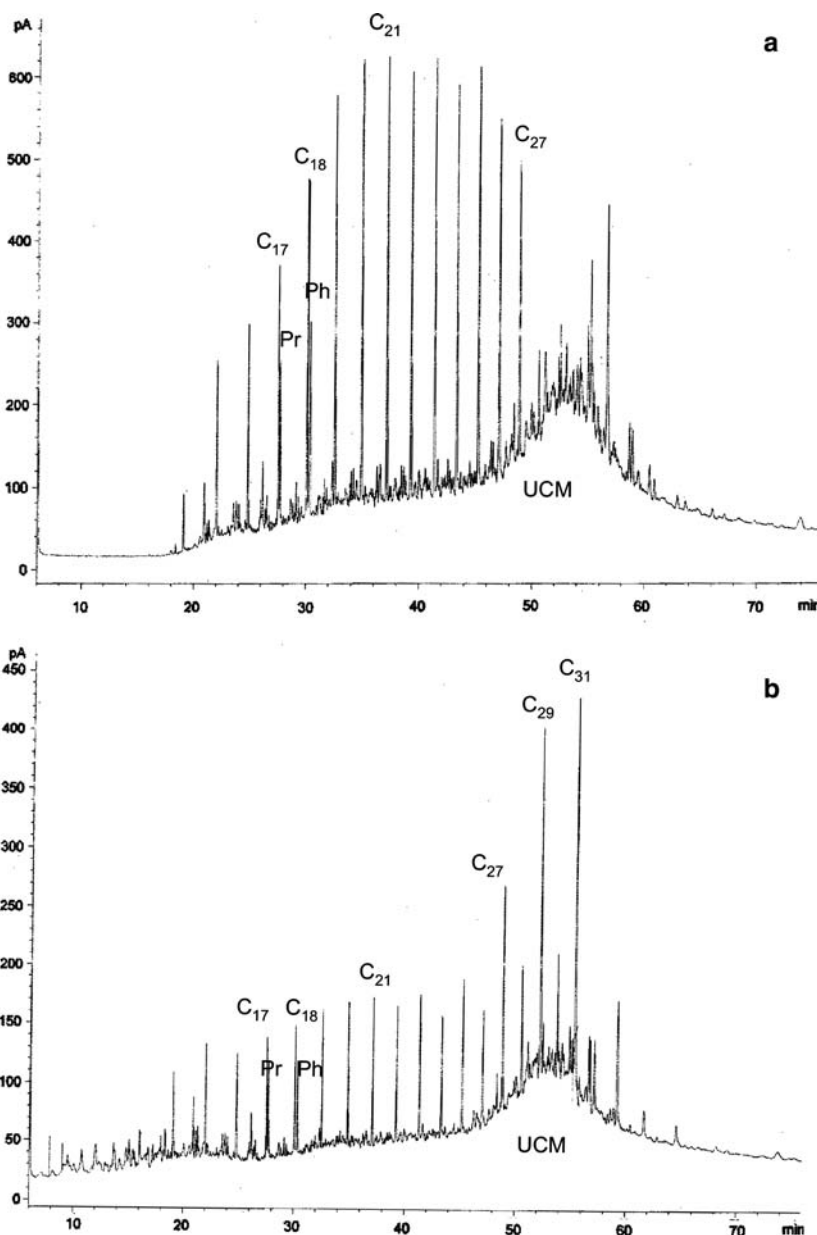
Both hopanes and steranes provided convincing
evidence that oil-derived hydrocarbons are widespread
in the sediments of the study area.

Polycyclic aromatic hydrocarbons

PAHs contents in sediments and toxic assessment

Polycyclic aromatic hydrocarbons are pollutants that
are ubiquitous in aquatic environments and a product
of combustion and fossil fuels as well as from oil pol-
lution. Total PAH concentrations (sum of the 16 EPA
priority pollutants) for the six analyzed samples ranged
from 17.7 to 407.7 ng g^{-1} dry wt with the mean value of

212.7 ng g^{-1} (Table 2). If the relatively high PAH
value for S15 (407.7 ng g^{-1}) sourced from combustion
(discussed later), PAH levels in Beiluohe were
<100 ng g^{-1}, which is indicative of low pollution
(Baumard et al. 1998). Total concentration of poten-
tially carcinogenic PAHs (PCPAH7) including BaA,
Chry, BbF, BkF, BaP, Indeno, DBahA (Savinov et al.
2003) ranged from 5.2 to 232.9 ng g^{-1} dry wt in this
study. The geometric mean of PCPAH7 is
119.8 ng g^{-1} dry wt. The greatest concentration of
PCPAH7 was also detected at location S15
(232.9 ng g^{-1}).

Concentration levels of total 16 PAHs in surface
sediments from the Beiluohe River were relatively low
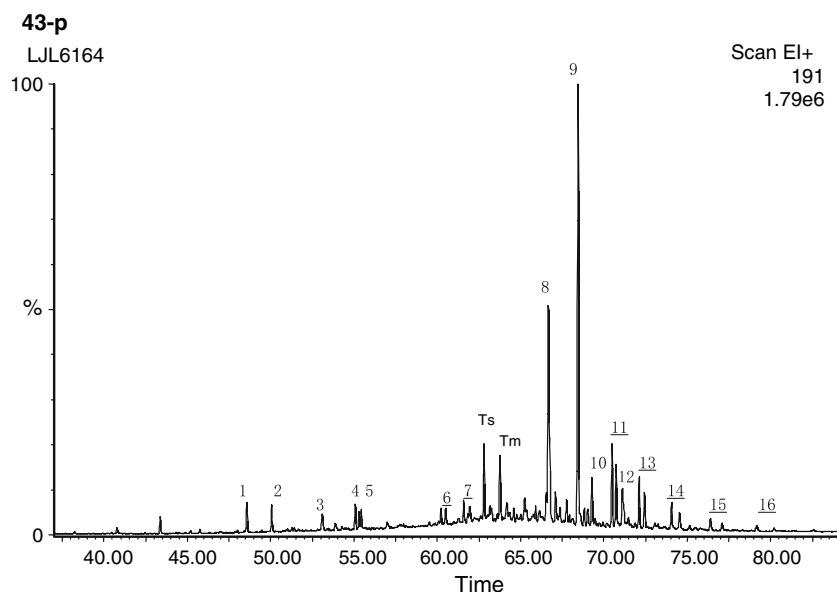
Fig. 3 Representative mass fragmentograms of m/z 191 for terpanes from sediment at site S43. *1–7* Tricyclic terpane; *Ts* 18α(H)22,29,30-tris-norhopanes; *Tm* 17α(H)22,29,30-tris-norhopanes; *8* 17α(H),21β(H),30-norhopanes; *9* 17α(H),21β(H)-hopanes; *10* 17β(H),21α(H),30-hopane (moretane); *11* 17α(H),21β(H)-homohopane (22S), 17α(H),21β(H)-homohopane (22R); *12* Gammacerane; *13* 17α(H),21β(H)-bishomohopane (22S), 17α(H),21β(H)-bishomohopane (22R); *14* 17α(H),21β(H)-trishomohopane (22S), 17α(H),21β(H)-trishomohopane (22R); *15* 17α(H),21β(H)-tetrakishomohopane (22S), 17α(H),21β(H)-tetrakishomohopane (22R); *16* 17α(H),21β(H)-pentakishomohopane (22S), 17α(H),21β(H)-pentakishomohopane (22R)

Fig. 4 Representative mass fragmentograms of m/z 217 for steranes from sediment at site S43. *1* $C_{27}ααα$-cholestane(22S); *2* $C_{27}αββ$-cholestane(22R); *3* $C_{27}αββ$-cholestane(22S); *4* $C_{27}ααα$-cholestane(22R); *5* $C_{28}ααα$-ergostane(22S); *6* $C_{28}αββ$-ergostane(22R); *7* $C_{28}αββ$-ergostane(22S); *8* $C_{28}ααα$-ergostane(22R); *9* $C_{29}ααα$-stigmastane(22S); *10* $C_{29}αββ$-stigmastane(22R); *11* $C_{29}αββ$-stigmastane(22S); *12* $C_{29}ααα$-stigmastane(22R)
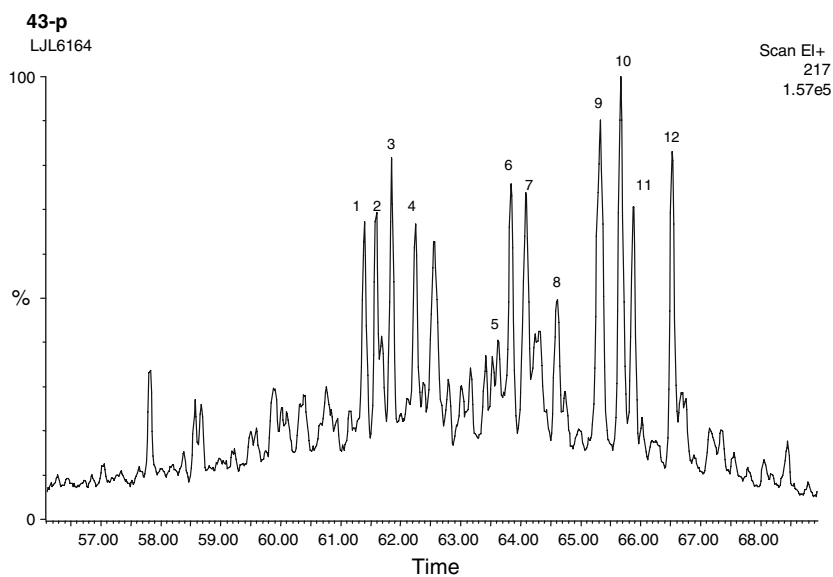
in comparison with many other aquatic systems in China (Ma et al. 2001; Wu et al. 2003; Zhang et al. 2004; Qiao et al. 2006). In order to assess whether sediments in Beiluohe River will cause toxic effect, the PAH levels in sediment were compared against effect-based guideline values such as the effect range-low (ER-L) (4,002 ng g^{-1}) and effect range-median (ER-M) (44,792 ng g^{-1}) developed by the US Natural Oceanic and Atmospheric Administration (Kim et al. 1999). The concentrations below the ER-L value represent a minimal-effect range, i.e., adverse biological effect would rarely be observed below the ER-L. On the other hand, if the concentration was higher than the ER-M value, adverse effects on biological systems will frequently occur. The concentration of total 16 PAHs is significantly lower than the ER-L value. Of

Table 2 Concentrations (ng g^{-1} dry wt) and characteristics of PAHs in surface sediments from Beiluohe River

Station	PAHs	PCPAH7	Fluor/Pyr	Phe/Ant	BaA/Chry	LMW/HMW
S15	407.7	232.9	1.22	5.34	0.86	0.17
S17	31	13.9	0.71	>10	0.18	0.55
S39	98.9	29.3	0.96	13.5	0.35	1.05
S40	17.7	5.2	1.15	37.7	0.32	0.78
S43	63.8	28.1	0.90	10.7	0.27	0.48
S64	21.9	8.3	1.20	18	0.45	0.52

LMW low molecular weight PAH (Nap + Acy + Ace + Flu + Phe + Ant), *HMW* high molecular weight PAH (Fluor + Pyr + BaA + Chry + BbF + BkF + Bap + IP + DBahA + BghiP)

the individual compounds, all PAHs in Beiluohe River did not exceed their respective ER-L values (Fig. 5). As a result, it may be concluded that PAHs will not cause immediately adverse biological effects in Beiluohe River sedimentary environment.

PAHs composition and possible sources

The study of the compositional patterns of PAH mixtures can provide useful information regarding their sources and transport pathways. In general, two types of PAHs are commonly found in aquatic sediments. Pyrolytic PAHs derived during the combustion of all the organic materials and petrogenic PAHs, which are contained in petroleum and its products. Pyrolytic PAH mixtures are characterized by predominance of parent compounds with four or more aromatic rings, whereas in petrogenic PAHs, the two to three aromatic ring compounds are most abundant components (Soclo et al. 1999). Several molecular ratios such as naphthalene/fluoranthene (Nap/Fluor), phenantharene/anthracene (Phe/Ant), fluoranthane/pyrene (Fluor/Pyr), benzo[a]anthracene/chrysene (BaA/Chry) and pyrene/benzo[a]anthracene (Pyr/BaA) have been developed

for interpreting PAH compositions and inferring the possible sources. The LMW/HMW is the ratio of the sum of the low molecular weight PAH concentrations to the sum of high molecular weight PAH concentrations, i.e., Nap + Acy + Ace + Flu + Phe + Ant/Pyr + BaA + Chry + BbF + BkF + BaP + IP + DBahA + BghiP. Since no alkylated PAHs derived from oil were determined in this study, concentration ratios of parent PAH including Phe/Ant, Fluor/Pyr, BaA/Chry and LMW/HMW, were used to identify the possible PAH origins in sediments from Beiluohe River (Table 2).

Petroleum often contains more thermodynamically stable compounds such as naphthalene, fluorine, phenanthrane and chrysene, while fluoranthene and pyrene are usually the most abundant compounds for pyrolytic PAHs. Therefore, the Fluor/Pyr ratio is obviously related to pyrolytic origins as the values greater than 1, while values less than 1 are attributed to petrogenic sources (Baumard et al. 1998). The Phe/Ant ratio is observed to be very high in PAH petrogenic pollution, but low in pyrolytic contamination cases (Gschwend and Hites 1981; Soclo et al. 2000). Budzinski et al. (1997) suggested that sediments with

Fig. 5 Composition of PAHs (ng g^{-1} dry wt) in sediments from the Beiluohe River. *Nap* naphthalene; *Acy* acenaphthylene; *Ace* acenaphthene; *Flu* fluorene; *Phe* phenanthrene; *Ant* anthracene; *Fluor* fluoranthene; *Pyr* pyrene; *BaA* benzo[a]anthracene; *Chry* chrysene; *BbF* benzo[b]fluoranthene; *BkF* benzo[k]fluoranthene; *Bap* benzo[a]pyrene; *IP* indeno[1,2,3-cd]pyrene; *DBahA* dibenzo[a,h]anthracene; *BghiP* benzo[ghi]perylene
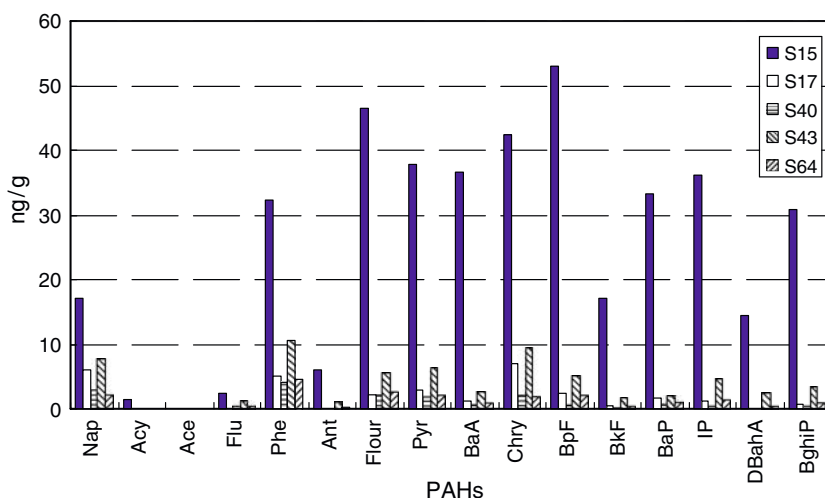
Phe/Ant > 10 were mainly contaminated by petrogenic inputs and Phe/Ant < 10 was typical of pyrolytic sources. At site S15, the ratio with Phe/Ant < 10 and Fluor/Pyr > 1, clearly indicates a pyrolytic source in sediment. In addition, the low ratio of LMW/HMW (0.17) supports its pyrolytic origin. At sites S17, S39 and S43, ratios of Phe/Ant were higher than 10 and ratios of Flu/Pyr were lower than 1, clearly indicating that PAH inputs were mainly from the petroleum contamination. Finally, sites S40 and S64 with the ratio of Phe/Ant > 10 and Fluor/Pyr > 1 were characteristic of a mix pattern of pyrolytic and petrogenic contamination. Similar results were observed for the BaA/Chry. Chrysene and benzo[a]anthracene are both derived from the combustion processes with BaA/Chry ratio lower than 1 (Gschwend and Hites 1981). The suggested ratio values for crude and fuel oil range from 0.24 to 0.40. The petrogenic PAH inputs at four sites (S17, S39, S40 and S43) in Beiluohe River are also confirmed by the BaA/Chry ratio, ranged between 0.18 and 0.32. But at sites S15 and S64, the ratio of BaA/Chry, which is 0.86 and 0.46, respectively, confirms their pyrolytic input.

Conclusions

The Beiluohe River showed to be only slightly or moderately contaminated by hydrocarbons in most surface sediments. Concentrations of "total" hydrocarbons in Beiluohe River sediments are shown to be substantially higher than those from pristine environments. The most contaminated stations (i.e., S87, concentrations >200 μg g^{-1}) are shown to be associated with illegal discharges of petroleum or petroleum wastewater from platforms and refinery factories. Samples taken from locations far from petroleum activities show comparatively little contamination (total hydrocarbon concentrations <15 μg g^{-1} dry wt). Gas chromatographic distribution patterns of n-alkanes show a strong UCM with a small predominance of odd on even numbered n-alkanes in most samples revealing a petroleum-related source. Besides oil-related hydrocarbon inputs at this region, and aliphatic hydrocarbons analysis showed also the presence of hydrocarbons of terrestrial origin at some sampling site, characterized by high CPI values. Both hopanes and steranes in analyzed samples provided convincing evidence that oil-derived hydrocarbons are widespread in the sediments of the study area.

In general, the concentrations of PAHs (sum of 16 isomers) in Beiluohe River sediments are low by comparison with those observed in other regions. The highest concentrations of total PAHs were observed at site S15 (407 ng g^{-1} dry wt). Total and individual PAHs in Beiluohe River did not exceed their respective ER-L values. It may be concluded that PAHs will not cause immediate adverse biological effects in Beiluohe River sedimentary environment. The molecular ratios indicate a pyrolytic source from the site S15. Petrogenic contributions were recorded at sites S17, S39 and S43. And a mixture of pyrolytic and petrogenic PAHs was observed in the sediments at sites S40 and S64. Except for site S15, good correlation between total hydrocarbons and PAH was observed indicating similar primary sources for the two classes of compounds.

References

Baumard P, Budzinski H, Michon Q, Garrigues P, Burgeot T, Bellocq J (1998) Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. Estuar Coast Shelf Sci 47:77–90

Bray EE, Evans ED (1961) Distribution of n-paraffins as a clue to recognition of source beds. Geochim Cosmochim Acta 22:2–15

Budzinski H, Jones I, Bellocq J, Pierard C, Garrigues P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar Chem 58:85–97

Clark RC, Macleod WD Jr (1977) Inputs, transportation mechanisms, and observed concentrations of petroleum in the marine environment. In: Malines DC (ed) Effects of petroleums in arctic and subarctic marine environments and organisms, vol 1. Academic, New York

Fu JM, Sheng GY (1989) Biological marker composition of typical source rocks and related oils of terrestrial origin in the People's Republic of China: a review. Appl Geochem 4:13–22

Gschwend PM, Hites RA (1981) Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochim Cosmochim Acta 45:2358–2367

Hostettler FD, Pereira WE, Kvenvolden KA, van Green A, Luoma SN, Fuller CC, Anima R (1999) A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment core. Mar Chem 64:115–127

Kim GB, Maruya KA, Lee RF, Lee JH, Koh CH, Tanabe S (1999) Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea. Mar Pollut Bull 38(1):7–15

Lin J, Wang B, Ma J, Tang X, Cheng J (2005) Oil exploration impact to eco-environment and protection countermeasure in loess hilly-gully area. J Northwest Univ (Nat Sci Edn) 35(1):105–108

Ma M, Feng Z, Guan C, Ma Y, Xu H, Li H (2001) DDT, PAH and PCB in sediments from the intertidal zone of the Bohai Sea and the Yellow Sea. Mar Pollut Bull 42:132–136

Mackenzie AS (1984) Applications of biological markers in petroleum geochemistry. In: Brooks J, Welte D (eds) Advances in petroleum geochemistry. Academic, London, pp 115–214

Mu CR (1994) Effects of oil exploration on ecological environment in the northwestern Loess Plateau. Geogr Res 13(4):19–27

Perters KE, Moildovan JM (1993) The biomarker guide: interpreting molecular fossils in petroleum and ancient sediment. Prentice-Hall, Englewood Cliffs

Qiao M, Wang C, Huang S, Wang D, Wang Z (2006) Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. Environ Int 32:28–33

Savinov VM, Savinova TN, Matishov GG, Dahle S, Næs K (2003) Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Guba Pechenga, Barents Sea, Russia. Sci Total Environ 306:39–56

Sheng G, Fu J, Zhang J, Xu Y, Simoneit BRT, Chen X (1993) Molecular marker study of extractable organic matter in aerosols from urban areas of China. Guangzhou Environ Sci 8:5–9

Soclo HH, Garrigues PH, Ewald M (1999) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar Pollut Bull 40:387–396

Soclo HH, Garrigues PH, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar Pollut Bull 40:387–396

Steinhauer MS, Boehm PD (1992) The composition and distribution of saturated and aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of Alaskan Beaufort Sea. Mar Environ Res 33:223–253

Sultan SA, Sameer JG (1997) Hydrocarbon distributions in sediments of the open areas of the Arabian Gulf following the 1991 Gulf War oil spill. Mar Pollut Bull 34:941–948

Volkman JK, Holdsworth DG, Neill GP, Bavor HJ Jr (1992) Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. Sci Total Environ 112:203–219

Witt G (1995) Polycyclic aromatic hydrocarbons in water and sediments from the Baltic Sea. Mar Pollut Bull 31:237–248

Wu Y, Zhang J, Zhu ZJ (2003) Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China. Mar Pollut Bull 46:619–625

Yunker MB, Macdonald RW, Cretney WJ, Fowler BR, McLaughlin FA (1993) Alkane, terpene and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie Shelf: riverine contributions to Beaufort Sea coastal sediment. Geochim Cosmochim Acta 57:3041–3061

Zhang ZL, Hong HS, Zhou JL, Yu G (2004) Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China. Sci Total Environ 323:71–86