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Petroleum Hydrocarbon Contamination in Surface Sediments of Beiluohe Basins, China

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Abstract Twenty-two surface sediment samples were collected from Beiluohe River, China, in 2005. Saturated hydrocarbons analysis was carried out on different river sediments in order to detect possible contaminations by petroleum development. Total concentrations of hydrocarbons in the sediments ranged from 6.4–147.3 $\mu g\ g^{-1}$ (dry wt) with an average of 76.8 $\mu g\ g^{-1}$, revealing relatively low to medium contamination in studied areas in spite of oil development for many years. The THC levels in the mainstream of Beiluohe River were relatively low. Sediment samples with higher total hydrocarbon concentrations were from the sites related to the petroleum activities or urban discharges. Gas chromatographic distribution patterns of n-alkanes are characteristic of petroleum in most samples. They show a strong unresolved complex mixture (UCM) with a small predominance of odd on even numbered n-alkanes. On the other hand, pentacyclic triterpanes and steranes occurred in all analyzed sediments and displayed similar signatures that are characteristic of mature organic matter contribution from oil contaminations. Hydrocarbons of terrestrial origin were also detected in the samples. However, contribution from plantwax hydrocarbons is overshadowed in samples by hydrocarbons of petroleum origin. This is obvious by the presence of the high relative abundance of UCM, and the identification of mature hopane and sterane in samples.

Keywords Sediment · Extractable organic matter · Saturated hydrocarbons · Biomarkers · Beiluohe River Basin

Hydrocarbons have been widely recognized as common organic contaminants in the environment and are of risk for ecosystems and human population health. They can enter river environments by direct discharge, surface run-off, atmospheric deposition and biogenic inputs (Afifa et al. 2001).

River Beiluohe, the second-order tributary of the Yellow River, is located in northern Shaanxi Province, geographically belonging to the Loess Plateau. In Yan'an areas, the Beiluohe River flow throughout six counties including Zhidan, Wuqi, Ganquan, Fuxian, Luochuan and Huangling. Most of these counties have enjoyed the fastest growth of economy due to petroleum development in this region. However, the rapid petroleum developments have resulted in the adverse impacts to its natural environment. For many years, the Beiluohe River has been the recipient of uncontrolled petroleum effluents containing high loads of organic matter, heavy metals and nutrients. Now Beiluohe River is seriously contaminated due to a long history of wastewater drainage from nearby petroleum industries.

Beiluohe is one of the important rivers for water supply, industry and irrigation in Yan'an areas, and most importantly it will serve as drinking water supply for the city of Yan'an in the future. Despite the significance of the Beiluohe River there is a lack of previous studies dealing with petroleum pollution. Especially, reliable data on concentrations and origin of petroleum hydrocarbon in the river sediments is scarce. Therefore, the objectives of this study were to determine the concentration, distribution and possible sources of hydrocarbons in river sediments in

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Beiluohe Basin using the following geochemical markers: n-alkanes, isoprenoid alkanes, petroleum biomarkers.

Materials and Methods

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 22 surface sediment samples coming from the Beiluohe River and its tributary were collected for extraction and fractionation in October 2005. Among these 22 samples, 12 samples were detected by gas chromatography with flame ionization detector (GC/FID) and 6 samples were selected for gas chromatography/mass spectroscopy detection. 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.

In the laboratory, about 100 g dry sediment samples were Xoxhlet-extracted with chloroform for a period of 72 h. Elemental sulphur 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 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.

Normal and isoprenoid alkanes analyses were conducted on a Hewlett Packard (HP) 6890 II gas chromatograph with flame ionization (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 PlatfromII 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 above. The MS operating conditions were: electron energy 70 eV, scanned from 50–600 amu. The samples were analyzed in the splitless mode.

Results and Discussion

The total solvent extractable organic matter (EOM) concentrations varied from 29 μg g^{-1} to 267 μg g^{-1} of dry sediment, with an overall average of 148 μg g^{-1} dry wt. In most of these samples, total hydrocarbons accounted for a major part of the EOM (from 31.3 to 80.3%). Concentrations of total hydrocarbons ranged between 6.4 and 147.3 μg g^{-1} dry sediment, with an average of 76.8 μg g^{-1}

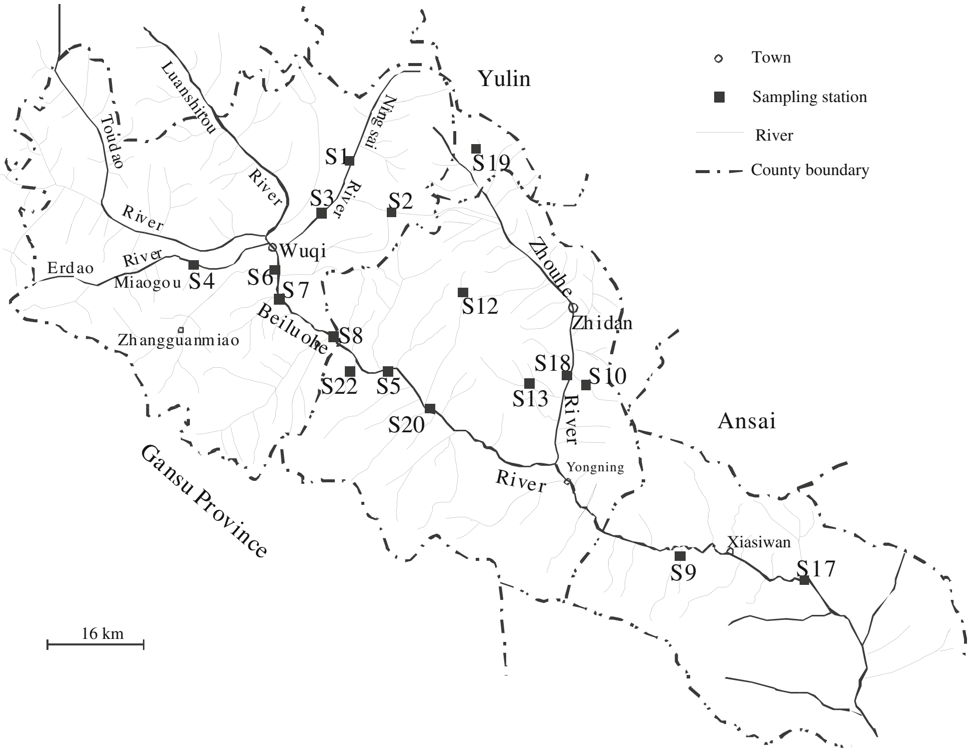


Fig. 1 Study areas and sampling location in the Beiluohe River, northern Shaanxi immediately until laboratory analysis

dry wt. 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 Macloed 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 6.4–15.6 μg g^{-1}. These low total hydrocarbon concentrations may be regarded as the natural background levels in the Beiluohe area. Results of THC values showed an unpolluted to slightly polluted levels in most sediment samples from the studied areas.

Figure 2 shows the spatial concentrations profiles of total hydrocarbons among different sampling stations. Samples taken from the mainstream of River Beiluohe displayed relatively low values of THC, ranging from 9.7 to 57.5 μg g^{-1}. Relatively high concentrations of total hydrocarbons were found in those sediments collected from locations S2, S3, S9, S12 and S20, associated with discharges of petroleum waste or urban wastewater. For example, sampling station S1 and S3 located on Ningsai River, are distributed upstream and downstream of a petroleum treatment factory respectivley. Station S3 received untreated petroleum waste every day and its THC is nine times higher than that from station S1. As a result, high value of THC in S3 may be mainly due to the continuous pouring of untreated petroleum waste into the Ningsai River. The Beiluohe River has a long history of polluted by crude oil. It is estimated that about 50,000 tons of oil waste water were discharged annually into the Yan'an reach of Beiluohe River alone. Therefore, the direct discharges of oil waste water are important sources of sediment hydrocarbon pollution in the region. Moreover, hydrocarbons are introduced into river environments by oil spills involving leakages from tank trucks and platform run-off.

The gas chromatographic profiles of total hydrocarbons in the river sediments are shown in Fig. 3. The GC traces are dominated by *n*-alkanes extending from C_{15} to C_{34} with relatively low CPI values. *N*-alkanes, representing two distinct sources, are evident on the basis of their distribution pattern in sediments collected (Fig. 3). (1) For station S10, the most abundant alkanes are generally those of medium molecular weight (C_{15}–C_{24}), while the least abundant are the n-alkanes of C_{27}, C_{29} and C_{31}. In addition, these stations contain abundant branched and cyclic alkanes. The dominance of the n-alkanes in the range C_{18}–C_{24}, suggests relatively recent oil input (Sultan and Sameer 1997). This has been verified by the presence of a strong unresolved complex mixture (UCM) in the GC profiles. Such compounds, resistant to biological degradation (Gough 1990), have been considered as the environmental indicators of long-term petroleum-related contamination (Sultan and Sameer 1997). The odd/even carbon preference index (CPI) is also an index used for determining the sources of n-alkanes. These stations presented lower values around 1.0 (between 1.0–1.1) indicating inputs of n-alkanes from crude oil related sources (Wang and Fingas 2003). The station S3 S12 and S21 can also be ranged in the group of predominant petroleum input. (2) At station S9, S14 and S20, the main features in GC profiles are notably different from the station S10. In these stations, the long chain compounds prevailed with the Cmax at C_{27}, C_{29} and C_{31} (Fig. 3) and presented an elevated odd to even carbon number preference as reflected in the high CPI2 values (3.0, 4.0 respectively). This pattern is characteristic of higher plant waxes and thus reveals the occurrence of prominent terrestrial inputs to these sampling sites (Patricia et al. 2005). However, the *n*-alkanes profile indicates that contribution from plantwax hydrocarbons is overshadowed in samples by *n*-alkanes of petroleum origin. This is obvious by the ratio of pristane to phytane and the presence of high relative abundance of UCM.

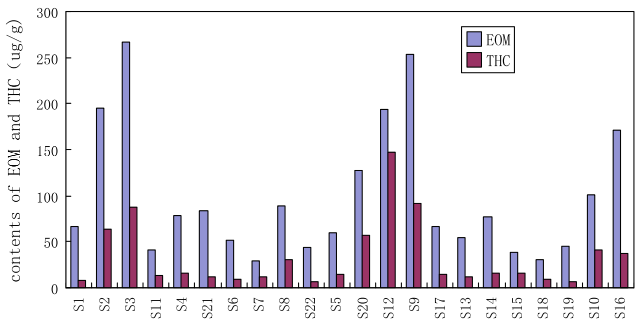


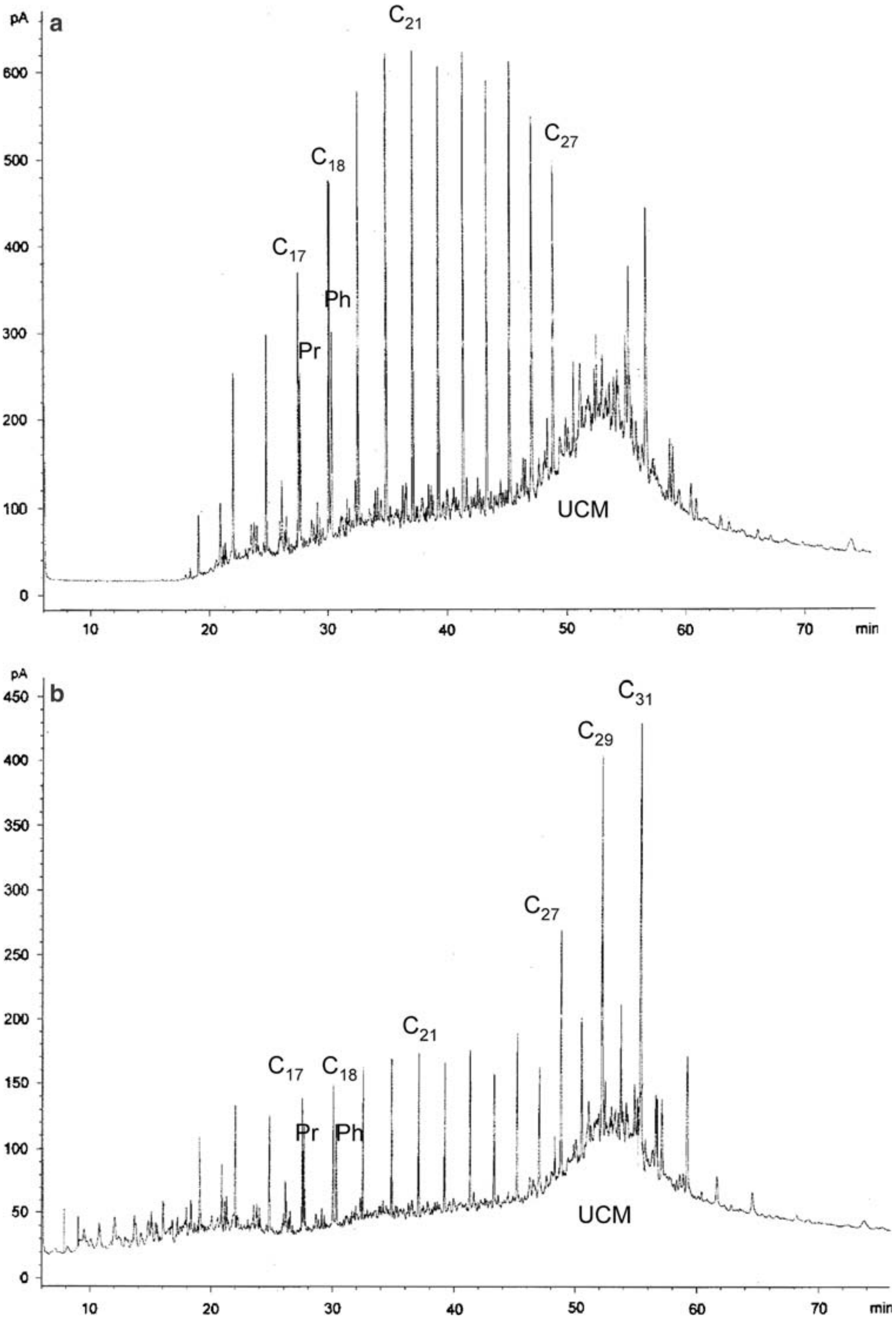
Fig. 2 The spatial concentration profiles of total hydrocarbons at sampling stations

The two isoprenoids, pristane (pr) and phytane (ph) were present in most sediment extracts. They are common indicators for petroleum pollution. The ratio of pristine to phytane varies between oils and is thought to reflect the depositional environment of the original source rocks (Didyk et al. 1978). A relative high concentration of pristane alone indicates a biogenic input possibly originating from algae and bacteria. In uncontaminated sediments, the ratio Pr/Ph is typically between 3 and 5 (Steinhauer and Boehm 1992). However, ratio of pristane to phytane was low (0.73–1.32) in most of the samples, indicating mainly petroleum source.

The presence of oil is also confirmed by the identification of the hopane and sterane series, which is determined in the GC-MS data by monitoring *m/z* 191 and 217 + 218, respectively, in Luohe Basin.

Figure 4 shows the characteristic m/z 191 mass fragmentogram. Fragmentograms reveal the presence of hopanes with 27–35 arbon atoms and triclycic terpanes with 23 and 24 carbon atoms. The hopanes distribution is characterized by the predominance of C_{30} 17α(H), 21β(H)-

Fig. 3 Gas chromatogram of saturated hydrocarbons from surface sediments at site S10 (**a**) and S9 (**b**). UCM-Unresolved Complex Mixture; Pr-Pritane; Ph-Phytane



hopane with a smooth decrease in the abundance of C_{31-35} homohopanes in these series. Homologues with number of carbon atoms $\geq C_{29}$ exhibited the thermodynamically more stable 17α(H), 21β(H) configuration, while the extended α-hopane series (C_{31}–C_{35}) occurred as 22S and 22R epimers. These patterns are characteristics of oil-derived hydrocarbons (Afifa et al. 2001). 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 values of the ratio 22S/22S + 22R epimers of αβ C_{31} homohopanes vary in a narrow range 0.58–0.59, close to the value of 0.6 for equilibrium of oil full maturity, suggesting petroleum-related hydrocarbon contamination in sediments (Mackenzie 1984). Therefore the occurrence of mature hopanes in river sediments clearly confirms the input of a fossil fuel contamination.

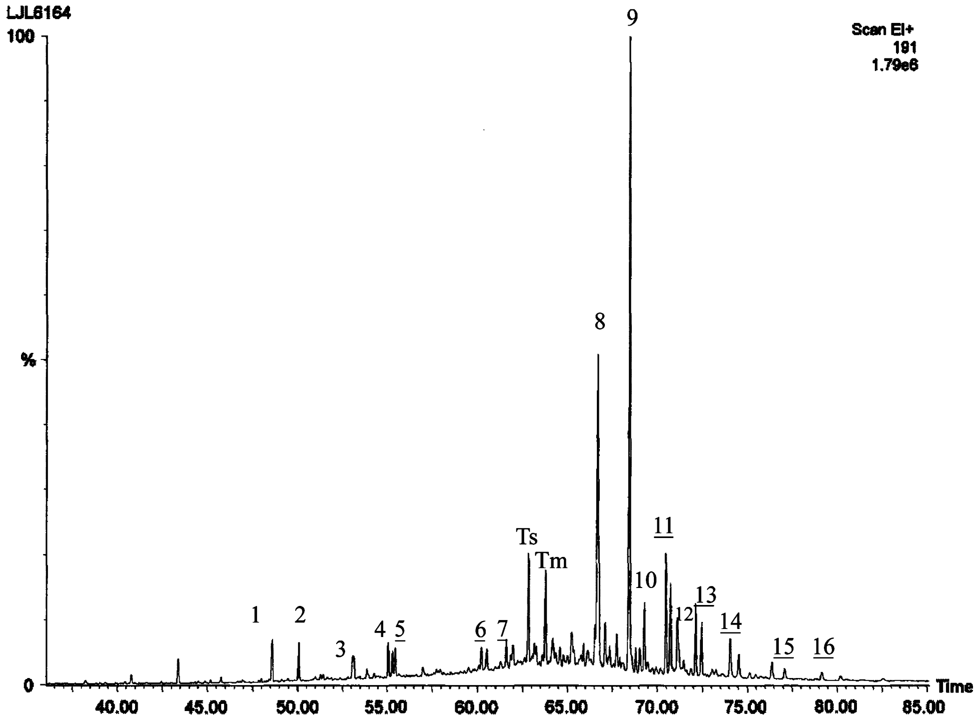


Fig. 4 Representative mass fragmentograms of m/z 191 for terpanes at site S12 1–7: Tricyclic terpane; Ts: 18α(H)22,29,30-tris-norhopanes; Tm: 17α(H)22,29,30-tris-norhopanes; 8: 17α(H), 21β(H), 30-norhopanes; 9: 17α(H), 21β(H)- hopanes; 10: 17β(H), 21α(H), 30-hopane (moretane); 11: 17α(H), 21β(H)-homohopane (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. 5 Representative mass fragmentograms of m/z 217 for steranes at site S12 1: $C_{27}\alpha\alpha\alpha$-cholestane(22S); 2: $C_{27}\alpha\beta\beta$-cholestane(22R); 3: $C_{27}\alpha\beta\beta$-cholestane(22S); 4:$C_{27}\alpha\alpha\alpha$-cholestane(22R); 5: $C_{28}\alpha\alpha\alpha$-ergostane(22S); 6: $C_{28}\alpha\beta\beta$-ergostane(22R); 7:$C_{28}\alpha\beta\beta$-ergostane(22S); 8: $C_{28}\alpha\alpha\alpha$-ergostane(22R); 9: $C_{29}\alpha\alpha\alpha$-stigmastane(22S); 10:$C_{29}\alpha\beta\beta$-stigmastane(22R); 11: $C_{29}\alpha\beta\beta$-stigmastane(22S); 12: $C_{29}\alpha\alpha\alpha$-stigmastane(22R)

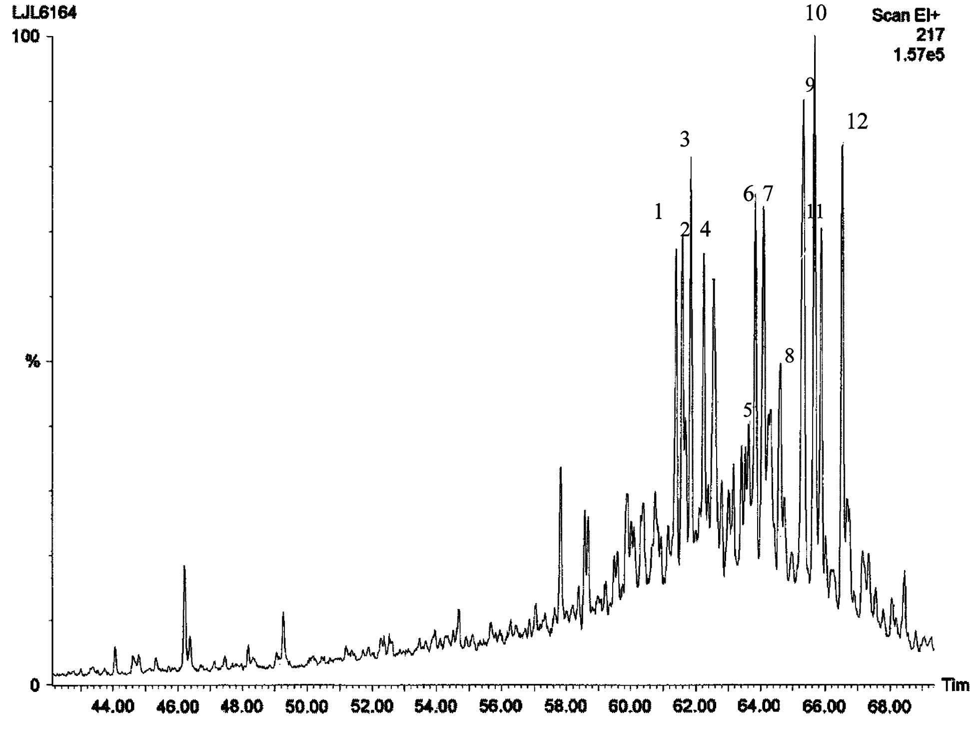


Table 1 Maturity indicators of biomarkers from the surficial sediments of the Beiluohe River

Sample station	Ts/Ts + Tm	$C_{31}\alpha\beta$ S/S + R	$\alpha\alpha\alpha C_{29}$ S/S + R
S8	0.44	0.58	0.61
S10	0.48	0.58	0.57
S12	0.51	0.58	0.59
S16	0.44	0.58	0.51
S20	0.61	0.58	0.61
S21	0.71	0.59	0.67

Figure 5 shows the characteristic m/z 217 mass fragmentogram. Steranes present in fossil fuels are also useful biomarker indicators for petroleum pollution. 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 20Repimers. The relative abundances of three regular sterane series are in an order of $C_{29} > C_{27} > C_{28}$, suggesting a lacustrine sourced oil 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) (Table 1) and have the high maturity level. Such sterane signatures also confirm the presence of mature petroleum in sediments.

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