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Baseline

An analysis of organic matter sources for surface sediments in the central South Yellow Sea, China: Evidence based on macroelements and *n*-alkanes

Shengyin Zhang [a,b], Shuanglin Li [b,c,*], Heping Dong [b,c], Qingfang Zhao [b,c], Xinchuan Lu [a], Ji'an Shi [a]

[a] Key Laboratory of Petroleum Resources, Gansu Province/Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Lanzhou 730000, China
[b] Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources, Qingdao, Shandong 266071, China
[c] Qingdao Institute of Marine Geology, Qingdao 266071, China

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ABSTRACT

By analyzing the composition of *n*-alkane and macroelements in the surface sediments of the central South Yellow Sea of China, we evaluated the influencing factors on the distribution of organic matter. The analysis indicates that the distribution of total organic carbon (TOC) was low in the west and high in the east, and TOC was more related to Al_2O_3 content than medium diameter (MD). The composition of *n*-alkanes indicated the organic matter was mainly derived from terrestrial higher plants. Contributions from herbaceous plants and woody plants were comparable. The comprehensive analysis of the parameters of macroelements and *n*-alkanes showed the terrestrial organic matter in the central South Yellow Sea was mainly from the input of the modern Yellow River and old Yellow River. However, some samples exhibited evident input characteristics from petroleum sources, which changed the original *n*-alkanes of organic matter in sediments.

Marginal seas on the continental shelf are a key area for energy conversion and the carbon cycle in the marine ecosystem. On average, more than 80% of organic matter in the sea is buried on the continental shelf and slope (Kao et al., 2006; Muller-Karger et al., 2005). Because of the effect of the sea-continent interaction, the source of organic matter is relatively complicated, and the sea on the edge of the continental shelf has a fast sedimentary accumulation and high biological production. It is significant to discuss the sources and distribution of organic matter on the edge of the continental shelf to examine the evolution of the marine ecosystem and the "source-sink" problem for the estuary-continental shelf (Alongi and McKinnon, 2005; Benner, 2004; Hu et al., 2009). Recently, with economic development in China, particularly the rapid increase of industrial levels in the Shandong Peninsula, the pollutants introduced into the Yellow Sea circulation through rivers and the atmosphere have increased yearly, and the effect of human activity on the marine ecosystem has become serious (Wu et al., 2001). It is necessary to determine the sources of organic matter to the marginal sea to evaluate and control environmental pollution in the ocean.

It has been realized that some compounds of organic matter are relatively stable over long-term geological evolution. In particular, because of the absorption of organic matter onto clay minerals in marine sediments, some compounds can maintain relatively stable structures, including *n*-alkanes, isoprenoid alkanes, sterane, and terpane (Brassell et al., 1987). Studying the geochemical characteristics of these organic compounds cannot only reveal important information, such as the source of the sediments, ancient sedimentary environment, and diagenetic evolution (Wu et al., 2001; Yunker et al., 1993), but also provide a necessary basis to track environmental pollution and to explore offshore oil and natural gas hydrates (Abrams, 1992, 2005; Simpson et al., 1996).

The Yellow Sea is a typical shelf sea formed under postglacial transgression. The average water depth is 50 m, and the maximum water depth is 100 m (Qin et al., 1989). After the Holocene, the Yellow Sea was affected by the Yellow and Yangtze rivers and received a large amount of terrestrial material (Qin et al., 1989). The sediments in the Yellow Sea were mainly from the discharge of the Yellow River, which was named the old Yellow River because it had been entering the Southern Yellow Sea from the estuary north of Jiangsu before 1855 (Fig. 1). The modern Yellow River passes

* Corresponding author at: Qingdao Institute of Marine Geology, Qingdao, Shandong 266071, China. Tel.: +86 532 80778389; fax: +86 532 85720553.
E-mail address: lishuanglin5335@hotmail.com (S. Li).

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through the north of the Shandong Peninsula to Bohai, and the discharged sediment bypasses the Shandong Peninsula to the South Yellow Sea. The circulation around the Yellow Sea formed the muddy deposition unique to the eastern sea of China (Dong et al., 2011; Lim et al., 2007). The study area is located in the central South Yellow Sea between latitudes 34°12′∼35°24′N and longitudes 121°12′∼124°E (Fig. 1), and the water depth in the study area is 40–90 m. The western region of the study area is a tongue-shaped system on the coast of North Jiangsu, and these sediments mainly consist of sandy slits, while the mid-eastern region is located on the plain of the central South Yellow Sea and developed large argillaceous sediments. In this paper, we examine the factors influencing the distribution of organic matter in the study area by analyzing the distribution characteristics of organic matter, particle size, and macroelements, including Al_2O_3, Fe_2O_3, CaO, K_2O, Na_2O, MgO, TiO_2, P_2O_5, and MnO, in the sediments. We further combined the compositional features of *n*-alkanes and isoprenoid hydrocarbons to discuss the provenance and destination of organic matter in the mud area of the central South Yellow Sea.

The study samples were from 501 stations, including 64 samples for saturated hydrocarbon gas chromatography analyses (Fig. 2, top). There were also 501 samples of macroelements, organic carbon, and particle size (Fig. 2, bottom). Surface sediment samples were collected using a vibro piston corer deployed from R/V Zhehaihuanjian of the State Oceanic Administration from August to October 2012. The vibro piston corer could obtain a 2.5–3.0 m core sample via vibrator on the upper device, and the sampling procedure did not significantly disturb the sediments. The top 3 cm of sediment from the core samples were selected as surface sediment samples on site and were packaged using aluminum foil without being contaminated. The samples were stored in a freezer at −20 °C in the laboratory until the organic analysis.

The macroelement, organic carbon, and particle size analyses were performed at the Qingdao Institute of Marine Geology. For the measurements of Al_2O_3, Fe_2O_3, CaO, K_2O, Na_2O, MgO, TiO_2, P_2O_5, and MnO, the sample was decomposed with 10 mL hydrofluoric acid and 5 mL nitric acid and heated for 30 min at low temperature. After the sample cooled, 2 mL perchloric acid was added for decomposition, and another 10 mL hydrochloric acid was added to dissolve the sample and prepare the solution. The samples were measured using compression X-ray fluorescence spectrometry (XRF) and plasma spectrometry (ICPOES). For the element analysis, we also performed repeat analyses for several duplicate samples, and the relative error of element analysis was less than 5%.

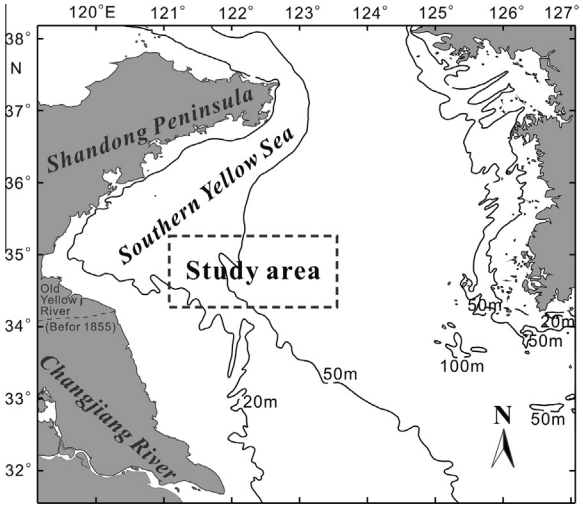

Fig. 1. The location of the study area.

The samples were freeze-dried for 48 h until the water content was completely removed and the weight of the sample did not change with freezing time. The lyophilized sample was ground into powder, passed through a 100-mesh sieve, lyophilized again, and then stored at room temperature. Approximately 1 g of the sample was placed into 10 mL 5% H_2O_2 for 24 h to eliminate the organic matter content, and diluted hydrochloric acid was then added to remove the carbonates. We then used an ultrasonic oscillator and ultrasonic waves to disperse the sample for 30 min. In this experiment, we used a laser particle size distribution meter (Mastersizer 2000) manufactured by the Malvern Company of the United Kingdom to analyze particle size. The range of measurement was 0.02–2000 μm with a resolution of 0.01 Φ and an analytical error of ±2%.

To measure organic carbon, we used acid to remove carbonate and then measured the percentage of carbon with an element analyzer. The detailed procedures were as follows: approximately 1 g of the sample was soaked three times with 10 mL 10% hydrochloric acid for approximately 8 h every time. The acid was discarded by centrifugation, and the sample was washed with water until neutral. We dried the sample overnight at 60 °C and then placed it in a desiccator and equilibrated to constant weight. One to ten milligrams of the sample was used to measure the percentage of carbon with an element analyzer (Vario EL-III Elemental Analyzer). We then used the difference in the weight before and after pickling to correct the measured percentage of carbon and calculated the percentage of organic carbon in the original sample.

The extraction, purification, and GC/MS analysis of organic matter were performed according to previous studies (Hu et al., 2009). The following basic procedures were used: the sediment sample was frozen, dried, and ground. We weighed approximately 20 g of the sample, and the organic matter was extracted with a Soxhlet extractor using dichloromethane for 72 h. A small amount of an activated copper sheet was placed on the bottom of the extract flask to remove the sulfur in the sample. The extracted solution was concentrated. The solution was transferred and passed through a silica/aluminum oxide (1:1) chromatographic column to be separated and purified. The sample was rinsed four times with 20 mL n-hexane, and the saturated hydrocarbon fraction was collected.

The quantitative analysis of saturated hydrocarbon chromatography used the Agilent 6890 N gas chromatograph. The chromatographic column was a 50 m × 0.20 mm × 0.3 μm PONA column, and the inlet temperature was 300 °C. The following GC temperature program was used: constant temperature of 35 °C for 10 min, then increased at a rate of 4 °C/min to 300 °C and hold for 50 min. The flow rate of the carrier gas was 1.0 mL/min, and the carrier gas was N_2.

The internal standard sample $C_{24}D_{50}$ (deuterated carbon 24 *n*-alkanes) was used to quantify the individual *n*-alkanes (C_{12}–C_{35}), which were identified based on retention times and mass spectra for target compounds. Relative response factors for the *n*-alkanes not included in the standard compounds were calculated by linear interpolation (Hu et al., 2009).

In the experiment, we applied recovery standards of five deuterated PAHs (naphthalene-d8; ace-naphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12} and perylene-d_{12}) in order to monitor matrix effects and procedural performance. The extracts from 1:2 alumina:silica was eluted by 20 mL hexane:dichloromethane (1:1, v:v) to separate the polyaromatic hydrocarbon fraction for evaluation of the five deuterated PAHs. The results showed that the recovery rate of the experiment was 91.5 ± 10%. In addition, we also applied a blank and spiked blank experiment for a control. In the blank experiment, there was no significant (<5%) interference on the targeted compound.

Based on the correlation between organic carbon (TOC), macroelements, and medium diameter (MD), we conducted an analysis