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Preliminary discussion on the source identification of oil spills based on the nitrogen isotopic characteristics

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Abstract. A preliminary evaluation of nitrogen isotope analysis as a novel, alternative method for identifying spilled oils is presented. The nitrogen isotopic compositions of crude oil from different oilfields in China may be significantly different, which provides a way of screening possible sources for spilled oil of unknown origin, especially in areas of heavy tanker traffic carrying oils from different geographical regions. The value of $\delta^{15}N$ increases gradually with the degree of biodegradation. This findings can be applied for correlation and differentiation of spilled oils at their lightly to moderately weathered stages.

Introduction

Oil exploitation and marine transportation have developed rapidly in China, bringing increased risk of oil spills. At present, China is the fifth largest oil producer and the second largest oil consumer in the world. China experienced 2,635 oil spill accidents in its seas and along its coastal areas from 1973 to 2006, including 69 major accidents. Oil spills cause extensive damage to marine and terrestrial life, human health, and natural resources. Therefore, characterization of chemical compositions and identification of oil spill sources are, in many cases, critical for providing forensic evidence in the investigation of oil spill accidents and settling disputes related to liability [1].

Correlation of crude oils and refined hydrocarbon products spilled in the environment with their respective sources is commonly undertaken using techniques such as gas chromatography (GC) or gas chromatography-mass spectrometry (GC–MS). The major elements in petroleum are carbon and hydrogen, and the stable isotope ratios of these elements have been the most intensively studied. Petroleum may also contain sulfur, nitrogen, and oxygen, and stable isotope ratios of these elements may provide additional information to correlate spilled material with sources. Stable carbon isotopic compositions of individual hydrocarbons in spilled oils and sediments may provide additional evidence that helps to trace oil spill sources [2-3]. Although sable isotope ratios of nitrogen have found increasing application in petroleum geochemistry [4-6] in recent years, there have a few reports of this for forensic oil spill investigations. Biodegradation of hydrocarbon by natural pollutions of microorganisms is general a long-term weathering process and represents the primary mechanisms by which petroleum are eliminated from the environment. Thus, biodegradation can be one of the most important processes in the environment [1,7]. The major aim of this paper is to assess the utilization of nitrogen isotopic characteristics as a correlation tool for hydrocarbons spilled with their suspected source(s). The study focuses on two main aspects: (i) determination of the effects of biodegradation processes on the nitrogen isotopic composition of crude oils; (ii) the evaluation of possibilities of $\delta^{15}N$ as a correlation tool in oil spill identification.

Experimental Section

2.1 Samples

A number of different samples from various origins were analyzed in this study. Microorganism may play an important role in nitrogen cycling. In view of this, a set of sequentially biodegraded oils from Liaohe oilfield were analyzed in order to elucidate the effect of biodegradation on distribution of the nitrogen isotopic composition of crude oils.

2.2 Analytical method

Oil is heated in strong sulfate acid. The organic nitrogen-bearing compounds in oil are decomposed and the nitrogen is transformed into ammonium stayed in the acid solution. Nitrogen gas was given out by adding NaBrO into the solution and then goes into MS instrument. The isotopic ratio is measured and calculated under the criterion of atmospheric N_2. The method and experimental steps can be seen in ref. [5]. The MS instrument in the paper is Finnigan-MAT251 made in USA.

. Result and discussion

3.1 Nitrogen isotopic characteristics of different crude oils

The nitrogen isotopic ratio distribution varies with different basins in China. An illustration of the nitrogen isotope distribution of crude oils formed in different depositional environments is shown in Fig. 1. The distribution can be divided into three types mainly based on the range of $\delta^{15}N$: limnic, basic saline to high salinity and marine carbonate sedimentary environments. Two kinds of distributions in Liaohe oil field represent those in most basins in Eastern China. For example, $\delta^{15}N$ values of oils (LH-A) forming in the limnic environment in Shahejie Formation of Shengli oil field ranged from 2.36‰ to 6.11‰, with the average of 5.08‰; and $\delta^{15}N$ values of oils (LH-B) in Minghua-zhen and Guantao Formations of Dagang oil field average 3.27‰ [6]. However, the values of most oils forming in the typical saline lake environment in Jianghan field are above 10‰, with the highest $\delta^{15}N$ being 17.12‰ [6]. The average $\delta^{15}N$ in Tazhong (TZ) has the lowest value compared with those of most oils in other zones; $\delta^{15}N$ in Lunnan is higher appreciably but it is still below zero on the whole, which reflects possibly the characteristic of the oil originating mainly from the organic matter in marine carbonate sediment [6]. In general, the stable nitrogen isotopic compositions of crude oils from different organisms under different sedimentary environments can be significantly different. This provides a way of screening possible sources for spilled oil or beach tars of unknown origin, especially in areas of heavy tanker traffic carrying oils from different geographical regions.

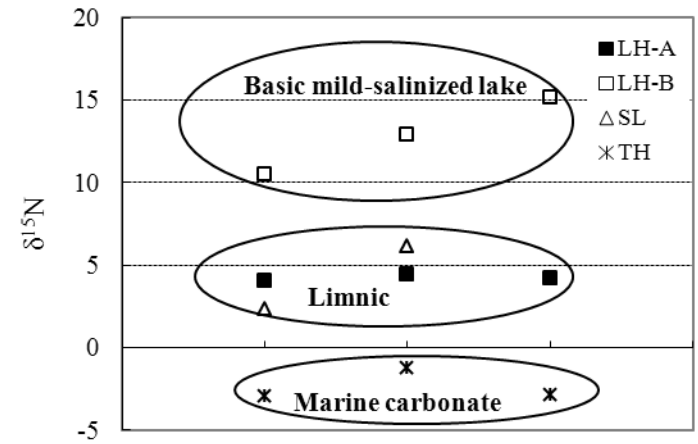

Fig.1 $\delta^{15}N$ values of different crude oils in China

The reason causing the $\delta^{15}N$ difference in two environments may be that saline environment is favorable for denitrification of bacteria. An anaerobic environment can form in the bottom of high saline water system easily. The bacteria transforms NO_3^- in water into N_2 under the anaerobic environment, so $^{15}NO_3^-$ is enriched in saline water [8].

3.2 Fractionation in oil biodegradation

The second step of the study was to determine if biodegradation processes can compromise correlations between pollutants and suspected sources. Fractionation in crude oil with high biodegradation from Liaohe oilfield, are selected as the example. The distributions of n-paraffin hydrocarbons in the samples studied are shown in Fig.2. The results show that *n*-alkanes are progressively depleted in crude oils with increasing extent of biodegradation in order of LH-A, LH-B and LH-C. As the easily degraded normal hydrocarbons (n-C_{17} and n-C_{18}) are lost, the more degradation resistant isoprenoids (pristane and phytane) are conserved, resulting in a significant increase of the ratios of Pr/n-C_{17} and Ph/n-C_{18} in the weathered oil residues samples. Three oils have

$\delta^{15}N$ values of 4.38‰, 6.52‰ and 10.63‰, respectively. The nitrogen isotopic ratio increased obviously when oil suffered biodegradation. Furthermore, $\delta^{15}N$ increases gradually with the degree of biodegradation. The standard deviations of $\delta^{15}N$ values of crude oils from different basin of China are 3.17% in this study, which is out of the range of the analytical error. Therefore, nitrogen isotopic analysis may be used for oil source identification for fresh or mildly weathered oil products.

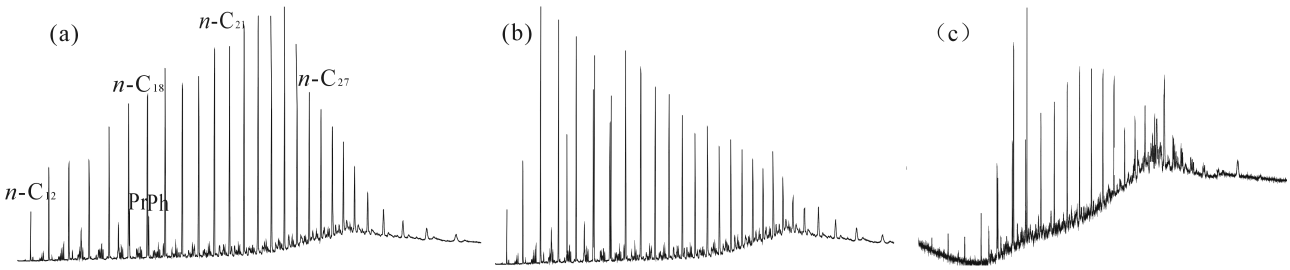

Fig.2. GC graphs and $\delta^{15}N$s of three oils in natural different biodegradation series

The mechanism of nitrogen isotopic fractionation caused by biodegradation is very complicated. Usually it is believed that biodegradation is caused by aerobic bacteria especially in the shallower reservoir. In general, bacteria prefer to utilize the compounds with light nitrogen isotope in metabolism, which results in the enrichment of the com-pounds with heavy nitrogen isotope in oil [6].

3.3 Case analysis

Bohai Bay is the largest oil and gas production base offshore China, among those owned by the China National Offshore Oil Corporation. There is always a leak risk of these materials which could lead to oil spill, fire and explosion accident. Nitrogen isotopic analysis was applied to identificate smaller oil spill happened in Bohai Bay. The oil residue (S1, S3, S4) had a very narrow $\delta^{15}N$ range (7.89±0.28), which is different from the oil S2 and S5 samples (5.72, 36.5) from drilling platforms there. However, the $\delta^{15}N$ distribution of the three oil residues samples correlated with oil sample S6 (7.85) obtained from a passing tanker. Thus, the oil residue was believed to be from the passing tanker.

Conclusions

The distinct characteristic nitrogen isotopic signatures of different crude oils can be potentially extended from oil migration studies to for identification of oil spill. The $\delta^{15}N$ distribution varies with different sedimentary types of basins. Oils formed in the limnic environment have lower $\delta^{15}N$ value, whereas the oils fromed in the saline or semi-saline environment have higher $\delta^{15}N$. Furthermore, $\delta^{15}N$ of the oil from marine carbonate rock of Tarim Basin is the lowest. The distribution range of $\delta^{15}N$ is affected by fractionation. $\delta^{15}N$ increases gradually with the degree of biodegradation. In this study, the standard deviations of $\delta^{15}N$ values of crude oils from different basin of China are 3.17%, which is out of the range of the analytical error. The results suggest that stable nitrogen isotope profile of crude oils can be a useful tool for tracing the source of an oil spill, especially for lightly weathered oils.

Acknowledgements

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