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# Characteristics of Aromatic Hydrocarbons and Its Stable Carbon Isotope Compositions in Crude Oils

Haixia Wang<sup>1</sup>, Jin Xu<sup>1\*</sup>, Qingming Wang<sup>3</sup>, Dawei Jiang<sup>2</sup> and Xibin Pang<sup>1</sup>

<sup>1</sup>Country Navigation College, Dalian Maritime University, Dalian, Liaoning Province, 116026, China

<sup>2</sup>College of Environmental Sciences and Engineering, Dalian Maritime University, Dalian, Liaoning Province, 116026, China

<sup>3</sup>Alumni Affairs and Cooperation Office, Dalian Maritime University, Dalian, Liaoning Province, 116026, China

\*Corresponding author's e-mail: jinxu@dlmu.edu.cn

**Abstract.** In this paper, relative contents, characteristic ratios and stable carbon isotope compositions of aromatic hydrocarbons in crude oils were determined from different areas. In terms of aromatic hydrocarbons relative contents, two kinds of crude oils have shown their own features. From the characteristics of the ratios of aromatic hydrocarbon in crude oil, the maturity parameters (MNR、TNR1、TNR2、MPR、MPI1、MPDF1 and MPDF2) reflected high maturity of all the crude oil. Other parameters, such as DNR1、DNR2 and TNR4, revealed the organic source and biodegradation of crude oil and other information. From the compositions of stable carbon isotope of aromatic hydrocarbons in crude oils, crude oils between the various regions have the differences. Plots of aromatic hydrocarbon ratios versus  $\delta^{13}\text{C}$  values of dimethylnaphthalene and phenanthrene were constructed to discriminate crude oils from different areas. The results demonstrate that this method can distinguish different kinds of crude oil more effectively.

## 1. Introduction

Recent statistical data shows that the average number of incidents involving large oil spills from tankers has reduced progressively for the last three and a half decades and has stood at an average of 1.8 large oil spills per year since 2010, but the total recorded amount of oil lost to the environment in 2015 was approximately 7,000 tons[1]. Particularly, with the industrial demand for petroleum increasing, marine oil spills by wrecked tanker or natural seep-age has been increasingly frequent[2-3]. Therefore, highly efficient identification of the types and sources of oil spills plays a critical role in pollution control of seas and investigations for accountability[4-5].

Gas chromatography–isotope ratio mass spectrometry (GC–IRMS), another analytical technology, is an effective method for oil spill identification[6-7]. The study has demonstrated the variation of n-alkane content and stable carbon isotope composition during short-term weathering of different types of oils[3]. It proved that the stable carbon isotopic composition of n-alkanes can be effectively applied to oil fingerprint identification during short-term weathering of oil spills[8]. Yanik et al. [9] studied the effect of biodegradation on the stable carbon isotope composition of PAHs in crude oil and proved that the  $\delta^{13}\text{C}$  values of PAHs have a positive trend with the increase in biodegradation degree. In the



existing oil sample identification studies, most of the normal paraffin carbon stable isotopes are used to distinguish oil samples, while the use of aromatic hydrocarbon carbon stable isotope to identify oil samples is less studied. In order to find out the aromatics geochemical index and the stable carbon isotope compositions which are suitable for oil samples identification, this paper studied the composition of aromatics and their stable carbon isotope composition in different areas, as well as to provide an alternative method for the identification of oil spills.

## 2. Materials and methods

### 2.1 Samples and reagents

Two crude oils and two fuel oils (Angolan crude oil and Brazil crude oil) were selected as research samples in this study. The seawater was filtered by nylon cloth of 500-mesh to remove suspended substances.

### 2.2 Sample preparation

About 0.2 g of each oil sample was dissolved in hexane (8 ml) and then subjected to ultrasonic concussion. The dissolved oil sample was transferred into a glass centrifuge tube, and 1 g of anhydrous sodium sulfate was added to it. The supernatant was collected for use after centrifugation at speed of 1500 r/min for 10 min. The column was packed with activated neutral alumina and washed with hexane before use. The supernatant was transferred to the column, and then the saturated hydrocarbons were eluted with hexane (20 ml) (component A). Total aromatics (component B) were eluted with hexane–dichloromethane mixture (20 ml, 3:1, v/v) and were concentrated to 0.5 ml under a nitrogen stream prior to analysis using GC–MS. In order to better meet the conditions for GC–IRMS, component B had to be separated by column chromatography. Hexane–dichloromethane solution (20 ml, 9:1, v/v) was used to elute diaromatics (component C), and hexane–dichloromethane solution (20 ml, 2:1, v/v) was used to elute tricyclic aromatics (component D). Finally, the components were concentrated to 0.5 ml and then stored in a sample bottle at low temperature for GC–IRMS[3].

### 2.3 Instrumental analysis

The samples were analyzed by a gas chromatography-isotopic ratio mass spectrometry (GC–IRMS) instrument (Thermo Fisher Scientific, USA). Carrier gas: He; Flow rate: 1–2 mL/min; Injection mode: splitless injection; inlet temperature: 280 °C; injection volume: 1 µL; temperature program: initial temperature 60 °C, 3 °C/min speed increased to 290 °C for 10 min; mass spectrometer, ion source temperature 230 °C, transmission line temperature 250 °C.

Carbon isotope ratios for individual aromatic hydrocarbons were calculated using CO<sub>2</sub> as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis and the stable isotope data are presented as delta (δ) values representing the deviation in parts per thousand (‰, per mil, or ppt) from an accepted standard. The isotope ratio for carbon was expressed as:

$$\delta^{13}\text{C} = [(R_{\text{samples}}/R_{\text{standard}}) - 1] \times 10^3$$

where  $R_{\text{samples}}$  and  $R_{\text{standard}}$  are the isotope ratio ( $^{13}\text{C}/^{12}\text{C}$ ) of the samples and recognized international standards Vienna Pee Dee Belemnite (VPDB) for  $\delta^{13}\text{C}$  values, respectively. The analytical precision was < 0.02‰ (1σ) for  $^{13}\text{C}$ .

PAHs of crude oils were identified by matching retention times of 16 PAH standards. Alkyl aromatic hydrocarbon compounds were identified by comparison of mass spectra and retention times against references[10–11].

### 2.4 Data analysis

The characteristic ratio information of crude oil polycyclic aromatic hydrocarbons is as follows:

(1)Methylnaphthalene Ratio, MNR: Concentration ratio of 2-methylnaphthalene (2-MN) to 1-methylnaphthalene (1-MN) in crude oil.

$$\text{MNR} = A(2\text{-MN}) / A(1\text{-MN})$$

where A are the concentration (peak area) of the corresponding component in the crude oil is calculated using the peak area of the component herein, the same below.

(2)Dimethylnaphthalene Ratio, DNR: The concentration ratio between different dimethyl naphthalenes (DMN) in crude oil.

$$\text{DNR1} = A(2,6+2,7\text{-DMN}) / A(1,3+1,7\text{-DMN})$$

$$\text{DNR2} = A(1,2\text{-DMN}) / A(1,3+1,7\text{-DMN})$$

(3)Trimethylnaphthalene Ratio, TNR: Concentration ratio between different trimethylnaphthalenes (TMN) in crude oil.

$$\text{TNR1} = A(2,3,6\text{-TMN}) / A(1,4,6+1,3,5\text{-TMN})$$

$$\text{TNR2} = A(1,3,7+2,3,6\text{-TMN}) / A(1,3,5+1,3,6+1,4,6\text{-TMN})$$

$$\text{TNR3} = A(1,3,7\text{-TMN}) / A(1,3,6\text{-TMN})$$

$$\text{TNR4} = A(1,2,5\text{-TMN}) / A(1,3,6\text{-TMN})$$

(4)Methylphenanthrene Ratio, MPR: Concentration ratio of 2-methylphenanthrene(2-MP) to 1-methylphenanthrene (1-MP) in crude oil.

$$\text{MPR} = A(2\text{-MP}) / A(1\text{-MP})$$

(5) Methylphenanthrene Index, MPI:

$$\text{MPI} = 1.5 \times A[(3\text{-MP}+2\text{-MP})] / A[(1\text{-MP}+9\text{-MP}+1\text{-MP})]$$

(6) Methylphenanthrene Distribution Fraction, MPDF:

$$\text{MPDF1} = A[(3\text{-MP}+2\text{-MP})] / A[(1\text{-MP}+2\text{-MP}+3\text{-MP}+9\text{-MP})]$$

$$\text{MPDF2} = 2 \times A[(2\text{-MP})] / A[(1\text{-MP}+2\text{-MP}+3\text{-MP}+9\text{-MP})]$$

### 3. Results and discussion

#### 3.1 Relative content distribution of aromatic components in crude oil

The relative content distribution of the aromatic components of the two crude oils is shown in Fig.1. The aromatic components of the two crude oils all contain naphthalene (N), alkyl naphthalene (ANs), hydrazine (Acp), biphenyl (Bip), hydrazine (F), dibenzothiophene (DBT), phenanthrene (P) and Alkylphenanthrene (APs) and compounds such as ruthenium (Py) and ruthenium (C). In Angolan crude oil, naphthalene (naphthalene and alkylnaphthalene, the same below) accounted for 79.94% of the total aromatic component, of which dimethylnaphthalene (C2-N) accounted for the highest, which was 34.25%. The proportion of lanthanum in all aromatics is 1%, the proportion of biphenyl series compounds is 1.93%, the bismuth series accounts for 2.67% of all aromatics, the proportion of dibenzothiophene series is 1.68%, and the proportion of phenanthrenes 11.18%, wherein the relative content of methylphenanthrene (C1-P) is 4.58%, which is the largest proportion in phenanthrene. The relative contents of lanthanum and cerium are relatively low, 0.45% and 0.43%, respectively. Among the Brazilian crude oils, the naphthalene series is also the dominant component of aromatic hydrocarbons, accounting for up to 80.85%, of which methyl naphthalene and dimethyl naphthalene account for 32.00% and 27.19%, respectively. The proportion of bismuth was 6.74%, and biphenyl, anthracene and dibenzothiophene accounted for 0.53%, 0.90% and 0.91%, respectively. The proportion of phenanthrene in all aromatics was 8.67%, and the proportion of phenanthrene monomer was 3.10%, and the content was the highest in phenanthrene. The relative content of cerium was 1.16%, and the relative content of cerium was the smallest, 0.24%.

Angolan crude oil contains more alkyl naphthalene series, while Brazilian crude oil contains more alkyl naphthalene series and rhodium. The result shows that different crude oils have their own characteristics in the distribution of the relative content of aromatic components.

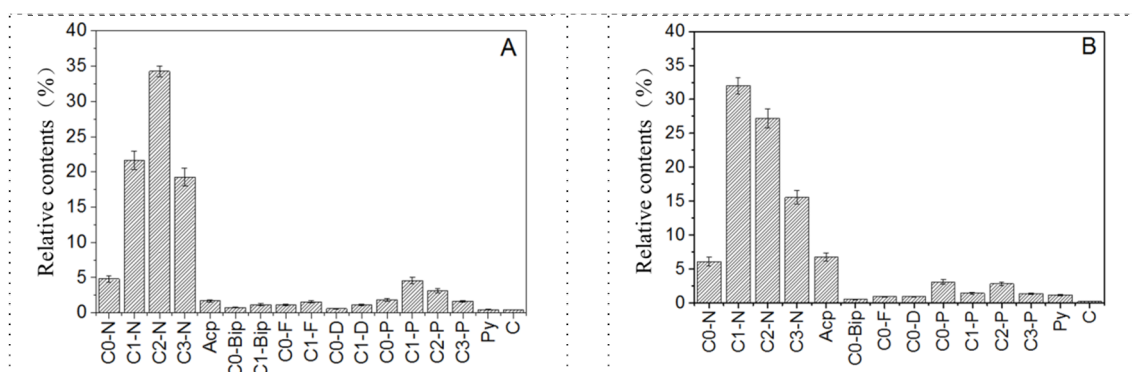


Figure 1. The relative contents of aromatic hydrocarbons in the crude oils

(A-Angolan; B-Brazil. N, Bip, AcP, F, D, P, Py, C stand for Naphthalene, Biphenyl, Acenaphthene, Fluorene, Dibenzothiophene, Phenanthrene, Pyrene and Chrysene, respectively. C0, C1, C2, C3 represent the number of substituent carbon atoms.)

### 3.2 Crude oil aromatics characteristic ratio

The characteristic parameters (ratio) of aromatic hydrocarbons in crude oil can reflect the crude oil's organic matter source, relative maturity, sedimentary environment, age, and so on. According to the paper[12], the commonly used aromatic hydrocarbons and their isomer characteristics were selected to analyze the two crude oils. The results are shown in Table 1.

Table 1. The characteristic parameters of aromatic hydrocarbons in all crude oils.

| characteristic parameters | MNR  | $\Sigma N/\Sigma PAH$ | $\Sigma N/\Sigma(N+P)$ | DNR1 | DNR2 | TNR1  | TNR2  | TNR3 |
|---------------------------|------|-----------------------|------------------------|------|------|-------|-------|------|
| Angolan crude oil         | 1.36 | 0.58                  | 0.73                   | 2.57 | 0.55 | 0.96  | 0.71  | 0.50 |
| Brazilian crude oil       | 1.80 | 0.38                  | 0.65                   | 2.34 | 1.64 | 0.92  | 1.24  | 1.80 |
| characteristic parameters | TNR2 | TNR3                  | TNR4                   | MPR  | MP11 | MPDF1 | MPDF2 |      |
| Angolan crude oil         | 0.71 | 0.50                  | 0.24                   | 1.37 | 0.99 | 0.53  | 0.76  |      |
| Brazilian crude oil       | 1.24 | 1.80                  | 1.32                   | 1.55 | 0.82 | 0.56  | 0.73  |      |

The aromatic components of the two crude oils all contain naphthalene (N), alkyl naphthalene (ANs), hydrazine (AcP), biphenyl (Bip), hydrazine (F), dibenzothiophene (DBT), phenanthrene (P) and Alkylphenanthrene (APs) and compounds such as ruthenium (Py) and ruthenium (C). Naphthalene and phenanthrene was the mainly aromatic content in crude oils, and the parent content of various aromatics is significantly smaller than the corresponding alkylated aromatics. More content of alkyl naphthalene series in Angolan crude oil, while Brazilian crude oil contains more alkyl naphthalene series and strontium

### 3.3 The carbon stable isotopic composition of aromatic hydrocarbons

With the increase of the number of aromatic hydrocarbons, the  $\delta^{13}C$  value of aromatic hydrocarbons( naphthalene, biphenyl, dibenzothiophene and phenanthrene) shows a negative trend, and in the alkylnaphthalene series. In the alkylnaphthalene series,  $^{13}C$  is significantly depleted with the increase in the number of methyl groups. The result is the same as the research of these papers[13-15]. The  $\delta^{13}C$  value of methyl dibenzothiophene is not found in Brazilian crude oil, in Fig.2. The carbon stable isotopic composition of aromatic hydrocarbons is between -28.8‰ and -22.5‰ in Brazil crude oil ( average value is -25.8 ‰). Most positive, consistent with the carbon stable isotope characteristics of the continental crude oil, and the curve fluctuates greatly. The carbon stable isotopic composition of

aromatic hydrocarbons is between -29.5‰ and -25.5‰ in Angola crude oil (average value is -27.3‰). From Fig. 3, the result showed that the difference in the carbon stable isotope composition of dimethylnaphthalene (C2-N) and phenanthrene (C0-P) is the most obvious among different oil samples.

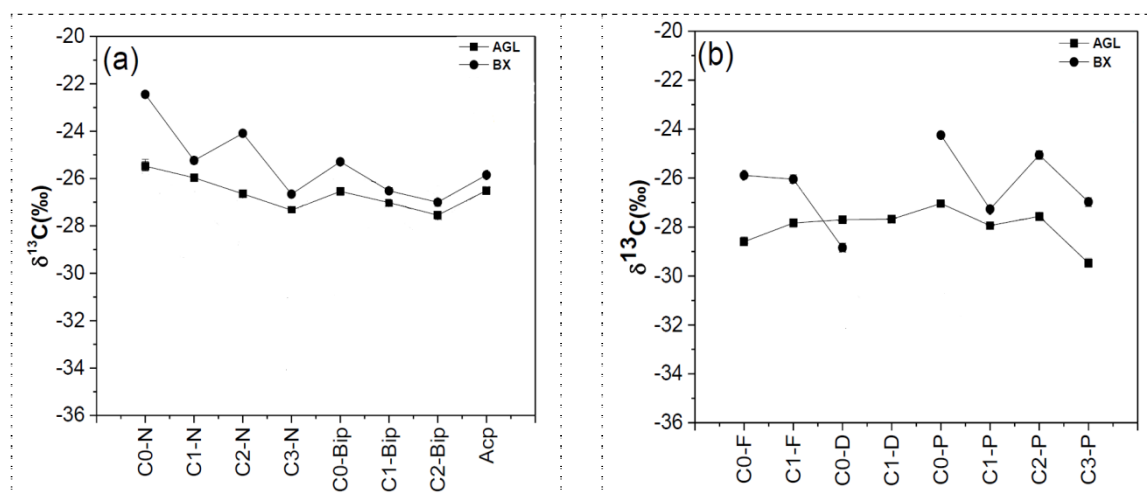


Figure 2. The carbon stable isotopic composition of aromatic hydrocarbons from crude oils (AGL-Angola; BX-Brazil. N, Bip, Acp, F, D, P, Py, C stand for Naphthalene, Biphenyl, Acenaphthene, Fluorene, Dibenzothiophene, Phenanthrene, Pyrene and Chrysene, respectively. C0, C1, C2, C3 represent the number of substituent carbon atoms.)

#### 4. Conclusions

Aromatic hydrocarbons contain plenty of geochemistry information as ubiquitous constituents of crude oils. Characteristics of aromatic hydrocarbons and its stable carbon isotope compositions are usually used to assess the source and thermal maturity. Component analysis was applied to the compositions of stable carbon isotope of aromatic hydrocarbons data sets in order to evaluate their different features. Indeed, there are diverse stable carbon isotope compositions characteristics and clear distinction among these crude oils. The use of aromatics stable carbon isotopic compositions of diverse oils can be applied on the identification of oil samples source. This study provides reference methods for the identification of oil products.

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