Effects of short-term weathering on the stable carbon isotope compositions of crude oils and fuel oils

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ABSTRACT

A short-term simulated weathering experiment was performed on two crude oils and two heavy fuel oils under natural conditions to evaluate the effects of natural weathering processes by using gas chromatography–mass spectrometry combined with gas chromatography–isotopic ratio mass spectrometry. The results of diagnostic ratios of n-alkanes show that only odd to even predominance (OEP1, OPE2) and carbon preference index (CPI) remain stabilized during the 28 d weathering process, but they cannot effectively distinguish the four types of oils. Statistical analyses based on paired sample *t*-test and principal component analysis (PCA) revealed that stable carbon isotope compositions of *n*-alkanes in the four studied oils have no significant changes over the weathering time, and that the carbon isotope discrimination ($\Delta\delta^{13}C$) of n-alkanes is < 3‰. We have provided evidence that the stable carbon isotope compositions of *n*-alkanes compared to *n*-alkanes diagnostic ratios significantly improve the efficiency and fidelity of the oil fingerprint identification.

1. Introduction

Statistical data for the past few years show that the average number of large oil-spill accidents (> 700 tons) resulting from oil exploration, shipping transportation, collisions, and unexpected events have gradually reduced, averaging at 1.8 large oil spills per year since 2010. However, the total recorded amount of oil spilled in 2015 has been > 7000 tons (ITOPF, 2015). Oil spills have physical effects and chemical toxicity, causing serious damage to marine and terrestrial ecosystems, human health, and natural resources (Beyer et al., 2016). Oil spilled into a marine environment is subjected to weathering processes, which strongly deplete the concentration of petroleum hydrocarbons and change the oil's chemical component distributions (Ezra et al., 2000; Yim et al., 2011; Samuels et al., 2013). For example, moderately biodegraded oils show an unresolved complex mixture (UCM), loss of short-chain *n*-alkanes ($n < C_{15}$), and moderate change in alkyl naphthalene distributions (Asif et al., 2009). Prince et al. (2002) found that the maximal total extent of weathering loss of hydrocarbon from an Arctic oil spill by biodegradation can reach 87%; in this process, approximately half of the four-ring chrysene series compounds were found to be heavily degraded by photooxidation over 20 years. Gas chromatography–flame ionization detection GC–FID and gas chromatography–mass spectrometry (GC–MS) are still the most widely used analytical techniques for oil spill fingerprinting. In these techniques, GC–FID and GC–MS profiles, source-specific target analytes, and diagnostic ratios of selected biomarkers are determined to trace spill sources (Fernández-Varela et al., 2009; Wang, Hu, He, Liu, & Zhao, 2013; Retnam et al., 2015). However, conventional chromatography cannot identify and quantify many compounds in UCMs below the baseline because of resolution and sensitivity limitations. These contain a large number of co-eluting compounds at low concentrations and overlap with the high-concentration chromatographic peaks, increasing the analytical uncertainty, especially in analyses of highly weathered oils, in which the concentration of petroleum hydrocarbons is lower than that in the original samples (Bayona et al., 2015; Wang, Chen, Zhang, He, & Zhao, 2013).

Compound-specific isotope analysis (CSIA, a highly specialized and complementary analytical technology (O'Malley et al., 1997), has been extensively applied in environmental forensic investigations related to petroleum pollution. It has also been applied in organic geochemistry, being used in inferring source materials for hydrocarbons, as well as in analysis of depositional environments and maturity (Maioli et al., 2012; Al-Areeq and Maky, 2015; Li and Guo, 2010). For example, Harvey et al. (2012) distinguished four diesel fuels from different sources or locations by measuring the carbon and hydrogen isotope ratios of *n*-alkanes, showing that compound-specific isotope analysis is a powerful

tool for distinguishing different fuel samples using δ^{13}C and δD values. Hall et al. (2014) determined the origin of asphaltites with moderate or severe weathering obtained from the coast of southern Australia on the basis of biomarker ratios and *n*-alkane isotopic profiles, confirming they have the same source.

Petroleum is mainly composed of aliphatic hydrocarbons and aromatic hydrocarbons, with aliphatic hydrocarbons (*n*-alkanes, branched alkanes, and cycloalkanes) usually occurring at the highest concentration in petroleum hydrocarbon, accounting for 50% of the oil (Tissot and Welte, 1984). However, the saturated components in oils are most vulnerable to weathering such as evaporation, photooxidation, and biodegradation, increasing the concentration of asphaltene and polar components in residual oil (Prince et al., 2003; Aeppli et al., 2012). In general, the loss of whole oil is mainly controlled by saturated hydrocarbons degradation, and the loss of the fuel oils is mainly dominated by the reduction of aromatic hydrocarbons (Li and Xiong, 2009). Despite its high specificity, CSIA may be limited when the oil spills show significant fractionation of stable carbon isotopes in moderate or severe biodegradation processes (Wang, Gao, Sun, Qin, Yin, & He, 2013). Studies indicate that *n*-alkanes are oxidized by aerobic microorganisms to oxidation products of alkyl alcohol, alkyl acid, and CO_2 via a series of transformation pathways. The ^{12}C–^{12}C bond usually has bond energy lower than that of ^{12}C–^{13}C and ^{13}C–^{13}C bonds prior to breaking in the aerobic biodegradation process, leading to ^{13}C-enrichment in the residual saturate fraction (Xiao et al., 2012; Sun et al., 2005; Wilkes et al., 2000). Therefore, fundamental research is essential to understanding the relationship between the weathering processes and the stable isotopic composition of *n*-alkanes as well as to determine whether carbon isotope ratios can be used as a weathering-resistance indicator. The effects on carbon isotopic fractionation have rarely been studied by simulation experiments.

The aim of this study is combine the methods gas chromatography–mass spectrometry with gas chromatography–isotopic ratio mass spectrometry to investigate the simultaneous changes in chemical composition and carbon stable isotope ratios of oil spills during the weathering process. A short-term 28-day simulated weathering experiment under natural conditions was performed on two types of oils (crude oils and fuel oils). Weathering characteristics were also analyzed and compared. Our results may provide technical support for studies on identification and characterization weathered oil spills.

2. Materials and methods

2.1. Weathering simulation experiment

A simulated weathering experiment was performed on crude oils and fuel oils (Table 1). Four different oils (each oil about 8 g) were separately added to four 2000 mL beakers with 1600 mL seawater. The seawater was pre-filtered through four layers of nylon cloth (500 mesh). The beakers were kept on an outdoor open-air platform for 28 d under natural conditions in order to approach the marine field environment.

Oil samples were taken periodically on the 0th, 1st, 3rd, 7th, 14th, 21st, and 28th d. All oil samples were stored in prewashed amber bottles at 4 °C in a refrigerator before experiments. In the weathering process, the average temperature, average wind speed, and average humidity were − 1.48 ± 3.55 °C, 7.23 ± 1.87 m/s, and 58 ± 4%, respectively.

2.2. Sample preparation

About 0.2 g of the oil sample was dissolved in 10 mL of hexane (HPLC grade, Tedia, Fairfield, USA) and then was centrifuged at 1409*g* for 10 min. The fractionation of saturates was conducted in a chromatographic column (0.47 cm i.d. × 12 cm). The column was dry-packed with 10 g of activated alumina (activated for 4 h at 200 °C, 100–200 mesh, AR) and was topped with a 1 cm thick layer of anhydrous sodium sulfate (activated for 4 h at 350 °C, AR). The column was conditioned with hexane and the eluent was discarded just prior to exposure of the sodium sulfate layer to air. About 200 μL of concentrated extract was quantitatively transferred. The aliphatic hydrocarbons were eluted with 15.0 mL of hexane. The *n*-alkanes were further isolated from branched hydrocarbon fractions by urea adduction (Barrie et al., 2016).

2.3. GC–MS

All processed samples were analyzed on mass spectrometer (ISQ, Thermo Fisher Scientific, USA) interfaced with a gas chromatograph (Thermo Fisher Scientific, CA, USA) equipped with a DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm; Agilent, Santa Clara, CA, USA). He (99.999% purity) was used as the carrier gas and introduced at a flow rate of 1.2 mL/min in constant-flow mode. The GC temperature program was started at 60 °C, which was ramped to 100 °C at 20 °C/min, held for 2 min, then from 100 to 280 °C at 6 °C/min, and held for 35 min isothermally. Injection was done with a volume of 1.0 mL in splitless mode. For MS, the injector, interface, and ion source were held at 280 °C, 250 °C, and 200 °C, respectively. The ion source was set in electron ionization mode at 70 eV. The mass spectrometer was operated in full scan mode. Scanning was done within the range of 50–550 amu at a rate of 0.2 s/scan. *n*-Alkanes were identified on the basis of the retention time of a standard mixture of *n*-alkanes ($nC_{10} − nC_{32}$, Sigma, USA).

2.4. Stable isotope analysis

CSIA was performed using a DELTA V stable isotope ratio mass spectrometer interfaced to a gas chromatograph (Thermo Fisher Scientific). The GC instrument parameters and the temperature program are consistent with the GC–MS analytic conditions described above. Isotopic analyses were carried out at the Environmental Information Institute, Dalian Maritime University (Dalian, China). The isotope ratio for carbon was expressed as follows:

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

where *R* represents ^{13}C/^{12}C. The δ^{13}C value is relative to that of Vienna Pee Dee belemnite. The analytical precision of δ^{13}C was < 0.06‰.

3. Results and discussion

3.1. Effects of weathering on the diagnostic ratios of n-alkanes

In this study, nine kinds of diagnostic ratios (Table 2) were selected to monitor weathering, to interpret chemical data from oil spills, and to differentiate or determine a match between the crude oils and fuel oils. Here, diagnostic ratios parameters were calculated from the chromatographic peak areas of *n*-alkane components; therefore, ratios only represent an approximation of the relative concentrations of each *n*-alkane fraction. Fig. 1 and Table 2 show the variations of nine

Table 1
Data of the oils samples.

Sample	Locations	Oil species	API gravity[a] (°)	Viscosity (50 °C, mm²/s)	IBP[b] (°C)	WAF[c] (mg/L)
KWT	Kuwait	Crude oil	31.8	6.965	55	8.96
AM	Oman	Crude oil	34.6	7.987	60	8.12
180#	China	Fuel oil	11.3	180	133	14.35
380#	China	Fuel oil	11.3	380	213	12.62

Note: WAF was quantified by UV spectroscopy using a UV1102 (Shanghai Techcomp Instrument Co.) according to GB 17378.4-2007.
[a] API gravity = 141.5/specific gravity (60 °F) − 131.5.
[b] IBP: initial boiling point.
[c] WAF: water accommodated fraction.