



## Fingerprint and weathering characteristics of crude oils after Dalian oil spill, China

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### ABSTRACT

In an attempt to analyze the chemical characterization of oil residues and examine the suitability of chemical fingerprinting methods in oil spill investigations, multiple parameters sensitive to both sources and degree of weathering were used to characterize oil residues from “7–16” Dalian oil spill, China. Oil residues collected 90 days to 120 days after the spill showed a weathering pattern where significant amounts of light to middle molecular weight normal alkanes were depleted with pristane and phytane as dominant peaks. Diagnostic ratios developed from *n*-alkane and selected isoprenoids (e.g. Pr/Ph, *n*-C<sub>17</sub>/Pr, *n*-C<sub>18</sub>/Ph, carbon preference index, LMW/HMW-alkanes ratio), all display obvious changes over weathering time, indicating that these ratios are not valid for oil source identification. Furthermore, the biomarker ratios of hopanes and steranes with relative standard deviations (RSDs) of 0.88–4.08% were useful for source identification even for severely weathered oil residues. In addition, RSD of  $\delta^{13}\text{C}$  values of individual *n*-alkanes in oil residue varied from 0.07% to 0.20%, which suggest that stable carbon isotope profile of *n*-alkanes can also be a useful tool for tracing the source of an oil spill.

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### 1. Introduction

The worldwide extraction, transportation, and use of petroleum inevitably results in its release to the environment. Therefore the coastal zone ecosystem is threatened due to the potential events such as tanker accidents, well explosions or pipeline leaks. Oil spills cause extensive damage to marine and terrestrial life, human health, and natural resources. On July 16, 2010, in the northeastern port city of Dalian, a coastal city in northeast China's Liaoning Province, two oil pipelines exploded, sent flames hundreds of feet into the air and burnt for over 15 h. The damaged pipes released thousands of barrels of oil, which flowed into the nearby harbor and the Yellow Sea. The total amount of oil spilled is about 1500 tons and the oil spread over 165 km<sup>2</sup>.

Once oil spilled into marine environment, it is subjected to a variety of weathering processes, including evaporation, dissolution, dispersion, flushing due to wave energy, emulsification, photochemical oxidation, microbial biodegradation, and adsorption to suspended matter and deposition on to the seafloor (Wang et al., 1997; Garrett et al., 1998; Ezra et al., 2000; D'Auria et al., 2009). Weathering processes may cause significant changes in the chemical composition of the spilled oil. The study on the chemical composition of oil spill cannot only be used to monitor the fate and behavior of the spilled oil in the marine environment, but also to refine the diagnostic values of the source recognition indices

(Wang et al., 1998; Yim et al., 2011; Wang et al., 2011). The combined effects of weathering can strongly modify the fingerprints and some common parameters used to correlate oil with its source on the basis of gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) analysis. Thus, the identification of spilled oil based on the basis of GC and GC–MS analysis becomes increasingly difficult with the lapse of time due to weathering processes. Stable carbon isotopic compositions of individual hydrocarbons in spilled oils and sediments may provide additional evidence that helps to trace oil spill sources (Mansuy et al., 1997; Mazeas and Budzinski, 2002; Wang and Fingas, 2003). The weathering processes under natural conditions are complicated and depend on a variety of factors such as the quantity and type of oil, the prevailing weather and sea conditions. Therefore, studies of weathering under natural conditions are essential for the understanding of these processes in the natural environment (Ezra et al., 2000; Prince et al., 2002; Braddock et al., 2003).

The Dalian oil spill provided an excellent opportunity to monitor the variation in the chemical composition of the spilled residual oil over time and characterize the weathering processes in the coastline of Dalian Bay under natural conditions. The oil spill has also given a better base for the source identification of oil spills using compound-specific carbon isotope analysis. The study focuses on three main aspects: (I) Weathered regulation of oil spilled in actual environment; (II) examining the suitability of chemical fingerprinting methods in oil spill investigations; (III) determination of the effects of natural weathering processes on the isotopic composition of individual *n*-alkanes and the evaluation of possibilities of GC–IRMS

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as a correlation tool in oil spill identification. To achieve these objectives, saturated hydrocarbons including alkanes and selected isoprenoids, biomarker compounds and the  $\delta^{13}\text{C}$  values of the *n*-alkane were quantitatively determined. In addition, a variety of diagnostic ratios were developed and evaluated for spill source identification and differentiation.

## 2. Experiments

### 2.1. Sample collection for oil spill in Dalian

The Dalian oil spill had been successfully controlled, 10 days after a pipeline blast leaked 1500 tons of heavy crude into the sea. Although large quantities of the pollutant have been successfully recovered, some oil residue attached to the rocks in Jinshatan was still found in the most affected area. A series of weathered oil residue in coastal zone from the Jinshatan were collected 10 days (DL-1), 30 days (DL-2), 60 days (DL-3), 90 days (DL-4) and 120 days (DL-5) after the oil spill occurred. In addition, a fresh crude oil sample (DL-0) was collected from the oil tank. Oil samples were carefully taken and placed in prewashed amber glass bottles using a solvent washed spatula and stored at about 2 °C in the freezer until analysis within a week.

### 2.2. Extraction, fractionation and GC–MS

In the laboratory, oil samples were Soxhlet-extracted with chloroform for a period of 72 h. The procedure used for separation and quantitation of individual alkanes and PAHs have been described elsewhere (Barakat et al., 2001; Duan et al., 2003). Briefly, an aliquot (50–100 mg) of the oil sample was dissolved in 20 ml *n*-alkane and spiked with 100–500 ml of hexane solutions of the deuterated alkane. The elemental sulfur was removed from the extracts using activated copper. The oil samples were deasphalted by precipitation with *n*-hexane followed by filtration. 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), respectively. The aliphatics was 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  $\text{N}_2$  gas. An aliquot of 1 ml of each extract was subjected to analysis. The saturated hydrocarbon fractions were distilled with *n*-hexane, and then analyzed by GC–MS. Straight chain hydrocarbons were separated from branched and cyclic hydrocarbons by treating the saturated fractions with 5A molecular sieve using the procedure described by Duan et al. (2003) and Grice et al. (2008). The purified *n*-alkane fractions were determined by Gas chromatography–isotope ratio mass spectrometry (GC–IRMS).

The saturated hydrocarbons were analyzed with a 6890N GC-5973N mass spectrometer. Sample extracts were injected in a splitless mode onto a HP-5 capillary column (50 m × 0.32 mm × 0.25 μm, Agilent Technologies, USA) at an initial temperature of 80 °C. The GC

oven temperature was programmed to 300 °C at 4 °C min<sup>-1</sup> and was held at the final temperature for 30 min. Helium was used as a carrier gas. Mass spectrometer conditions were electron ionization at 70 eV with an ion source temperature at 250 °C.

Individual *n*-alkanes were identified based on the retention time of the authentic standards (*n*C<sub>10–40</sub>, Sigma), and concentrations of each *n*-alkane were calculated based on the standard calibration curve of each corresponding standard compound. Biomarker ratios were calculated using peak areas from the *m/z* = 191 and 217 chromatograms.

### 2.3. GC–IRMS

GC–IRMS analyses were performed on a VG Isoprime instrument (GV Instruments Ltd., UK). The GC was equipped with a HP-5 capillary column (50 m × 0.32 mm × 0.25 μm) with helium as the carrier gas. The GC was held for 5 min at 70 °C, programmed to sequentially step from 70 °C to 290 °C at 3 °C min<sup>-1</sup>, and then held for 40 min at 290 °C. The combustion furnace was run at 880 °C. Carbon isotope ratios for individual alkanes were calculated using  $\text{CO}_2$  as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis, and the data was reported in per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard. A standard mixture of *n*-alkanes (*n*-C<sub>12</sub>–*n*-C<sub>32</sub>) with known isotopic composition was used daily to test the performance of the instrument. Replicate analyses of this mixture show that the standard deviation for each compound is less than 0.3‰.

## 3. Results and discussion

### 3.1. Alkane fingerprints

#### 3.1.1. Alkane distribution

Evaporation and emulsification occur in the first few hours after a spill and removes the more volatile hydrocarbons, and water-washing also occurs rapidly and removes the more water-soluble hydrocarbons, typically hydrocarbons below C<sub>15</sub> (Mansuy et al., 1997). At the same time, biodegradation will also start to affect the nature of the spilled oil by initially removing the *n*-alkanes before attacking the more complex branched and cyclic hydrocarbons and naphthenic compounds. A decrease in the overall concentrations of *n*-alkanes and isoprenoids indicated some loss of 50% in the spilled oil (Fig. 1). Within 120 days, these compounds were degraded largely and as a consequence, are of limited value in identifying the remaining oil residues.

The *n*-alkane envelope in the initial oil from the oil container is characterized by *n*-alkanes ranging from C<sub>9</sub> to C<sub>36</sub> and maximizing at *n*-C<sub>15</sub> and *n*-C<sub>31</sub> (Fig. 2a). Subsequently, there is an absence of aliphatic compounds <*n*-C<sub>11</sub> after 10 days and aliphatic compounds <*n*-C<sub>13</sub> 120 days after the spill (Fig. 2-b). Based on this observation, the low-molecular-weight alkanes (LMW alkanes) (*n*-C<sub>12</sub>–*n*-C<sub>21</sub>)

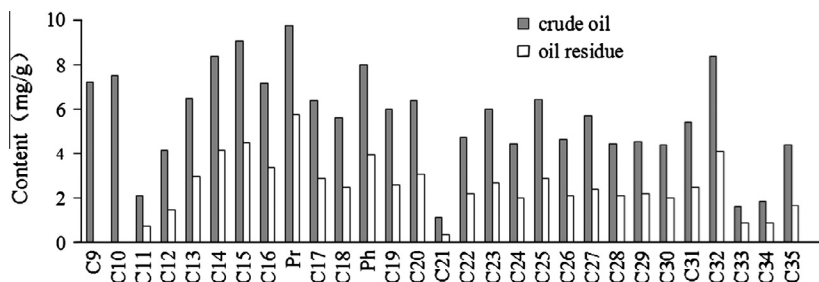


Fig. 1. Content of various alkane, pristane and phytane.

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