



## Chemical characterization of naturally weathered oil residues in the sediment from Yellow River Delta, China

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### ABSTRACT

With its close proximity to Shengli Oilfield, China's second largest oilfield, the Yellow River Delta is at high risk for crude oil contamination. The massive oil discharge in oilfield may offer a chance for a natural experiment to investigate compositional changes of oil residues and study the stability of source- and weathering-dependent molecular parameters in oil residues after spills. The results demonstrate that the conventional diagnostic ratios, such as  $C_{29}20S/(20S + 20R)$ ,  $C_{29}/C_{30}H$ ,  $C_{30}\beta\alpha/\alpha\beta$ ,  $C_{31}22S/(22S + 22R)$ ,  $C_2$ -DBTs/ $C_2$ -PHENS,  $C_3$ -DBTs/ $C_3$ -PHENS, DBT/MCHRY, CHRY/PHENS, are also valid for oil source identification even after extensive weathering of spilled oils in terrestrial environment, although some exceptions were encountered for extensively weathered sample. Moreover, the ratios of selected specific biomarkers (the oleanane index, the gammacerane index) have been developed and assessed as source indicators. Finally, we find that some maturity parameters based on alkyl naphthalenes and methyl phenanthrenes in petroleum geochemistry, such as the methyl naphthalene ratios (TMNr, TeMNr, PMNr), the methylphenanthrene ratios (MPI-1, MPDF), can be applied for the source identification and correlation at their lightly to moderately weathered stage.

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### 1. Introduction

As industrialization processes speed up and demands for energy grow worldwide, oil spills have become a global problem. Oil spills may occur during the process of oil exploitation, storage, transportation, production or consumption. Crude oil is a complex mixture of thousands of different organic compounds formed from a variety of organic materials that are chemically converted under differing geochemical conditions over long period of time. Once crude oil is released to the environment, it undergoes various physical, chemical, and biological alterations, collectively called weathering. The weathering processes can be divided into (1) physical weathering (e.g., evaporation, dissolution, adsorption to particles, emulsification), (2) biological weathering (mainly microbial degradation) and (3) chemical weathering (e.g., photodegradation) (Garrett et al., 1998; Behara et al., 2006; D'Auria et al., 2009). The weathering processes under natural conditions are complicated and depend on a variety of factors. A detailed understanding of natural weathering processes that oil is subjected to is required in order to reduce environmental damage and develop effective protection

strategies. These processes change the compositions of the oil and some of them are the key to identifying the spilled oil. Hence it is very important to understand the relationship between the weathering processes and the composition changes. In recent years, numerous studies concerned with the origin, type, fate and behavior of spilled oils in aquatic environments have been reported (Hostettler et al., 1992; Bence et al., 1996; Boehm et al., 1997; Barakat et al., 2001; Prince et al., 2002; Wang and Fingas, 2003; Wang et al., 2004; Malmquist et al., 2007). However, less is known about the long-term fate of oil spilled in the terrestrial environments (for example, in contaminated soil of this study), which may not only contribute to tracking spilled oils, but also offer some guidance for oil spill bioremediation in terrestrial environment.

Yellow River Delta (YRD), a newly born wetland in China, is one of the most active regions of land-ocean interaction among the large river deltas in the world. Yellow River Delta National Nature Reserve (YRDNNR, 118°33'–119°20'E longitude, 37°35'–38°12'N latitude), was established in 1992 for protection of the newborn wetland ecosystem. However, Shengli Oilfield, the second largest oilfield of China, is located here. The pollution due to oil well blow-outs, leaks and spills from underground tank, pipelines and illegal disposals may pose a threat to the ecosystem of YRD. These weathered oil residues may provide an excellent opportunity to test the stability of several molecular parameters in identifying the source

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of degraded oils, and to investigate source and weathering-dependent changes in a number of molecular parameters during natural weathering. The main objectives of the study were: (1) to analyse the changes in the chemical composition of the oil residues from sediments and assess the stability of molecular markers after weathering in natural environment; and (2) to investigate the fate of such spilled oil in the natural environment of YRDNR; (3) to evaluate on some new ratios of selected PAHs to use for tracking spilled oils and identifying spill sources during natural weathering process.

## 2. Experimental

### 2.1. Samples

The sampling sites in Xintan Oilfield and Hongliu Oilfield of YRDNR, are illustrated in Fig. 1. In the petroleum polluted soil, the pollutant is mainly within 0–40 cm. The accumulated residue soil/oil mixture samples from two locations were collected from different depths, to represent different degrees of weathering. Both surface and subsurface samples at different depths to 40 cm (total accumulation depth over the spill history) were collected. Sediments were obtained utilizing a stainless-steel grab and placed in precleaned brown glass jars. All samples were frozen immediately and transported to the laboratory and kept in the refrigerators at  $-18^{\circ}\text{C}$  before analysis. On the basis of previous results (Prince et al., 2003), we may regard the soil/oil mixtures (0–10 cm from the surface) as the highly weathered oil sample in this study. In addition, a fresh crude oil sample (S1-0, S2-0, S3-0) was systematically collected and stored frozen until analysis.

### 2.2. Extraction and fractionation

After being centrifuged and freeze dried, all soil samples were rubbed to granular powder to pass through a 20-mesh sieve and homogenized. In the laboratory, about 100 g dry sediment samples were Soxhlet-extracted with chloroform for a period of 72 h. Elemental sulfur was removed from the extracts using activated copper. The crude oils and extractable organic matter of soils were deasphalted by precipitation with *n*-hexane followed by filtration. The extract was fractionated into aliphatic hydrocarbons 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 aliphatic and aromatic fractions were 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.

### 2.3. Instrumental analysis

The saturated hydrocarbons and aromatic hydrocarbons were analyzed on a Hewlett-Packard 6890 gas chromatograph interfaced with a Hewlett-Packard 5973 mass-selective detector made by Agilent (USA). Helium was used as the carrier gas. Sample extracts were injected in a splitless mode onto a  $30\text{m}\times 0.2\text{m}$  ( $0.25\ \mu\text{m}$  film thickness) H-5 fused capillary column at an initial temperature of  $80^{\circ}\text{C}$ . The temperature was programmed at  $4^{\circ}\text{C}/\text{min}$  to  $290^{\circ}\text{C}$  and held at the final temperature for 30 min. The injector temperature was  $250^{\circ}\text{C}$ . The mass spectrometer was operated at an electron energy of 70 eV with an ion source temperature of  $250^{\circ}\text{C}$ .

Individual *n*-alkanes were identified based on the retention time of the authentic standards ( $n\text{C}_{10-40}$ , Sigma), and concentrations of each *n*-alkane were calculated based on the standard calibration curve of each corresponding standard compound. On the other hand, Individual PAHs were quantified based on the retention time and *m/z* ratio of an authentic PAH mixed standard (Sigma), and concentrations of each PAH were calibrated based on the standard calibration curve. The minimum method detection limits for an individual aliphatic or aromatic compound is 10 ppb. Biomarker ratios were calculated using peak areas from the *m/z* = 85, 191 and 217 chromatograms. The unresolved complex mixture (UCM) concentration was calculated from the average of the response factors for *n*-alkanes over the retention time range for the UCM.

## 3. Results

### 3.1. Alkanes distribution

From Table 1, it can be seen that the higher concentration of total petroleum hydrocarbons (TPH) was found at S1-1, which suggest that the oil contamination mainly remained in the topsoil (0–10cm). Although alkanes are not particularly useful for

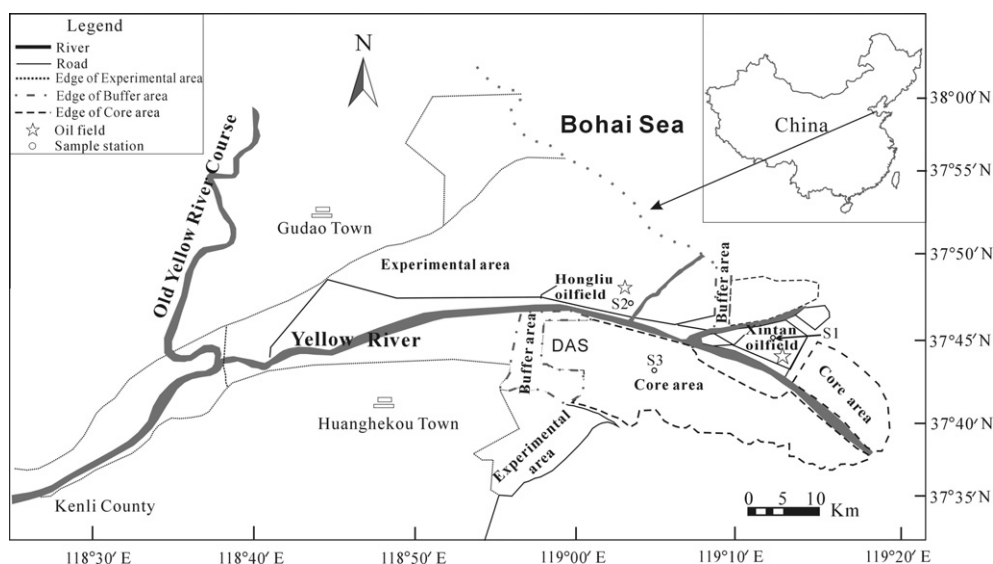


Fig. 1. Study areas and sampling location in the YRDNR.

**Table 1**  
Sample description and aliphatic hydrocarbon ratios in the oil residue samples.

Sample	Depth/cm	<sup>a</sup> TPH	<sup>b</sup> UCM/TPR	Pr/Ph	Pr/ <i>n</i> -C <sub>17</sub>	Ph/ <i>n</i> -C <sub>18</sub>	<sup>c</sup> WR
S1-1	0-10	651.16	11.54	0.48	2.34	3.46	1.15
S1-2	10-20	77.72	5.37	0.56	1.85	2.43	1.35
S1-3	20-30	52.09	4.40	0.53	2.25	3.10	0.99
S1-4	30-40	25.54	4.10	0.55	1.76	2.79	1.07
S1-0	n.d.	n.d.	4.35	0.62	0.81	1.43	0.45
S2-1	5-10	354.6	9.87	0.69	0.99	0.92	0.82
S2-0	n.d.	n.d.	4.52	0.87	0.10	0.38	0.45
S3-1	1-10	186.45	7.96	0.52	1.56	2.68	1.88
S3-0	n.d.	n.d.	2.35	0.66	0.26	0.55	0.66

n.d.: not available.

<sup>a</sup> TPH: total petroleum hydrocarbon (μg/g);

<sup>b</sup> Unresolved to resolved hydrocarbon compounds;

<sup>c</sup> *n*-C<sub>23</sub> to *n*-C<sub>34</sub> alkanes relative to the sum of *n*-C<sub>11</sub> to *n*-C<sub>22</sub> alkanes.

determining the sources of the spill, they can give some information on the degree of weathering or freshness of the sample (Udoetok and Osuji, 2008). The distributions of alkanes in the studied samples are shown in Fig. 2. The results show that *n*-alkanes are progressively depleted in crude oils with increasing extent of degradation. The weathering ratio (WR) is essentially changed for the spilled oil sample compared to that of the reference crude oil (Table 1). Other evident from the GC-MS in Fig. 2 is the large unresolved complex mixture (UCM) or “hump” in the samples, being more accentuated with increasing biodegradation. These UCMs are interpreted as either the result of low maturity or biodegradation. In this particular case, the UCMs are only interpreted to be the result of biodegradation because all three samples appear to be of the same source and maturity.

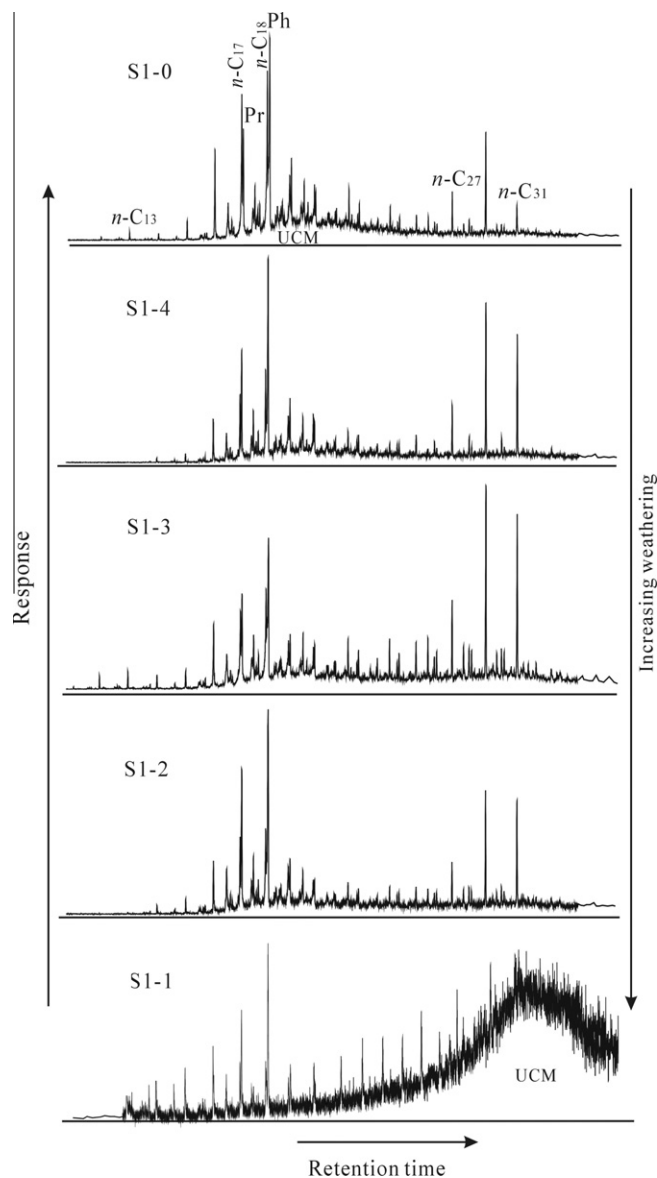
Pr/Ph ratio, widely invoked as an indicator of the redox condition in the depositional environment, also decrease from 0.62 and 0.87 to 0.69, respectively. In agreement with the interpretation of Bao *et al.* (2002), we believe that such change in Pr/Ph is likely due to the more readily biodegradation of pristane than phytane. Furthermore, pristane/*n*-C<sub>17</sub> (Pr/*n*-C<sub>17</sub>) and phytane/*n*-C<sub>18</sub> (Ph/*n*-C<sub>18</sub>) indices have been widely used as indicators of oil biodegradation (Kennicutt, 1988; Barakat *et al.*, 2001; Wang and Fingas, 2003). As the easily degraded normal hydrocarbons (*n*-C<sub>17</sub> and *n*-C<sub>18</sub>) are lost, the more degradation resistant isoprenoids (pristane and phytane) are conserved, resulting in a significant increase of the ratios of Pr/*n*-C<sub>17</sub> and Ph/*n*-C<sub>18</sub> in the weathered oil residues samples. Samples from S1-2, S1-3, and S1-4 displayed little change in the ratios of Pr/*n*-C<sub>17</sub> and Ph/*n*-C<sub>18</sub> with values in the range of 1.76–2.25 and 2.43–3.10, respectively, which indicated similar degree of weathering for these samples. In contrast, samples from S1-1 and S2-1 were degraded to a much greater extent.

### 3.2. Biomarker distributions

Much of the knowledge of biomarkers and their diagnostic ratios comes from the oil geochemistry (Peters and Moldovan, 1993). In this study, steranes and terpanes were the primary biomarkers to be evaluated because these compounds are common in crude oils and more resistant to degradation than *n*-alkanes and isoprenoid hydrocarbons. A number of ratios of selected terpanes and steranes have been defined and increasingly used for tracking spilled oils and identifying spill sources.

#### 3.2.1. Steranes distribution

As known, the sterane distributions can be used as effective source facies discriminators to group oils in a region on the basis of genetic relationships. The steranes detected in all samples are comprised mainly of the 5 $\alpha$ ,14 $\beta$ ,17 $\beta$  and minor 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$  configurations, both occurring as 20S and 20R epimers (Fig. 3). The



**Fig. 2.** GC-MS chromatograms (m/z 85) of the degraded oil compared to the initial oil.

sterane distribution dominated by high abundance of C<sub>29</sub> steranes is typical of crude oils generated from source rocks rich in terrigenous organic matter. The epimer ratios of 20S/(20S + 20R) and  $\beta\beta/(\alpha\alpha + \beta\beta)$  for the C<sub>29</sub>-steranes are commonly used as maturity parameters (Mackenzie *et al.*, 1980) and as source tracers of weathered oil residues (Wang *et al.*, 1994; Kvenvolden *et al.*, 1995).

Preferential removal of the C<sub>27</sub> homologue results in a decrease in the C<sub>27</sub>/C<sub>29</sub> steranes ratio (Table 2). This confirms previous observations of the removal in the order C<sub>27</sub>>C<sub>28</sub>>C<sub>29</sub> steranes and selective removal of the 5 $\alpha$  20R C<sub>29</sub>-sterane compared to the 20S epimer (Pieri *et al.*, 1996; Peters *et al.*, 2005). The average values of these ratios for all residue samples (S1-1, S1-2, S1-3, S1-4) are: 0.48±0.03 and 0.33±0.02 for C<sub>29</sub> 20S/(20S + 20R) and lower C<sub>29</sub>  $\beta\beta/(\alpha\alpha + \beta\beta)$ , respectively, as compared to the values of 0.46, and 0.33 for the source oil (S1-0). The higher C<sub>29</sub> 20S/(20S + 20R) and lower C<sub>29</sub>  $\beta\beta/(\alpha\alpha + \beta\beta)$  ratios in S1-1 (surface) may be caused by the selective loss of sterane isomers during the severe weathering processes.

Another difference of the highly weathered oil sample S1-1 and S2-1 from other samples is that the concentrations of the lighter

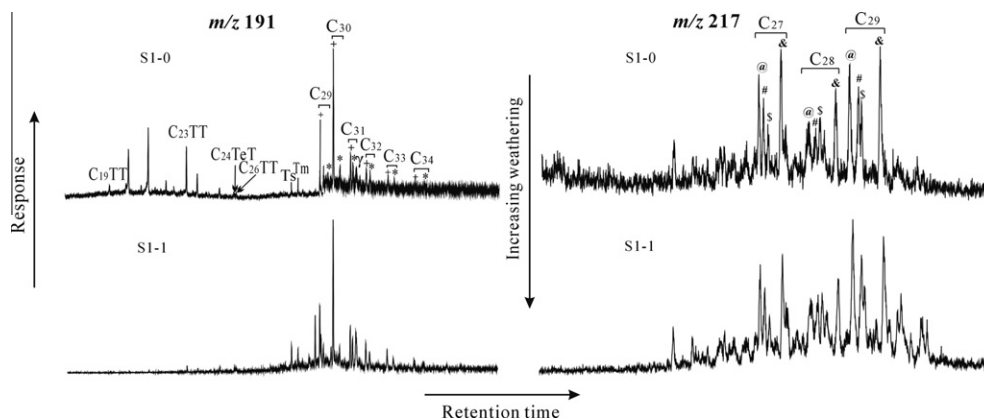


Fig. 3. Representative  $m/z$  191 and  $m/z$  217 mass fragmentograms showing distribution of terpanes and steranes from sediment.

$C_{21}$  and  $C_{22}$  steranes were greatly decreased in their abundance relative to the  $C_{27}$ – $C_{29}$  steranes. The severely weathered sample S1-1 has a lower value for the pregnane index (PI) (0.03 as compared to 0.61 for the fresh oil samples), indicating a greater extent of weathering of S1-1 compared to the source oil. Moreover, the depletion of short chain steranes are also observed in the samples from S1-2 (10–20 cm), S1-3 (20–30 cm), S1-4 (30–40 cm), suggesting that these samples might also have undergone extensive weathering and degradation. The extensive volatilization, coupled with biodegradation and other physical and chemical reactions, could have caused the changes in the compositions of most hydrocarbons in S1-1, even for the relatively stable biomarkers.

### 3.2.2. Terpanes distribution

Terpanes are another group of biomarker compounds that are commonly used in oil correlation, source identification, and maturity determination (Zhang et al., 2005). The terpane distribution shown in Fig. 3 between the residue sample and the fresh oil are nearly identical. The terpene distribution is dominated by  $C_{27}$  to  $C_{35}$  pentacyclic hopanes, maximizing at the  $C_{30}$  homologue. The  $7\alpha(H),21\beta(H)$  isomers are the major components of hopanes with minor amounts of the  $17\beta(H),21\alpha(H)$  isomers. Furthermore,  $C_{24}$  tetracyclic terpanes and  $C_{19}$ – $C_{29}$  tricyclic terpanes are also identified in the residue samples.

A number of ratios of selected terpanes, in general, vary in different oils and are dependent upon sources, depositional environment and maturity. Generally, the presence of tricyclic terpanes was indicative of mixed contribution of marine/terrestrial source

material in their source rocks; and the  $C_{23}$  member is often the dominant homologue in crude oils of a marine source while the  $C_{19}$  and  $C_{20}$  members are more abundant in terrestrial oils (Peters and Moldowan, 1993). It is known that the proportion of  $C_{24}$  tetracyclic terpane relative to triterpanes (the triplet ratio in Table 3) may be facies dependent, with relatively high concentrations in source rocks and oils with terrigenous input, or in sediments of low clastic content (Peters and Moldowan, 1993). The ratios of  $\beta\alpha$ -moretane/ $\alpha\beta$ -hopane and  $22S/(22S + 22R)$  was typically used as maturity parameters in petroleum geochemistry (Kvenvolden et al., 1995). Moreover, the ratio of  $C_{29}/C_{30}$  was found to be a very good indicator for oil correlation and source tracking (Wang et al., 1994).

According to the analysis mentioned above, the commonly used molecular ratio parameters for terpanes in source identification and maturity determination are shown in Table 3. Such parameters were almost the same in the weathered residues and in the source oil, regardless of weathering extent of the samples. The average values of these ratios for all residue samples (S1-1, S1-2, S1-3, S1-4) are:  $0.91\pm 0.23$ ,  $0.53\pm 0.06$ ,  $0.57\pm 0.02$ ,  $0.42\pm 0.04$ , and  $0.15\pm 0.01$  for  $(C_{19} + C_{20})/C_{23}TT$ , triplet ratio,  $22S/(22S + 22R)$ ,  $C_{29}/C_{30}$ , and  $\beta\alpha/\alpha\beta$ , respectively, as compared to the values of 1.09, 0.50, 0.58, 0.46, and 0.16 for the source oil (S1-0). The similarity of these parameters between the weathered residue samples and the fresh oil also suggests that weathering processes does not alter the biomarker parameters and these terpane molecular parameters were good tracking indices of weathered oil. Although both Ts and Tm were degraded in oil sample, a slight increase in the Ts/Tm ratio was observed (Table 3), implying that Tm is more readily biodegraded than Ts.

Finally, the tricyclic terpane index (TriTI in Table 3) suggests that tricyclic terpanes are more readily degraded than pentacyclic terpanes at higher weathering stages. The differential weathering of tricyclic terpanes versus pentacyclic terpanes was more pronounced in the highly weathered samples obtained from S1-1 and S2-1 as indicated by the lower values of TriTI. This is consistent with the generally accepted sequence of increasing resistance to aerobic bacterial alteration of petroleum compound: diasterane >  $C_{27}$ steranes > tricyclic terpanes > pentacyclic terpanes > norhopanes >  $C_{29}$   $\alpha\beta\beta$ -steranes (Wang and Fingas, 2003).

### 3.2.3. Distribution of "specific" biomarker

Except terpanes and steranes, a few "specific" biomarker compounds are found to exist only in certain oils and, therefore, can be used as unique markers to provide an interpretational advantage in fingerprinting sources of spilled oils (Wang and Fingas, 2003). Gammacerane, a biomarker common to most Chinese crude

Table 2  
Steranes biomarker parameters.

Sample	Steranes abundance (%)			<sup>a</sup> $C_{27}/C_{29}$	<sup>b</sup> $20S/(20S + 20R)$	<sup>c</sup> $\beta\beta/(\alpha\alpha + \beta\beta)$	<sup>d</sup> PI
	$C_{27}$	$C_{28}$	$C_{29}$				
S1-1	31.61	26.88	41.51	0.76	0.53	0.32	0.03
S1-2	30.07	27.00	42.93	0.70	0.48	0.34	0.05
S1-3	33.08	24.74	42.18	0.78	0.46	0.34	0.09
S1-4	34.92	25.33	39.75	0.88	0.48	0.33	0.09
S1-0	35.33	23.79	40.88	0.86	0.46	0.31	0.61
S2-1	33.31	21.57	45.12	0.74	0.54	0.31	0.11
S2-0	35.27	21.19	43.54	0.81	0.58	0.30	0.05
S3-1	29.85	21.32	48.33	0.61	0.52	0.51	0.11
S3-0	32.50	18.92	48.58	0.67	0.56	0.48	0.06

<sup>a</sup>  $C_{27}/C_{29}$   $5\alpha(H),14\alpha(H),17\alpha(H)$ -20R-steranes;

<sup>b</sup>  $20S/(20S + 20R)$  for  $C_{29}$ - $5\alpha(H),14\alpha(H),17\alpha(H)$ -steranes;

<sup>c</sup>  $5\alpha(H),14\beta(H),17\beta(H)/[5\alpha(H),14\beta(H),17\beta(H) + 5\alpha(H),14\alpha(H),17\alpha(H)]$  for  $C_{29}$ -steranes;

<sup>d</sup> Pregnane index, sum of concentrations of  $C_{21}$  and  $C_{22}$  steranes (pregnanes) over total concentration of steranes.

**Table 3**  
Terpane biomarker parameters.

Sample	<sup>a</sup> (C <sub>19</sub> + C <sub>20</sub> )/C <sub>23</sub> TT	<sup>b</sup> Triplet ratio	<sup>c</sup> TriTI	<sup>d</sup> C <sub>29</sub> /C <sub>30</sub> H	<sup>e</sup> Ts/Tm	<sup>f</sup> 22S/22S + 22R	<sup>g</sup> βα/αβ	<sup>h</sup> γ/C <sub>30</sub> H	<sup>i</sup> O/C <sub>30</sub> H
S1-1	0.38	0.63	0.05	0.42	1.20	0.59	0.13	0.24	0.12
S1-2	0.67	0.56	0.13	0.36	0.90	0.58	0.13	0.17	0.07
S1-3	1.24	0.54	0.18	0.44	0.77	0.55	0.16	0.21	0.07
S1-4	1.17	0.53	0.19	0.43	0.85	0.57	0.16	0.17	0.06
S1-0	1.09	0.50	0.45	0.46	0.69	0.58	0.16	0.26	0.07
S2-1	0.56	0.32	0.15	0.37	1.64	0.57	0.14	0.19	0.05
S2-0	0.97	0.34	0.11	0.42	0.82	0.55	0.21	0.21	0.04
S3-1	0.75	0.46	0.33	0.38	1.22	0.57	0.21	0.31	0.06
S3-0	0.87	0.42	0.32	0.44	0.95	0.54	0.23	0.32	0.05

<sup>a</sup> (C<sub>19</sub> + C<sub>20</sub>)/C<sub>23</sub> tricyclic terpanes;

<sup>b</sup> C<sub>24</sub>-tertracyclic terpane/C<sub>26</sub>-Tricyclic terpanes;

<sup>c</sup> Tricyclic triterpane index, sum of concentrations of C<sub>19</sub> to C<sub>30</sub> tricyclic terpanes/total concentration of pentacyclic terpanes;

<sup>d</sup> 17α, 21β (H)-30-norhopane/17α, 21β (H)-hopane;

<sup>e</sup> 18α(H)-22,29,30-trisnorneohopane/17α(H)-22,29,30-trisnorhopane;

<sup>f</sup> 22S/22S + 22R for C<sub>31</sub>-17α, 21β (H)-homohopane;

<sup>g</sup> 17β, 21α(H)-moretane/17α, 21β (H)-hopane;

<sup>h</sup> Gammacerane/17α, 21β (H)-hopane;

<sup>i</sup> 18α(H)-oleanane/17α, 21β (H)-hopane.

oils derived geologically from lacustrine sources (Fu and Sheng 1989), and 18α-Oleanane, an indicator of age and terrestrial organic matter input (Petters and Moldowan 1993), were also present in the analyzed sediments. Results in Table 3 show that the ratios of gammacerane index (GI) and oleanane index (OI) are almost constant for most samples and generally similar to the fresh source oil. This result provides additional evidence for the stability and utility of GI and OI as diagnostic source ratios over a wide range of weathering and biodegradation. The slight shift of GI and OI ratios to higher values for the extremely degraded samples might be the result of the slightly greater stability of Gammacerane and 18α-Oleanane compared to terpanes.

As mentioned above, terpanes and steranes retained their molecular compositions during the weathering process of moderate degradation and could be used in tracking the origin and sources of hydrocarbon pollution in the terrestrial environment. However, it should be noted that in severely weathered or long-term weathered oil, biodegradation of some sterane and terpane biomarkers was also observed (Bost et al., 2001; Bao and Zhu, 2008).

### 3.3. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) can provide more detailed compositional data that can be used to identify both the source and extent of degradation of released oils (Page et al., 1995; Douglas et al., 1996; Hegazi et al., 2004), which largely because PAHs are more complex and more resistant to biodegradation than alkanes. The GC-MS analytical results indicated that the aromatic hydrocarbons of the weathered petroleum residues consist primarily of five families of PAH compounds: naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes. The quantitation results of the total concentrations of the alkylated PAH homologues in each compound type and selected diagnostic ratios are summarized in Tables 4 and 5. Concentrations of total PAHs in all samples decrease from 7.19 to 4.14 and 12.35 to 9.32 μg/g of extracellular organic matter (EOM), respectively, indicating that almost all PAH compounds are degraded to a certain extent.

#### 3.3.1. Evaluation of the conventional diagnostic ratios

In previous works (e.g., Douglas et al., 1996; Zakaria et al., 2001; Asif et al., 2009), some PAH ratios have been used as weathering indicators of varying sensitivity for different stages and indicators for oil spill identification. The relative abundance of the PAH alkyl homologue ratios, C<sub>2</sub>-DBTs/C<sub>2</sub>-PHENs and C<sub>3</sub>-DBTs/C<sub>3</sub>-PHENs, vary

among oils having different sulfur contents. Furthermore, they were previously shown to remain relatively constant as oil weathers and prove useful in distinguishing and correlating hydrocarbon inputs to heavily weathered oil residues (Page et al., 1995; Barakat et al., 2001; Wang and Fingas, 2003).

As noted by other investigators, the degree of PAH degradation in the environment decreases with increasing ring size and decreases with increasing alkylation within a homologous series. Results in Table 4 show that the ratios of C<sub>2</sub>-DBTs/C<sub>2</sub>-PHENs and C<sub>3</sub>-DBTs/C<sub>3</sub>-PHENs are almost constant for most samples and generally similar to the fresh source oil, which provide additional evidence for the stability and utility of C<sub>2</sub>-DBTs/C<sub>2</sub>-PHENs and C<sub>3</sub>-DBTs/C<sub>3</sub>-PHENs as diagnostic source ratios over a wide range of weathering and biodegradation. The slight shift of C<sub>2</sub>-DBTs/C<sub>2</sub>-PHENs and C<sub>3</sub>-DBTs/C<sub>3</sub>-PHENs ratios to higher values for the extremely degraded samples (S1-1 and S2-1) might be the result of the slightly greater stability of DBTs compared to PHENs. Moreover, CHRYs exhibits the most marked increase in their relative concentrations due to their very low solubility in water and high resistance to degradation. As a result, relative concentrations of CHRYs to other major PAH components increase with the increased weathering of oil residues (DBTs/MCHRYs, CHRY/PHENs, Table 4). Based on this, it can be concluded that photooxidation seems to have played an important role in removing larger polycyclic aromatic hydrocarbons from exposed surface samples, and as exemplified by the pattern of loss of the DBTs and PHENs.

Alkyl dibenzothiophene is the common sulfur-containing aromatic compounds in crude oils. Methyl dibenzothiophene ratios (4-MDBT/1-MDBT, MDR) are often used to assess the maturity of organic matter in the marine source rocks without vitrinite and crude oils (Chakhmakhchev et al., 1997). MDR have been also successfully used to discriminate different oil samples and to identify the sources of spilled oils (Wang et al., 1995). However, the two ratios gradually decrease with increase in the biodegradation degree for biodegraded oils in this study. The reason is that during biodegradation process, 4-methyl, 2 + 3-methyl dibenzothiophene isomers with higher thermally stability can be easily destroyed by bacteria than 1-methyl dibenzothiophene with lower thermally stability.

#### 3.3.2. New diagnostic ratios based on the maturity parameters from PAHs

Maturity parameters and indicators of the depositional environment from PAHs in petroleum geochemistry, are potentially useful in distinguishing petroleum in the natural environment after spill

**Table 4**  
Source and weathering diagnostic ratios of PAHs.

Sample	PAHs( $\mu\text{g/g}$ EOM)	C <sub>2</sub> -DBTs/C <sub>2</sub> -P	C <sub>3</sub> -DBTs/C <sub>3</sub> -P	DBTs/MCHRYs	CHRY/P	MDR
S1-1	4.40	0.11	0.09	0.09	1.25	2.01
S1-2	5.64	0.07	0.05	0.11	0.67	2.50
S1-3	4.91	0.08	0.07	0.10	0.74	1.04
S1-4	5.29	0.07	0.06	0.08	0.82	n.d.
S1-0	7.19	0.08	0.08	0.14	0.65	3.18
S2-1	9.32	0.13	0.08	0.18	0.16	2.92
S2-0	12.35	0.11	0.07	0.22	0.10	4.52
S3-1	6.58	0.12	0.10	0.36	0.24	2.68
S3-0	8.25	0.10	0.09	0.43	0.18	4.23

n.d.: not available; P: phenanthrenes; DBTs: dibenzothiophenes; CHRY: chrysenes.

**Table 5**  
Variability of aromatic indicators among biodegraded oils and their source oils.

Sample	<sup>a</sup> TMNr	<sup>b</sup> TeMNr	<sup>c</sup> PMNr	<sup>d</sup> MPI-1	<sup>e</sup> Rc	<sup>f</sup> MPDF
S1-1	0.49	0.54	0.45	0.60	0.73	0.45
S1-2	0.47	0.46	0.44	1.04	1.02	0.59
S1-3	0.50	0.47	0.47	0.98	0.99	0.48
S1-4	0.45	0.45	0.42	0.86	0.92	0.41
S1-0	0.45	0.48	0.43	0.92	0.95	0.56
S2-1	0.86	0.82	0.67	0.49	0.69	0.38
S2-0	0.77	0.71	0.68	0.55	0.73	0.48
S3-1	1.02	0.71	0.68	0.57	0.65	0.47
S3-0	0.97	0.65	0.70	0.62	0.69	0.52

<sup>a</sup> TMNr: 1,3, 7-TeMN/(1,3, 7- +1,2,5-TeMN);

<sup>b</sup> TeMNr: 1,3,6,7-TeMN/(1,3,6,7- +1,2,5,6- +1,2,3,5-TeMN);

<sup>c</sup> PMNr: 1,2,4,5,7-TeMN/(1,2,4,5,7- +1,2,3,5,6-TeMN);

<sup>d</sup> MPI-1:  $1.5 \times (3\text{-MP} + 2\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})$ ;

<sup>e</sup> Rc:  $0.6 \times \text{MPI-1} + 0.4$ ;

<sup>f</sup> MPDF:  $(3\text{-MP} + 2\text{-MP}) / \Sigma\text{MP}$ .

accidents, but little work has been reported on this topic. We propose the following ratios to assess the effect of the weathering process on the distribution of the oil samples investigated in this study. At the same time, the variation of those aromatic geochemical parameters usually used and the reasons resulting in those changes will be discussed.

A number of maturity parameters based on alkyl naphthalenes have been developed over the years (Radke, 1988; van Aarssen et al., 1999). The distribution of methylated naphthalenes is highly variable as they are controlled by the effects of source, thermal stress and biodegradation. The ratios trimethylnaphthalene (TMNr), tetramethylnaphthalene (TeMNr) and pentamethylnaphthalene (PMNr) (Table 5) are based on the increase of the stable isomers relative to the less stable isomers and are thought to be determined by 1,2-methyl shift and methyl transfer in the naphthalene carbon skeleton (van Aarssen et al., 1999; Sivan et al., 2008). Biodegradation affects the different classes of methylnaphthalenes. For trimethyl-naphthalenes (TMN) isomers, 1,3,7-TMN was much less susceptible to microbial attack than 1,2,5-TMN. This implies that TMNr will increase as a consequence of biodegradation. With increasing levels of biodegradation the distribution of tetramethyl-naphthalenes (TeMNs) and even pentamethyl-naphthalenes (PMNs) will become affected (van Aarssen et al., 1999). Differences in physical conditions during degradation could also result in varying compositions, particularly for volatile compounds. On the other hand, enhanced maturity will lead to the rearrangement of methyl phenanthrenes on the basis of thermodynamic stability, with the 2-MP and 3-MP isomers being more stable than 1-MP and 9-MP isomers. Thus, the methylphenanthrene ratio (MPI-1, Rc, MPDF) could be used as a tracer of thermal history based on their isomer abundance. Moreover, MPI-1 proposed by Radke and Welte (1983) is perhaps the most widely used molecular maturity parameter based on aromatic hydrocarbons. Due to its

linear relationship with vitrinite reflectance throughout the conventional oil window, MPI-1 is often used to derive the equivalent vitrinite reflectance value (% Rc) for crude oils (Radke and Welte, 1983; Radke, 1988). The results showed that that the maturity parameters based on alkyl naphthalenes and methyl phenanthrene may be still an effective maturity indicator or for moderately biodegraded oils, but for severely biodegraded oils, the indexes could not be used as maturity indicator (Table 5). Thus, such ratios are good candidates for source ratios that will remain reasonably constant as oil is degraded.

#### 4. Conclusion

This study attempts to characterize the natural weathering processes of residual oil pollution in soil environment by detailed monitoring of changes in its chemical composition with different rank of degradation. Major compositional changes of steranes, terpanes and PAHs observed were consistent with previous studies. The most pronounced features were: (1) tricyclic terpanes are preferentially degraded relative to pentacyclic terpanes; (2) C<sub>29</sub>20S/(20S + 20R), C<sub>29</sub>20S/(20S + 20R), C<sub>29</sub>/C<sub>30</sub>H, C<sub>30</sub> $\beta$  $\alpha$ / $\alpha$  $\beta$ , and C<sub>31</sub>22S/(22S + 22R) were found to be most suitable for the source identification and correlation; (3) the ratios C<sub>2</sub>-DBTs/C<sub>2</sub>-PHENS, C<sub>3</sub>-DBTs/C<sub>3</sub>-PHENS, DBT/MCHRY, CHRY/PHENS, MDR, were stable in a terrestrial environment, after which the ratios become slightly higher due to the slightly faster biodegradation of PHENS and DBTs. Moreover, the gradual increase of the oleanane index and gammacerane index and sharp decrease of the pregnane index were found with increased weathering. This case study implies that the maturity parameters based on alkyl naphthalenes and methyl phenanthrenes in petroleum geochemistry, such as TMNr, TeMNr, PMNr, MPI-1, Rc, MPDF, may also provide another useful diagnostic means for spilled source identification.

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