



GC–MS analysis of two types of mixed oils, a comparison of composition and weathering patterns



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ABSTRACT

In order to compare the effects of weathering on two types of mixed oil, simulated weathering experiments were performed. The first sample was a mixture of two fresh oils and the second sample was a mixture of one fresh oil and another oil sample that had undergone a serious weathering process. Comparative studies evaluated decay rates and changes in diagnostic ratios of some fingerprinting biomarkers. Results showed that the mixing process affected the weathering rate of some compounds in the oils and also that certain diagnostic ratios are more suitable for estimating mixing proportions. A $\text{Pr}/n\text{-C}_{17}$ versus $\text{Ph}/n\text{-C}_{18}$ plot can be used to identify the end-numbers of mixed oils and the $(\text{C}_{13} + \text{C}_{14})/(\text{C}_{25} + \text{C}_{26})$ ratio is a useful diagnostic ratio to detect the degree of weathering. Finally, hopane, sterane, and alkylated PAH fingerprints were found to give useful insights about the sources of the mixed oils.

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1. Introduction

Recent statistical data has shown a slightly increasing trend of large oil spills from tankers (ITOPF, 2014). These massive releases of oil pose a significant threat to marine and coastal ecosystems; not only because of the extensive environmental harm they cause, but also because of the economic damages associated with their consequences (Garza-Gil et al., 2006; McCreath-Strub et al., 2011). Therefore, tracing the liable sources of these pollutants, as a primary stage, as well as understanding their fate and behavior so as to assess their potential long-term impact on the environment is extremely important (Wang et al., 2004; Hayworth et al., 2015). The technique of chemical fingerprinting has been widely employed and is able to provide specific information on the chemical composition of a crude oil in order to link it to a suspected source (Stout et al., 2001; Wang and Fingas, 2003; Radović et al., 2014). However, field samples in most actual spills are multi-source oils, which confounds the chemical fingerprints of the spilled oils and by extension the candidate sources (Christensen and Tomasi, 2007; Douglas et al., 1996; McKenna et al., 2013). When an oil pollution incident may involve mixed sources, the liability must be carefully separated and allocated to

the different responsible parties (Kvenvolden et al., 1995; Li and Xiong, 2009; Kao et al., 2015). Though the crude oils and petroleum products in multi-source oils spills have distinct chemical fingerprints, these cannot be easily detected or recognized, especially if they have undergone a weathering process that can alter the chemical fingerprints. Hence, determining potential sources as well as qualifying or even quantifying the contribution from each source become a large challenge when the problem involves mixed oils.

Some end-member candidate oils collected after actual marine spill events may be either tar balls that have weathered for a long time or seriously weathered oils re-released after being deposited onto a sea bed. It is widely acknowledged that hydrocarbons are able to migrate through shallow marine sediment on the ocean floor at continental margins and form an oil layer on the ocean surface (Kvenvolden, 1993). Therefore, in addition to weathering, the mixing of the oil with the background contaminants could affect the inherent fingerprints of spilled oil in the marine environment (Stout and Wang, 2007). A severe challenge in spill interpretation may arise whenever oil residues from previous chronic pollution or other fresh oils are mixed in with oil spill samples that need to be analyzed. The question thus becomes how, over short weathering periods, the changes seen in chemical fingerprints are different when two fresh oils are the end members versus when the candidate end members are weathered sample (e.g. tar balls)

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and a fresh oil. To investigate this question, we have conducted a weathering simulation experiment on artificially mixed oils.

The major aims of this paper are, therefore: (i) to compare the chemical compositions of both mixed products, (ii) to assess how the mixed oils evolve over time (fifteen days) after being spilled under controlled conditions, and (iii) to select useful diagnostic ratios to evaluate weathering processes for mixed oils.

2. Experimental

2.1. Weathering simulation experiment

Two crude oil samples were collected from different oilfields, Shengli oilfield (oil-1) and Tarim oilfield (oil-2). The Shengli oil is

a heavy crude oil with a density (at 20 °C) of 0.9551 g/cm³ and a viscosity (at 50 °C) of 96.63 mPa s. The Tarim oil is a lighter crude oil with a density (at 20 °C) of 0.8259 g/cm³ and a viscosity (at 50 °C) of 14.3 mPa s. Two oil mixtures were then prepared, the first, group FO, (made using two fresh oils) was a mixture of oil-1 and the fresh Tarim crude oil (oil-2-0). The second mixture, group OO (made using an older oil and a fresh oil) was prepared using oil-1 and an older Tarim crude oil sample (oil-2-1) that had passed an artificial weathering process for 210 days. Samples from each of the two groups were then prepared at different mixing proportions, weighed (around 5 g), and poured into 50-ml graduated centrifuge tubes. Appropriate volumes of dichloromethane (DCM) were added in order to dissolve all mixed samples under ultrasonic oscillation (180 W, continuous mode) and

Table 1
Sample information of single-source and mixed oils.

Sample ID	Mixed proportion (%/oil-2)	Weathering time (day)	Σ alkanes (mg/g) ^a			Σ sterane (μg/g) ^b			Σ hopane (μg/g) ^c			Σ alkylated PAHs (μg/g) ^d		
			Actual	Estimated ^e	E/A ^f	Actual	Estimated	E/A	Actual	Estimated	E/A	Actual	Estimated	E/A
SO ^g	Oil-1 0	Initial	13.44	13.44	1.00	2072.64	2072.64	1.00	3355.52	3355.52	1.00	108.00	108.00	1.00
		1	8.91	11.80	1.32	1427.46	1819.98	1.27	2264.65	2946.47	1.30	69.55	94.83	1.36
		5	7.76	7.02	0.90	1306.31	1082.01	0.83	2195.33	1751.74	0.80	67.18	56.38	0.84
		15	7.43	1.91	0.26	1353.08	294.88	0.22	2105.55	477.40	0.23	46.32	15.37	0.33
		Initial	189.22	189.22	1.00	369.78	369.78	1.00	2480.03	2480.03	1.00	1359.61	1359.61	1.00
	Oil-2-0 100	1	133.36	166.15	1.25	308.15	324.71	1.05	2070.18	2177.70	1.05	1223.05	1193.87	0.98
		5	181.29	98.78	0.54	388.08	193.04	0.50	2581.55	1294.69	0.50	964.21	709.78	0.74
		15	137.89	26.92	0.20	296.95	52.61	0.18	2086.31	352.84	0.17	918.22	193.44	0.21
		Initial	127.33	127.33	1.00	186.81	186.81	1.00	1294.00	1294.00	1.00	5155.17	5155.17	1.00
		1	163.74	111.81	0.68	292.52	164.04	0.56	2086.52	1136.26	0.54	3441.82	4526.73	1.32
	Oil-2-1 100	5	165.98	66.47	0.40	339.50	97.52	0.29	2319.00	675.53	0.29	1670.07	2691.23	1.61
		15	154.85	18.12	0.12	358.29	26.58	0.07	2463.54	184.10	0.07	1390.77	733.45	0.53
		Initial	14.08	14.08	1.00	1323.93	1323.93	1.00	2110.31	2110.31	1.00	366.52	366.52	1.00
		1	11.79	12.37	1.05	1335.07	1162.53	0.87	2166.33	1853.05	0.86	191.30	321.84	1.68
		5	8.33	7.35	0.88	946.60	691.15	0.73	1553.03	1101.68	0.71	121.37	191.34	1.58
FO ^h	FO-1 9.8	15	6.68	2.00	0.30	963.97	188.36	0.20	1542.14	300.24	0.19	58.17	52.15	0.90
		Initial	27.38	27.38	1.00	1421.16	1421.16	1.00	2457.08	2457.08	1.00	1082.57	1082.57	1.00
		1	19.01	24.04	1.26	1078.90	1247.92	1.16	1837.28	2157.55	1.17	351.52	950.60	2.70
		5	13.33	14.29	1.07	902.32	741.91	0.82	1487.27	1282.71	0.86	165.62	565.15	3.41
		15	9.29	3.90	0.42	703.71	202.19	0.29	1238.96	349.58	0.28	87.20	154.02	1.77
	FO-2 30.2	Initial	32.81	32.81	1.00	1268.50	1268.50	1.00	2329.30	2329.30	1.00	1354.76	1354.76	1.00
		1	22.17	28.81	1.30	975.81	1113.87	1.14	1203.16	2045.35	1.70	363.77	1189.61	3.27
		5	14.91	17.13	1.15	753.86	662.22	0.88	1388.26	1216.00	0.88	230.31	707.24	3.07
		15	7.17	4.67	0.65	511.27	180.47	0.35	945.88	331.40	0.35	72.46	192.75	2.66
		Initial	33.26	33.26	1.00	925.40	925.40	1.00	1817.36	1817.36	1.00	1552.25	1552.25	1.00
	FO-3 40.6	1	27.59	29.20	1.06	873.21	812.59	0.93	1606.43	1595.82	0.99	860.39	1363.03	1.58
		5	21.44	17.36	0.81	791.81	483.10	0.61	1422.32	948.75	0.67	326.14	810.35	2.48
		15	16.21	4.73	0.29	672.98	131.66	0.20	1302.61	258.56	0.20	169.33	220.85	1.30
		Initial	22.53	22.53	1.00	2321.95	2321.95	1.00	3950.92	3950.92	1.00	245.26	245.26	1.00
		1	16.65	19.79	1.19	1831.67	2038.89	1.11	3044.64	3469.28	1.14	139.52	215.36	1.54
OO ⁱ	OO-1 10.1	5	11.49	11.76	1.02	1264.66	1212.16	0.96	2053.35	2062.56	1.00	94.53	128.04	1.35
		15	13.04	3.21	0.25	1670.69	330.35	0.20	2676.35	562.11	0.21	86.32	34.89	0.40
		Initial	25.08	25.08	1.00	1756.79	1756.79	1.00	2990.23	2990.23	1.00	246.85	246.85	1.00
		1	21.07	22.02	1.05	1528.51	1542.63	1.01	2481.31	2625.71	1.06	199.71	216.76	1.09
		5	21.47	13.09	0.61	1495.30	917.13	0.61	2573.20	1561.04	0.61	198.17	128.87	0.65
	OO-2 31.0	15	18.01	3.57	0.20	1316.67	249.95	0.19	2297.72	425.43	0.19	134.12	35.12	0.26
		Initial	32.65	32.65	1.00	1628.43	1628.43	1.00	2978.45	2978.45	1.00	341.30	341.30	1.00
		1	24.74	28.67	1.16	1282.29	1429.92	1.12	2227.04	2615.36	1.17	256.51	299.70	1.17
		5	19.38	17.04	0.88	1013.35	850.11	0.84	1883.01	1554.89	0.83	200.06	178.18	0.89
		15	17.90	4.65	0.26	1058.30	231.68	0.22	1927.89	423.76	0.22	128.53	48.56	0.38
	OO-3 40.3	Initial	37.50	37.50	1.00	1350.92	1350.92	1.00	2623.25	2623.25	1.00	406.14	406.14	1.00
		1	24.73	32.93	1.33	1136.96	1186.24	1.04	2198.04	2303.47	1.05	254.42	356.63	1.40
		5	24.70	19.58	0.79	1123.26	705.24	0.63	1974.18	1369.46	0.69	232.83	212.02	0.91
		15	22.28	5.34	0.24	1161.97	192.20	0.17	2079.79	373.22	0.18	167.68	57.78	0.34
	OO-4 50.1	Initial	24.73	32.93	1.33	1136.96	1186.24	1.04	2198.04	2303.47	1.05	254.42	356.63	1.40
		1	24.70	19.58	0.79	1123.26	705.24	0.63	1974.18	1369.46	0.69	232.83	212.02	0.91
		5	22.28	5.34	0.24	1161.97	192.20	0.17	2079.79	373.22	0.18	167.68	57.78	0.34
		Initial	24.73	32.93	1.33	1136.96	1186.24	1.04	2198.04	2303.47	1.05	254.42	356.63	1.40
		1	24.70	19.58	0.79	1123.26	705.24	0.63	1974.18	1369.46	0.69	232.83	212.02	0.91

^a Sum of normal alkanes from C₁₀ to C₃₈.

^b Sum of 18 selected pentacyclic hopanes.

^c Sum of 12 selected steranes.

^d Sum of alkylated naphthalenes, phenanthrenes and dibenzothiophenes.

^e All estimated weathering values were calculated by the decay equations (Boehm et al., 1995): $HC = HC_0 e^{-0.13t}$, where HC is the hydrocarbon concentration at any given time, HC₀ is the hydrocarbon concentration in the initial time, t = days after the spill.

^f Estimated values/actual values.

^g Single-source oils.

^h Group FO. Four samples (FO-1, FO-2, FO-3 and FO-4) are mixed with the oil-1 and the oil-2-0 with different mixing proportion.

ⁱ Group OO. Four samples (OO-1, OO-2, OO-3 and OO-4) are mixed with the oil-1 and the oil-2-1 with different mixing proportion.

samples were then shaken for 5 min. The numbering system and the mixing proportions are listed in Table 1.

All mixed samples were then added to 400 ml beakers containing approximately 200 ml of seawater with an approximately 5 cm thick layer of sand at the bottom. Next the beakers were set in two tanks ($L \times B \times H = 80 \text{ cm} \times 30 \text{ cm} \times 50 \text{ cm}$, respectively) as seen in Fig. 1. The beakers were then placed in a BOXUN SPX-400 IC environmental test chamber with settings of humidity at 70% RH, illumination at 12,000 LX, and temperature at 26 °C during the day, and with settings of humidity at 60% RH, illumination at 0 LX, and temperature at 20 °C at night, in order to simulate the summer climate of the Yellow Sea. For each of the single-source and mixed oils, the weathering times tested were 1, 5, and 15 days.

2.2. Extraction, fractionation and instrumental analysis

Oil samples were weighed (approximately 0.1–0.2 g) and then dissolved in 10 ml of *n*-hexane in 15 ml centrifuge tubes. After ultrasonic oscillation for 15 min, each of the oil sample extracts were dehydrated using anhydrous sodium sulfate (certified ACS grade), filtered through a 0.2 μm nylon filter, and finally transferred to 5 ml screw cap auto-sampler vials. A mixture of internal standards composed of 50 μl each of 10 mg/l tetracosane-*d*50 (Sigma-Aldrich Co. USA), 5- α -androstane, and 4-terphenyl-*d*14 (both obtained from J&K SCIENTIFIC Ltd. CHN) was injected into the final sample extracts just prior to GC-MS analysis.

Further sample treatment and analysis was performed according to previously described methods (Stout and Wang, 2007;

CEN/TR 15522-2, 2012). Briefly, analysis was completed using a 6890 N gas chromatograph connected to a GC-5973 N mass spectrometer (energy 70 eV, m/z 50–800, and the source at 230 °C and quadrupole at 150 °C) in the EI mode, equipped with a HP-5 capillary column (50 m \times 0.32 mm \times 0.25 μm , Agilent Technologies, USA). The oven temperature was first held at 50 °C for 2 min and then programmed to rise from 50 to 300 °C at a rate of 6 °C/min and maintain the final temperature for 16 min. Helium was used as the carrier gas at a flow rate of 1.0 ml/min. The present *n*-alkanes were identified based on the retention time of the standards (*n*C_{10–40}, Sigma), and the concentrations of each *n*-alkane were calculated based on a standard calibration curve prepared for each corresponding standard compound.

3. Results and discussions

3.1. Degradation rates and quantification of the mixed oils

The exponential decay equation was used to estimate the weathering values for the oils (Boehm et al., 1995). The apparent decay-rate constants in nature vary from -0.008 to -0.01 day^{-1} due to the various decay rates of different organic compounds (Yim et al., 2011). The average decay-rate constant k for this work was set at -0.13 day^{-1} , considering that actual values are almost equivalent to estimated values (Table 1). The average decay-rate constant k represents an estimated decay-rate of $-12.19\% \text{ day}^{-1}$. Colombo et al. (2005) had previously reported the decay-rate constants in soils relative to sediments (-0.006 versus -0.003 day^{-1} , respectively). Even though dispersants were added to the weathering oil, the decay-rate constant k for oils in sea water is only -0.008 day^{-1} and -0.035 day^{-1} for total alkanes and total aromatics, respectively. Venosa et al. (1996) studied the estimated decay-rate of a sandy beach with aerated soils for the control plots, and reported decay-rates of -2.6% and $-2.1\% \text{ day}^{-1}$ for total alkanes and total aromatics, respectively. A similar work showed a lower decay-rate for coastal marshes, with a rate of $-0.39\% \text{ day}^{-1}$ observed for the total alkane pool (Turner et al., 2014). For the works mentioned, the decay-rate constants in the artificial weathering simulation experiments were lower than what has been observed in the natural environment. However, the decay rate in this experiment was observed to be faster than the weathering process in nature, and indicates that the conditions in this chamber are able to speed up the oil weathering process. One former study showed that evaporation, dissolution, and dispersion are the major oil weathering processes (Joo et al., 2013). Three factors (plenty of ventilation, constant illumination, and high temperature

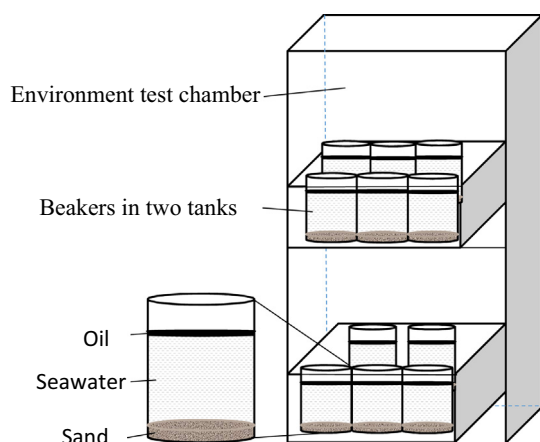


Fig. 1. Mimic diagram of the simulation test device.

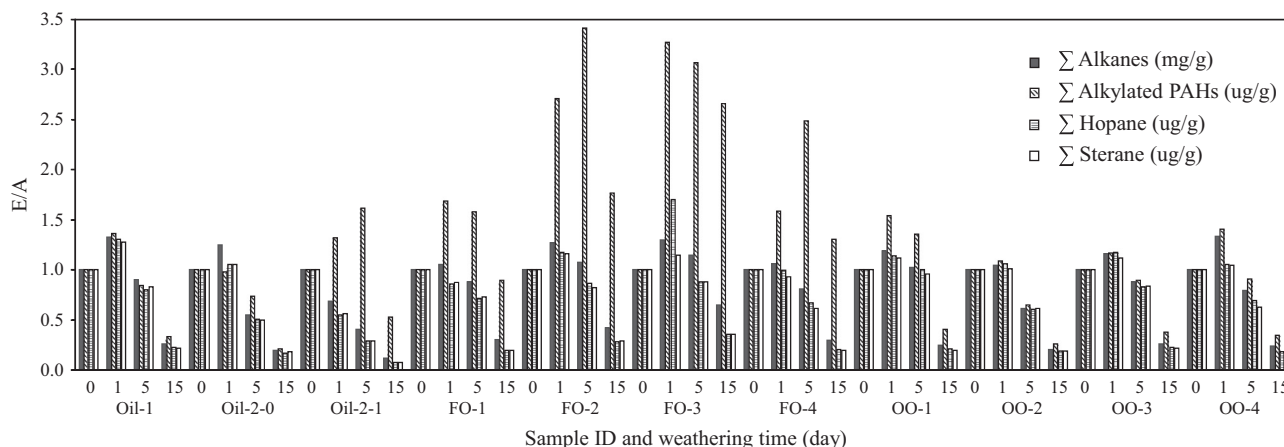


Fig. 2. Estimated values versus actual observed values of content of compounds in different oils.

Table 2

Comparisons with the actual and estimated initial values of selected diagnostic ratios of mixed oils.

Sample ID			FO				OO				RSD% ^a
			FO-1	FO-2	FO-3	FO-4	OO-1	OO-2	OO-3	OO-4	
Ratios	$(C_{13} + C_{14})/(C_{25} + C_{26})^b$	Actual	0.73	0.94	1.04	1.13	0.29	0.22	0.19	0.17	99.50
		Estimated ^c	0.34	0.27	0.24	0.21	0.48	0.72	0.82	0.93	
		AC/ES ^d	2.17	3.46	4.33	5.31	0.60	0.31	0.23	0.18	
Pr/ <i>n</i> -C ₁₇ ^e		Actual	0.52	0.39	0.36	0.33	0.53	0.40	0.37	0.34	6.88
		Estimated	0.68	0.59	0.54	0.51	0.68	0.59	0.55	0.51	
		AC/ES	0.77	0.66	0.67	0.66	0.77	0.68	0.66	0.67	
Ph/ <i>n</i> -C ₁₈ ^f		Actual	1.42	0.72	0.55	0.39	1.30	0.79	0.53	0.39	29.20
		Estimated	2.27	1.77	1.51	1.31	2.25	1.76	1.54	1.31	
		AC/ES	0.62	0.41	0.36	0.30	0.58	0.45	0.35	0.30	
C ₂₇ /C ₂₉ ^g		Actual	0.76	0.75	0.76	0.73	0.78	0.78	0.71	0.72	13.21
		Estimated	0.73	0.60	0.54	0.49	0.72	0.59	0.54	0.48	
		AC/ES	1.04	1.25	1.42	1.50	1.09	1.31	1.33	1.50	
C ₂₉ β/C ₂₉ ^h		Actual	27.94	31.08	31.91	32.69	30.99	31.32	31.23	32.93	5.84
		Estimated	31.86	35.89	37.99	39.65	32.19	36.60	38.58	40.67	
		AC/ES	0.88	0.87	0.84	0.82	0.96	0.86	0.81	0.81	
C ₃₁ S/(S + R) ⁱ		Actual	0.44	0.45	0.44	0.44	0.44	0.45	0.44	0.44	1.70
		Estimated	0.45	0.44	0.44	0.43	0.45	0.44	0.44	0.43	
		AC/ES	0.98	1.01	1.01	1.02	0.97	1.01	1.01	1.01	
C ₃₂ S/(S + R) ^j		Actual	0.55	0.56	0.55	0.56	0.54	0.55	0.56	0.56	0.68
		Estimated	0.55	0.56	0.57	0.57	0.55	0.56	0.56	0.57	
		AC/ES	0.99	0.99	0.98	0.98	0.98	0.99	0.99	0.99	
MDBT/DBT ^k		Actual	1.89	2.05	2.02	2.03	1.99	2.29	2.13	2.55	29.05
		Estimated	1.96	2.78	3.20	3.54	1.68	1.86	1.94	2.02	
		AC/ES	0.96	0.74	0.63	0.57	1.19	1.23	1.10	1.26	
MPR-2 ^l		Actual	0.51	0.55	0.55	0.58	0.63	0.73	0.75	0.79	28.13
		Estimated	0.56	0.67	0.73	0.78	0.51	0.53	0.54	0.55	
		AC/ES	0.92	0.82	0.75	0.75	1.23	1.37	1.40	1.45	
MPR-3 ^m		Actual	0.54	0.54	0.55	0.56	0.57	0.70	0.71	0.73	26.17
		Estimated	0.49	0.61	0.67	0.73	0.44	0.47	0.49	0.50	
		AC/ES	1.11	0.88	0.81	0.77	1.29	1.47	1.45	1.45	

^a Relative standard deviation (%).^b *n*-Alkanes ($n-C_{13} + n-C_{14})/(n-C_{25} + n-C_{26})$.^c All estimated initial values of diagnostic ratios of group FO were calculated by the following equations: $R_{\text{mixed}} = R_{\text{oil-2-0}}X + R_{\text{oil-1}}(1-X)$, and group OO by $R_{\text{mixed}} = R_{\text{oil-2-0}}X + R_{\text{oil-1}}(1-X)$. Where R_{mixed} is the estimated initial values of diagnostic ratios of mixed oils, $R_{\text{oil-1}}$, $R_{\text{oil-2-0}}$ and $R_{\text{oil-2-1}}$ are the actual determined values of diagnostic ratios of three single-source oils, respectively. *X* denotes contribution mass proportion of one end-numbers (given by Table 1), and $1-X$ corresponds to the contribution mass proportion of another end-numbers.^d Actual values/estimated values.^e Pristane to *n*-C₁₇ alkane.^f Phytane to *n*-C₁₈ alkane.^g Ratio of sum of 5α(H), 14α(H), 17α(H)-C₂₇-steranes (S + R) and 5α(H), 14α(H), 17α(H)-C₂₇-steranes (S + R) to sum of 5α(H), 14α(H), 17α(H)-C₂₉-sterane (S + R) and 5α(H), 14β(H), 17β(H)-C₂₉-sterane (S + R).^h 100 × ratio of 5α(H), 14β(H), 17β(H)-C₂₉-sterane (S + R) to sum of 5α(H), 14α(H), 17α(H)-C₂₉-sterane (S + R) and 5α(H), 14β(H), 17β(H)-C₂₉-sterane (S + R).ⁱ Ratio of 17α(H), 21β(H)-C₃₁-hopane (S) to sum of 17α(H), 21β(H)-C₃₁-hopane (S) and 17a(H), 21b(H)-C₃₁-hopane (R).^j Ratio of 17α(H), 21β(H)-C₃₂-hopane (S) to sum of 17α(H), 21β(H)-C₃₂-hopane (S) and 17a(H), 21b(H)-C₃₂-hopane (R).^k Ratio of sum of 1-methyldibenzothiophene, 2-methyldibenzothiophene and 4-methyldibenzothiophene to dibenzothiophene.^l Ratio of C₂-phenanthrene to C₀-phenanthrene.^m Ratio of C₃-phenanthrene to C₀-phenanthrene.

conditions) are able to influence these oil weathering processes and accelerate the oil decay rate in an environmental test chamber.

The large difference in decay rates between single-source oils and mixed oils are shown in Fig. 2. These results reveal that over time the ratios of the estimated values compared to the actual observed values (*E/A*) for all oils becomes increasingly smaller, indicating that the decay due to the weathering process becomes slower overall. As can be seen from Fig. 2, oil-2-0 has a faster decay-rate for alkylated PAHs (*E/A* ≥ 1 over 1, 5, and 15 days) as compared to oil-1. In addition, the group FO has a faster decay-rate for alkylated PAHs than is seen in group OO. This most likely means that the mixing process is able to change the weathering rate of some compounds in oils.

By comparing the calculated values with the actual values of different diagnostic ratios (Table 2), useful diagnostic ratios estimating the mixed mass proportions can be obtained using the following principle: the relative deviation (RSD%) of the ratios comparing actually determined values to the estimated values for the diagnostic ratios of all samples should be less than 5. Therefore, in terms of a practical investigation of two suspected

oil sources, some diagnostic ratios, such as C₃₁S/(S + R) and C₃₂S/(S + R) are most suitable for estimating mixing proportions.

3.2. Biomarker fingerprints

3.2.1. *n*-Alkanes and isoprenoid fingerprints

n-Alkanes and isoprenoid hydrocarbons are commonly used to characterize the source composition of spill oils (Wang and Fingas, 2003; Liu et al., 2009). Some diagnostic ratios, such as $(C_{13} + C_{14})/(C_{25} + C_{26})$, represent one of multiple weathering characteristics, evaporation in this case (Diez et al., 2007). Yim et al. (2011) used this ratio to categorize the oil weathering process into four stages: the initial weathering stage ($(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio over 1.0), the moderate weathering stage ($(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio between 0.1 and 1.0), the advanced weathering stage ($(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio between 0.01 and 0.1), and the extreme weathering stage ($(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio of less than 0.01). Fig. 3 and Table 3 show that the $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio measured for oil-2-1 changed the most dramatically out of the three single-source oils, most likely due to

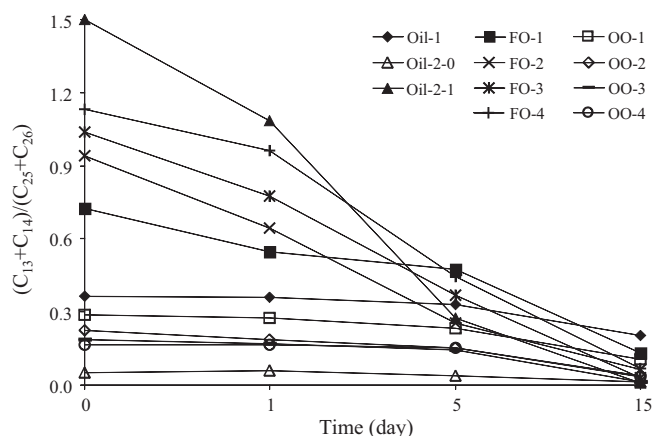


Fig. 3. Change mode of $(C_{13} + C_{14})/(C_{25} + C_{26})$ of oils. Refer to Table 2 for abbreviations.

the fact that it is the lightest crude oil, and suggests that this oil has undergone an extensive transformation. Furthermore, it was also shown that the initial $(C_{13} + C_{14})/(C_{25} + C_{26})$ values of the samples in the two groups become increasingly closer to the initial $(C_{13} + C_{14})/(C_{25} + C_{26})$ value of oil-1 as the mixing mass proportions of oil-1 increase. The $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratios of the mixed oils are positively correlated to the proportion of oil-2-0 in the FO group. In contrast, there is a negative correlation between the $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio of mixed oils in the OO group and the proportion of oil-2-1. The $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio of the OO group mixed oils changed less significantly than for the FO group, indicating that the ratio of fresh oil mixed with an older oil has a lower $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio (lower than 0.3) and also changes only slightly during a short-term weathering process. Therefore, if the $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratios measured for actual spill cases are larger than that of the potential source, the spill is most likely due to fresh oil. If, however, the $(C_{13} + C_{14})/(C_{25} + C_{26})$ ratio of a field

Table 3
Selected diagnostic ratios used for source identification of single-source and mixed oils.

Sample ID	Weathering time (day)		Diagnosis ratios ^a										
			$(C_{13} + C_{14})/(C_{25} + C_{26})$	Pr/n-C ₁₇	Ph/n-C ₁₈	C ₂₇ /C ₂₉	C ₂₉ ββ/C ₂₉	C ₃₁ S/(S + R)	C ₃₂ S/(S + R)	(N + N1)/N2 ^b	MDBT/DBT	MPR-2	MPR-3
SO	Oil-1	Initial	0.36	0.73	2.50	0.78	30.00	0.54	0.55	1.49	1.59	0.51	0.43
		1	0.36	0.72	2.59	0.83	29.94	0.54	0.55	1.47	1.66	0.51	0.44
		5	0.33	0.72	2.54	0.79	30.27	0.54	0.54	1.41	1.54	0.52	0.46
		15	0.20	0.75	2.55	0.78	27.87	0.56	0.52	1.37	1.68	0.49	0.42
	Oil-2-0	Initial	1.50	0.09	0.29	0.48	51.30	0.59	0.58	1.10	2.44	0.58	0.58
		1	1.09	0.09	0.28	0.48	52.88	0.59	0.57	0.61	2.48	0.58	0.57
		5	0.28	0.09	0.30	0.44	50.18	0.59	0.58	0.90	2.82	0.64	0.63
		15	0.01	0.12	0.25	0.43	51.68	0.59	0.58	1.12	3.22	0.86	0.88
	Oil-2-1	Initial	0.05	0.30	0.10	0.43	49.39	0.59	0.58	1.58	4.43	1.15	1.11
		1	0.06	0.27	0.08	0.40	50.11	0.60	0.59	1.10	4.19	1.05	1.03
		5	0.04	0.27	0.08	0.41	49.69	0.60	0.58	0.73	4.39	1.15	1.11
		15	0.01	0.30	0.10	0.39	50.37	0.59	0.59	1.10	5.07	1.26	1.20
FO	FO-1	Initial	0.73	0.52	1.42	0.76	27.94	0.56	0.55	1.19	1.89	0.51	0.54
		1	0.55	0.54	1.59	0.84	30.23	0.55	0.55	0.97	1.84	0.56	0.50
		5	0.48	0.55	1.54	0.79	30.33	0.55	0.55	0.96	1.84	0.56	0.50
		15	0.13	0.54	1.61	0.78	27.98	0.55	0.54	1.14	1.94	0.58	0.58
	FO-2	Initial	0.94	0.39	0.72	0.75	31.08	0.55	0.56	1.14	2.05	0.55	0.54
		1	0.64	0.41	0.72	0.74	30.15	0.55	0.56	0.77	2.04	0.58	0.55
		5	0.25	0.41	0.75	0.77	28.54	0.55	0.55	1.16	2.15	0.60	0.58
		15	0.06	0.44	0.74	0.83	31.24	0.56	0.55	1.08	2.54	0.71	0.68
	FO-3	Initial	1.04	0.36	0.55	0.76	31.91	0.56	0.55	1.13	2.02	0.55	0.55
		1	0.77	0.39	0.58	0.94	38.72	0.56	0.55	0.81	1.98	0.58	0.55
		5	0.37	0.39	0.58	0.78	31.75	0.56	0.55	0.86	2.05	0.58	0.56
		15	0.03	0.40	0.61	0.78	29.44	0.56	0.55	1.36	2.65	0.74	0.69
	FO-4	Initial	1.13	0.33	0.39	0.73	32.69	0.56	0.56	1.10	2.03	0.58	0.56
		1	0.96	0.35	0.44	0.76	29.68	0.56	0.56	0.82	2.05	0.57	0.56
		5	0.44	0.36	0.42	0.69	29.65	0.57	0.55	0.81	2.32	0.59	0.57
		15	0.07	0.38	0.44	0.76	32.56	0.57	0.55	0.93	2.68	0.74	0.70
OO	OO-1	Initial	0.29	0.53	1.30	0.78	30.99	0.56	0.54	1.54	1.99	0.63	0.57
		1	0.28	0.52	1.45	0.77	30.97	0.55	0.55	1.47	1.85	0.69	0.62
		5	0.23	0.54	1.47	0.86	30.37	0.56	0.55	1.36	1.85	0.65	0.66
		15	0.10	0.55	1.52	0.78	28.21	0.56	0.52	1.42	2.09	0.71	0.71
	OO-2	Initial	0.22	0.40	0.79	0.78	31.32	0.55	0.55	1.49	2.29	0.73	0.70
		1	0.19	0.42	0.75	0.77	28.72	0.56	0.58	1.40	2.36	0.76	0.68
		5	0.15	0.41	0.76	0.77	30.87	0.55	0.55	1.27	2.17	0.79	0.74
		15	0.04	0.43	0.79	0.73	30.01	0.56	0.56	1.48	2.41	0.90	0.81
	OO-3	Initial	0.19	0.37	0.53	0.71	31.23	0.56	0.56	1.55	2.13	0.75	0.71
		1	0.17	0.36	0.56	0.74	29.08	0.57	0.55	1.47	2.42	0.77	0.71
		5	0.15	0.39	0.54	0.77	32.08	0.56	0.55	1.21	2.52	0.81	0.74
		15	0.01	0.41	0.55	0.74	31.35	0.55	0.55	1.63	3.07	0.85	0.82
	OO-4	Initial	0.17	0.34	0.39	0.72	32.93	0.56	0.56	1.53	2.55	0.79	0.73
		1	0.16	0.36	0.47	0.75	31.93	0.56	0.56	1.51	2.39	0.77	0.73
		5	0.15	0.36	0.49	0.76	29.20	0.57	0.55	1.33	2.65	0.83	0.77
		15	0.03	0.39	0.48	0.74	29.15	0.57	0.55	1.45	2.83	0.85	0.92

^a Pr/n-C₁₇ and Ph/n-C₁₈ values of oil-1, oil-2-1 and the FO group refer to He et al. (2014); C₂₇/C₂₉, C₃₁S/(S + R), C₃₂S/(S + R), MDBT/DBT, MPR-2 and MPR-3 values of oil-1, oil-2-1 and the FO group refer to He et al. (2015).

^b Ratio of the sum of C₀-naphthalene and C₁-naphthalene versus C₂-naphthalene.

sample is less than that of a potential source, fresh oil from the source may have become mixed with previously spilled older oil.

The ratio of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ has been widely used to identify the changes over time seen for organic matter and organic matter maturation and even recover the individual depositional environments (Connan and Cassou, 1980; Peters et al., 1999; Baban and Ahmed, 2013). From a cross plot of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ (Fig. 4A), mixing was clearly seen in the $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ double plot, where oil-1 and oil-2-0, and oil-1 and oil-2-1 are the endpoints of the two group oils, respectively. There is a significant ($P < 0.05$) linear relationship between $Pr/n-C_{17}$ and $Ph/n-C_{18}$ as shown in Fig. 4A. Samples from group FO and the OO group displayed little change in the ratios of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$, with values ranging from 0.33 to 0.55 and 0.39 to 1.52, respectively. Furthermore the samples with the same mass proportions of oil-1 (e.g. FO-1 and OO-1) were quite close to each other, indicating a similar degree of weathering for these samples and that the two mixed oil groups are closely related. The weathering process did not cause large scattering in the data plots, indicating that the influence of the mixed

proportion on the degree of change of $Pr/n-C_{17}$ and $Ph/n-C_{18}$ is larger than seen from the degree of weathering. An increase in the $Pr/n-C_{17}$ and $Ph/n-C_{18}$ of oil always indicates a relative increase in the degree of oil biodegradation (Formolo et al., 2008). The result that $Pr/n-C_{17}$ and $Ph/n-C_{18}$ values of each oil examined in this work did not change significantly indicates that biodegradation is not a dominant factor in such a short-term weathering process.

3.2.2. Hopane, sterane and PAHs fingerprints

In general, because they are high molecular weight organic compounds, hopane and sterane biomarkers are more resistant to degradation than *n*-alkanes and isoprenoids (Barakat et al., 2002; Suneel et al., 2013). In this work, the influence of the weathering process on the oils' $C_{31}S/(S+R)$ and $C_{32}S/(S+R)$ ratios are related to hopane and the C_{27}/C_{29} and $C_{29}\beta\beta/C_{29}$ ratios are related to sterane, and are of interest because they own qualities that can be used to differentiate oil sources (Table 3). As shown in Table 3, the combined ratios of the selected pairs of terpanes and steranes, especially the ratios of $C_{31}S/(S+R)$ and $C_{32}S/(S+R)$, were apparently independent of weathering effects and therefore very useful in identifying spilled oil sources. Oil-2-0 and oil-2-1 samples have similar $C_{31}S/(S+R)$ ratio values, and are lower than the values measured for the two groups of mixed oils and oil-1. The plots of the two groups in Fig. 4B are similar to each other and lie between the values of the three single sources in the double plot (Fig. 4B). The $C_{31}S/(S+R)$ and $C_{32}S/(S+R)$ values of the two groups are increasingly near to the values of oil-1 as the proportion of oil-1 increases. The double ratio plots of $C_{31}S/(S+R)$ and $C_{32}S/(S+R)$ could be used to identify sources and further define the mixing of oil-1 and oil-2-0, as well as oil-1 and oil-2-1 (Fig. 4B). Oil-2-0 and oil-2-1 have similar C_{27}/C_{29} and $C_{29}\beta\beta/C_{29}$ values that are higher than the values of the two group mixed oils and oil-1 (Fig. 4C). The values of the two groups of mixed oils are also close together and almost between the values of the three single sources in the double plot (Fig. 4C). The fact that the C_{27}/C_{29} and $C_{29}\beta\beta/C_{29}$ values of the mixed oils (including their short-term weathered oils) are close to the values measured for oil-1 reveals that some

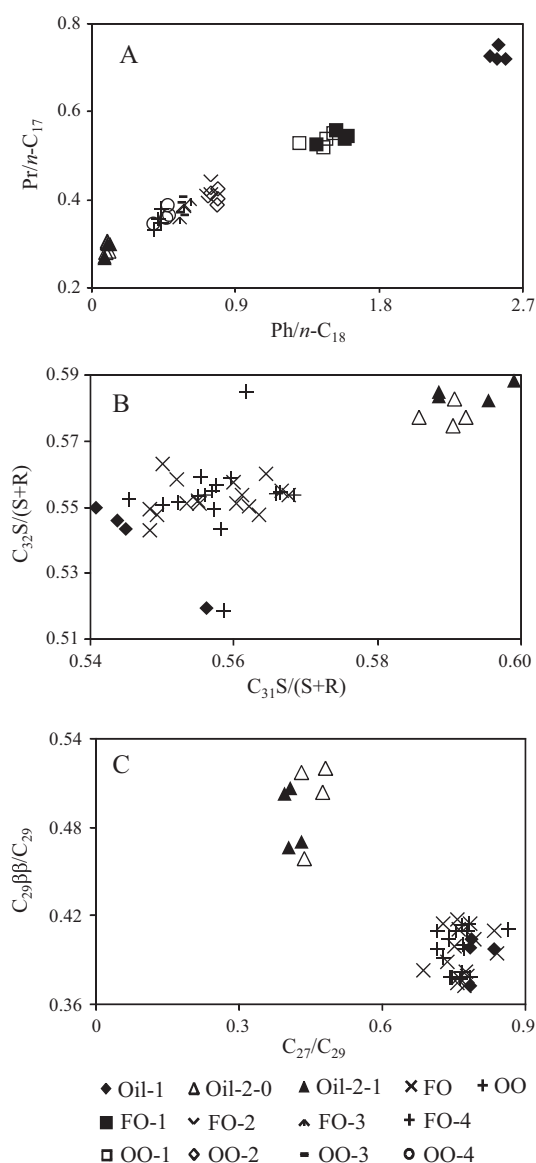


Fig. 4. Cross-plots of biomarker parameters. (A) $Ph/n-C_{18}$ versus $Pr/n-C_{17}$. (B) $C_{31}S/(S+R)$ versus $C_{32}S/(S+R)$. (C) C_{27}/C_{29} versus $C_{29}\beta\beta/C_{29}$.

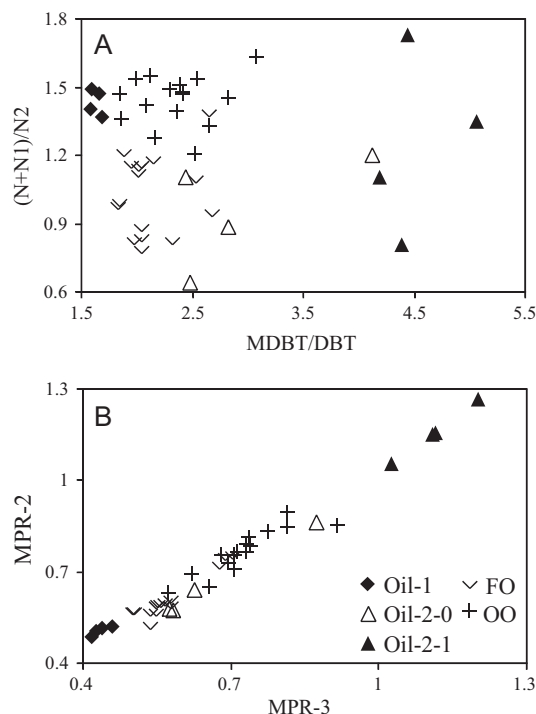


Fig. 5. Double ratio plots using alkylated phenanthrenes and dibenzothiophenes. (A) $MDBT/DBT$ versus methylanththalenes $[(N+N1)/N2]$, (B) $MPR-3$ versus $MPR-2$.

diagnostic ratios of mixed oils could be used as excellent indicators to identify their individual oil source endpoints.

Alkylated homologues of polycyclic aromatic hydrocarbons have high stability and are much more easily quantified than *n*-alkanes (Wang and Fingas, 1995; Ezra et al., 2000). The cross-plot of the two ratios MDBT/DBT and $(N+N1)/N2$ was adopted to describe the variations in abundance of naphthalene and dibenzothiophene compounds (Fig. 5A). The OO group oils have higher values of the sum of C_0 -naphthalene and C_1 -naphthalene versus C_2 -naphthalene than the FO group oils. The OO group oils have similar values for the ratio of MDBT/DBT as the group FO oils. High values for the ratio of $(N+N1)/N2$ as well as the comparable ratio values measured for the MDBT/DBT ratio in both group OO and group FO oils suggest that the MDBT/DBT ratios in the mixed oils are more stable over time than the $(N+N1)/N2$ ratio. Generally, indicators in the naphthalene and phenanthrene series (e.g. the MPR-2 and MPR-3 indices) are used in the identification of oil spills. Even though the MPR-2 index, similar to other conventional naphthalenes including the methyl-dibenzothiophene and phenanthrene indices, is able to separate oil-1 from two mixed oil groups after the weathering process, it can also differentiate between oil-1 and the other samples in the same group (Fig. 5B). As seen in the cross plot of MPR-2 and MPR-3 (Fig. 5B), mixing is also clear in the MPR-3 versus MPR-2 double plot, where oil-1 and oil-2-0, and oil-1 and oil-2-1 are the endpoints of two oil groups, respectively. The seriously weathered single-source sample (oil-2-1) displayed more dramatic changes than oil-2-0 for the ratios of MPR-2 and MPR-3 with values in the range of 1.05–1.26 and 1.03–1.20, respectively. This response can identify oil-2-1 in both of the mixed oil groups (Fig. 5B). Data plots of MPR-2 and MPR-3 values for oil-2-0 are mixed with the data plots of the two mixed groups (ranging from 1.56 to 1.95) and in between the values of oil-1 and oil-2-1 (ranging from 0.51 to 0.86 and 0.50 to 0.92, respectively.) Based on this data, it seems that oil-1 and oil-2-1 are the representative end-members of the two group oils. A significant correlation coefficient value of 0.86 ($p < 0.05$, $n = 44$) was measured between MPR-2 and MPR-3, and shows that there is a significant relationship between MPR-2 and MPR-3.

4. Conclusion

In this study, simulated weathering experiments were performed on two oils and two oil mixtures containing a series of artificially mixed oils in order to detect the differences in identification and quantification between these mixed oils after a short term weathering process. This artificial oil weathering experiment conducted in a controlled environmental test chamber was able to simulate the weathering process which occurs in nature. The decay-rates for a single day in the environmental test chamber are nearly equal to the decay-rate for a month under natural conditions, allowing the test chamber to accelerate the oil weathering process. The decay rates for single-source oils versus the mixed oils are different, and the mixing process changed the weathering rates of some individual compounds in the oils. The decay-rate constant under the artificial weathering simulation experiment was lower than the decay-rate constants observed in the natural environment, indicating that the decay rates measured during this experiment were higher than the natural weathering process.

To determine whether an accidental oil spill mixed with other oils, a short-term artificial weathering test is needed. In this test, the resulting $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ plot can identify whether the spilled oil samples are correlated to one single oil that always appears as one of the end-numbers and the major oil contained in the spill. The $(C_{13}+C_{14})/(C_{25}+C_{26})$ ratio can be used to clarify

whether the mixed oils are older than the spill being investigated. Multiple biomarker fingerprints (e.g. C_{27}/C_{29} , $C_{29}\beta\beta/C_{29}$, $C_{31}S/(S+R)$, $C_{32}S/(S+R)$, MPR-2, and MPR-3) can give additional information about the source of the spilled oil. The changes to degradation rates of oils in a short-term weathering test can also indicate characteristics useful to distinguish the different sources of spilled oils. Finally, some diagnostic ratios, such as $C_{31}S/(S+R)$ and $C_{32}S/(S+R)$, are most suitable to use in order to estimate mixing proportions.

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