Fingerprint and weathering characteristics of stranded oils after the Hebei Spirit oil spill

Un Hyuk Yim, Sung Yong Ha, Joon Geon An, Jong Ho Won, Gi Myung Han, Sang Hee Hong, Moonkoo Kim, Jee-Hyun Jung, Won Joon Shim *

Oil and POPs Research Group, South Sea Research Institute, KORDI, Geoje, Republic of Korea

ABSTRACT

After the Hebei Spirit oil spill in December 2007, mixtures of three types of Middle East crude oil were stranded along 375 km of coastline in Western Korea. Stranded oils were monitored for their identity and weathering status in 19 stations in three provinces. The results obtained using a weathering model indicated that evaporation would be a dominant weathering process immediately after the spill and the sequential changes of chemical composition in the field verified this prediction positively. In the early stages of weathering, the half-life of spilled oil was calculated to be 2.6 months. Tiered fingerprinting approaches identified background contamination and confirmed the identity of the stranded oils with the spill source. Double ratios using alkylated phenanthrenes and dibenzothiophenes in samples after the spill clearly reveal the impact of weathering on oil. However, to derive defensible fingerprinting for source identification and allocation, recalcitrant biomarkers are extremely useful. Weathering status of the stranded oils was evaluated using composition profiles of saturated hydrocarbons, polycyclic aromatic hydrocarbons and various weathering indices. Most samples collected 8 months after the spill were categorized in either the advanced or extreme weathering states. Gradual increase in toxic components in the residual oil through weathering emphasizes the need for adaptive ecotoxicological approaches.

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1. Introduction

On 7 December 2007, the Hong Kong registered tanker Hebei Spirit (146,848 GT), laden with 209,000 ton of crude oil, was struck by the crane barge Samsung No. 1, while anchored about five miles off Taean on the west coast of the Republic of Korea. About 10,900 ton of crude oil escaped into the sea from the Hebei Spirit. The collision punctured tanks No. 1, 3 and 5 of the oil tanker from which three different kinds of crudes were spilled, namely UAE Upper Zakum crude (UZC), Kuwait export crude (KEC) and Iranian heavy crude (IHC). The spilled oil polluted three of the four provinces along the west coast of Korea to varying degrees. In total more than 375 km of coastline has been affected [1,2].

Once in the marine environment, the spilled oil is immediately subject to a variety of weathering processes, including evaporation, dissolution, emulsification, microbial degradation, photo-oxidation, adsorption to suspended matter, and deposition on the sea floor, that determine its ultimate fate and impact on the environment [3]. In the early stages of weathering, evaporation is often the dominant process and in the later stages biodegradation plays a dominant role.

Weathering processes cause significant changes in the chemical composition of the spilled oil that can be used to monitor the fate and behavior of the spilled oil in the marine environment, and to refine the diagnostic values of the source recognition indices [4]. Together with weathering, mixing with the background could affect the inherent fingerprints of spilled oil in the marine environment [5]. The average number of spills and amount of oil spilled in Korea over the past ten years (1998–2007) excluding the Hebei Spirit oil spill (HSOS) are 388 and 827 kl, respectively [1]. Even after HSOS, small scale spills occurred in the West Coast where HSOS residual oils were mixed with newly stranded oils. For example, during summer sampling campaign in Jeungdo Island in 2008, bunker C oil from a different spill was found in locations previously studied for HSOS. Therefore, recognizing and distinguishing this background contamination from target sources is an important component of the oil spill investigation.

Detailed knowledge of stranded oil can provide an effective cleanup strategy and potential ecotoxicological information

* Corresponding author. Tel.: +82 55 639 8671; fax: +82 55 639 8689.
E-mail address: wjshim@kordi.re.kr (W.J. Shim).

[6,7]. For remediation of residual oils, weathering information can be used to evaluate the efficacy of bioremediation products and other oil-spill treating products. Information on the chemical composition of residual oil is crucial for designing the toxicity tests on weathered oil which should inherently mimic the naturally weathered oil using artificial weathering method [7].

This study mainly focused on differentiating potential sources of hydrocarbons, and determining the weathering extent of the spilled oil. To achieve these objectives, total petroleum hydrocarbons (TPH), saturated hydrocarbons (SHCs) including alkanes and selected isoprenoids, polycyclic aromatic hydrocarbons (PAHs), and biomarker compounds were quantitatively determined. In addition, a variety of diagnostic ratios were developed and used for spill source identification and differentiation. These interpretative tools provide an estimation of the weathering extent of spilled oils for further ecotoxicity and bioremediation tests.

2. Materials and methods

2.1. Materials

High purity chromatographic solvents (Burdick & Jackson, GC^2 grade) were used. Calibration standards used for the determination of individual and total petroleum hydrocarbons include n-alkane standards from C8 to C32 including pristane and phytane, PAH standards (SRM 2260) from the National Institute of Standards and Technology (NIST), and biomarker (hopanes and steranes) standards from Chiron Laboratory of Norway.

2.2. Study area and sample collection

Twenty-eight stranded oil samples were collected from nineteen stations covering most of the spill impacted area including Chungnam Province and Jeolla Province (Fig. 1; Table 1). In Chungnam Province, samples were taken from December 2007 to August
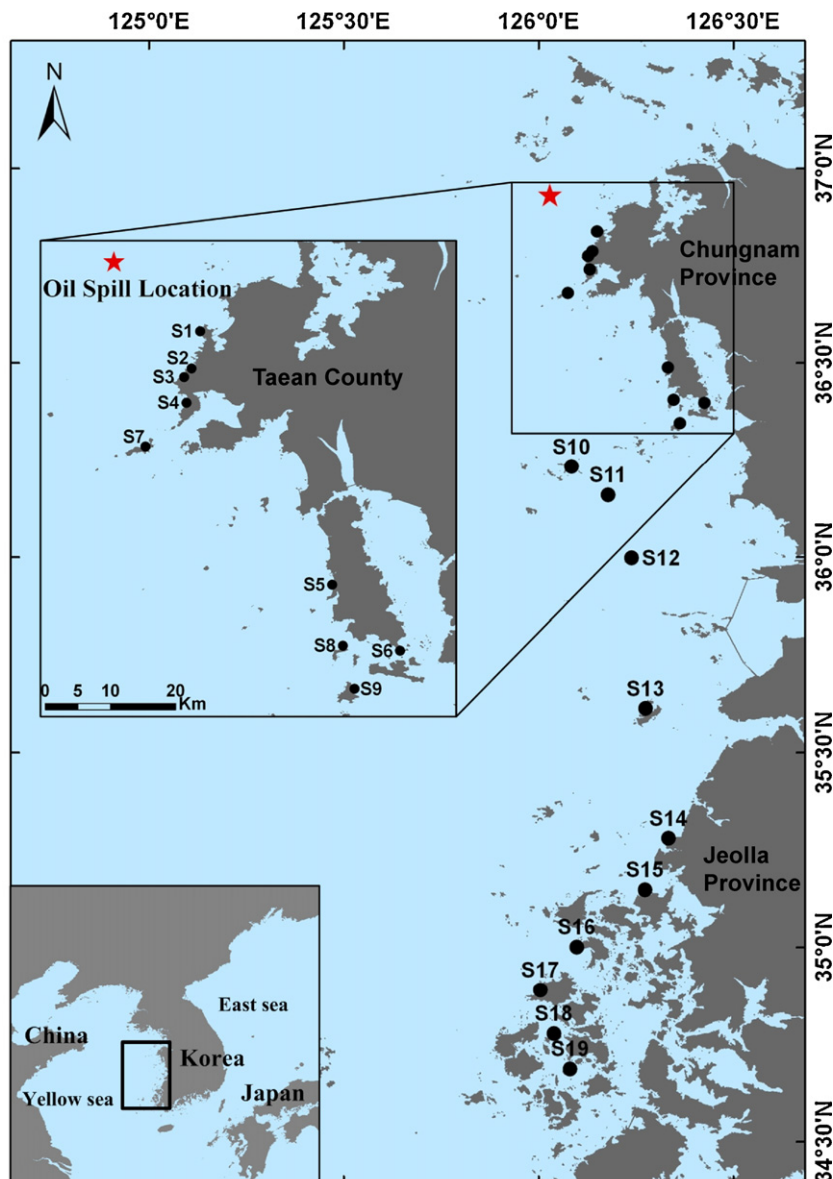

Fig. 1. Location map of stranded oil sampling sites.

Table 1
Sample information of spilled source and stranded oils.

Location	Sample ID	Sampling date	[a]TPH (mg/g)	[b]Σ Alkanes (mg/g)	[c]16 PAHs (µg/g)	[d]Σ Alkylated PAHs (µg/g)	[e]Σ Hopane (µg/g)	[f]Σ Sterane (µg/g)	Weathering stage
Cargo Oil	IHC	7 December 2007	241	9.90	277	6763	621	330	
	KEC	7 December 2007	212	19.9	130	4511	677	153	
	UZC	7 December 2007	227	34.6	236	8259	532	138	
Taean Penninsula	S 1-1	14 December 2007	247	12.0	145	6285	638	266	I
	S 1-2	26 December 2007	120	4.91	18.1	1297	255	100	II
	S 2	13 December 2007	88.4	4.54	39.0	1581	151	67.0	I
	S 3	16 December 2007	226	12.9	127	5455	515	234	I
	S 4	14 December 2007	310	17.1	118	5680	744	249	I
Islands of Chungnam Province	S 5	15 December 2007	162	6.81	30.3	2106	488	182	II
	S 6	17 December 2007	157	6.15	40.8	2296	494	193	II
	S 7-1	26 December 2007	250	12.3	87.1	4350	587	232	II
	S 7-2	18 February 2008	145	3.86	91.2	4918	585	290	II
	S 7-3	21 August 2008	119	1.74	27.4	2940	814	304	IV
	S 8	25 December 2007	183	8.06	50.2	2668	369	140	II
	S 9-1	25 December 2007	195	6.89	68.8	3837	544	226	II
	S 9-2	22 February 2008	165	5.28	68.6	3809	642	265	II
	S 9-3	21 August 2008	14.3	0.52	3.07	241	54.6	22.1	II
	S 10-1	25 February 2008	233	11.3	73.6	3981	759	329	II
	S 10-2	21 August 2008	118	0.95	18.1	1391	608	253	III
	S 11	21 December 2007	163	6.68	43.0	2260	540	231	II
Beaches & Islands of Jeolla Province	S 12	10 March 2008	177	7.42	42.7	2470	511	198	II
	S 13	10 March 2008	161	6.73	36.6	2436	575	207	II
	S 14-1	4 March 2008	187	8.39	83.7	4114	622	251	II
	S 14-2	21 September 2008	6.83	2.19	7.04	3.91	nd[g]	nd	Non-match
	S 15	22 September 2008	10.7	0.05	3.21	264	96.9	40.9	IV
	S 16-1	5 March 2008	142	3.33	43.9	2735	419	170	II
	S 16-2	23 September 2008	5.94	0.82	34.1	885	7.15	2.54	Non-match
	S 17-1	7 March 2008	128	1.42	41.2	2708	349	142	II
	S 17-2	24 September 2008	29.5	0.67	4.47	296	167	69.9	III
	S 18	7 March 2008	165	7.06	31.7	1934	508	182	II
	S 19	8 March 2008	177	9.00	150	3716	610	178	II

[a] Sum of GC–FID resolved peaks and unresolved complex mixture (UCM).

[b] Sum of normal alkanes from C8 to C40.

[c] Sum of US EPA 16 priority PAHs.

[d] Sum of alkylated naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysens.

[e] Sum of 15 selected pentacyclic hopanes.

[f] Sum of 9 selected steranes, refer to supplementary material for target biomarker compounds.

[g] Not detected.

2008. In Jeolla Province, the sampling commenced in March 2008 due to inaccessibility of the remote islands. Oil samples were carefully taken and placed in prewashed amber bottles using a solvent washed spatula and stored in the freezer until analysis. Three different cargo oil samples (UZC, KEC, and IHC) were obtained from the Korea Coast Guard (KCG).

2.3. Analytical method

Approximately 0.4 g of the oil sample was accurately weighed, dissolved in hexane and made up to final volume of 5.0 ml. From this a 200 μl volume of the oil solutions was taken and spiked with appropriate surrogates (100 μl of 200 ppm *o*-terphenyl and 100 μl of a mixture of deuterated acenaphthene, phenanthrene, chrysene, and perylene, 10 ppm each). These were transferred to a 3 g activated silica gel column topped with ~1 cm anhydrous granular sodium sulfate for sample clean-up and fractionation [8].

Half of the hexane fraction (F1) was used for analysis of saturates and biomarker compounds; half of the 50:50 hexane:dichloromethane fraction (F2) was used for analysis of alkylated PAH homologues and other target PAH. The remaining half of F1 and F2 were combined (F3) and used for determination of total GC-detectable TPH, GC-resolved peaks, and the GC-unresolved complex mixture of hydrocarbons (UCM). These three fractions were concentrated to appropriate volumes, spiked with internal standards (5-α-androstane and C30-ββ-hopane, terphenyl-*d*14, and 5-α-androstane for F1, F2 and F3, respectively), and then adjusted to an accurate preinjection volume of 1.00 ml for GC/FID and GC/MS analysis. Analyses for *n*-alkane distribution and TPH were performed on a Agilent 7890 gas chromatograph equipped with a flame-ionization detector (FID). Analyses of PAH and biomarker compounds were performed on HP 5890 GC equipped with HP 5972 mass selective detector (MSD). System control and data acquisition were achieved with an HP G1034C MS ChemStation. For detailed analytical procedure, chromatographic conditions, analysis quality control, and quantification methodology, refer to Refs. [8,9].

3. Results and discussion

3.1. Physical properties and weathering simulation

The proportional spill volume of the three cargo oils, KEC, IHC, and UZC are 43.4%, 42.8% and 13.8%, respectively (Table 2). Their physical properties such as density, viscosity and pour point are similar. However, their asphalthene and resin contents, which are known to affect the formation of emulsion, showed significant differences. Laboratory experiments revealed that IHC and KEC produced stable water-in-oil emulsions, while UZC resulted in meso-stable emulsion. Due to high wind and rough sea conditions, water-in-oil emulsion was formed right after the spill and most of the intertidal area was affected by this visco-elastic oil with high water content.

Weathering simulation using the NOAA ADIOS 2 model [10] indicated that at the initial stage of the spill, the major weathering process was evaporation, followed by dispersion. Four days after the spill, 22–30% of the spilled oil had evaporated and 0.7–10% had dispersed depending on the oil type, and approximately 60–76% of the spilled oil remained.

3.2. Degradation rates and half-lives

The temporal changes of TPH, alkanes, PAHs in the stranded oils can be used for estimating degradation rates and environmental half-lives of residual oils. Apparent first-order rate constants and environmental half-lives were obtained from chemistry data

Table 2
Physical properties and initial weathering model results of the three cargo oil spilled after Hebei Spirit oil spill.

Sample ID	Cargo oil name	Percentage of spilled amount (%)	Density (g/ml) @40°C	Viscosity (mm²/s) @40°C	Sulfur content (%)	Pour point (°C)	Asphalthene (%)	Resin (%)	Emulsion formation	ADIOS2 model (4 days after)		
										Evaporation (%)	Dispersion (%)	Remains (%)
IHC	Iranian Heavy	42.8	0.88	10.53	2.17	−17.5	5.6	5.6	Stable	23.3	0.7	76
KEC	Kuwait Export	43.4	0.88	9.69	2.88	−20	4.5	4.1	Stable	22.0	4.0	74
UZC	Upper Zakum	13.8	0.85	5.86	2.06	−7.5	3.0	2.8	Meso-stable	30.0	10.0	60

Table 3
Degradation rates and half-lives of spilled oil.

	Apparent decay-rate constant (k)	Half-lives (months)
TPH	−0.009	2.6
Total alkanes	−0.01	2.3
16 PAHs	−0.008	2.9
Alkylated PAHs	−0.01	2.3

for samples collected during December 2007 to September 2008 (Table 1). Rate constants for the loss of TPH, alkanes, EPA 16 priority PAHs (16 PAHs) and alkylated PAHs were calculated by fitting the data to the following exponential decay equations [11]:

$$[\text{Concentration at any given time}] = [\text{concentration at time zero}]\,e^{-kt},$$

where t = days after the spill and k = the apparent decay-rate constant.

The environmental half-life is defined as the time required for a given initial concentration of target compounds to decay to half of its original level and is computed as $t_{1/2} = 0.693/k$. Decay-rate constants for the target compounds groups varied from −0.008 to −0.01, where alkanes and alkylated PAHs showed the highest and 16 PAHs the lowest (Table 3). As the low molecular weight alkylated naphthalenes comprise more than 50% of the initial volume of alkylated PAHs, this highly volatile PAH series would account for relatively high decay of alkylated PAHs compared to the 16 PAHs. The half-life estimate ranges from 2.3 to 2.9 months depending on the group of target compounds.

The half-life values reported here are generally consistent with the data reported from other studies. Boehm et al. [11] presented data yielding a half-life of 2–3.8 months within the first 17 months after the Exxon Valdez oil spill (EVOS). And Berne and Marchand [12] reported a half-life of 2.4 months for Amoco Cadiz spill. However, following the rapid weathering and physical removal period, rates of dispersion and degradation diminished through time for the sequestered oil which has physical barriers to disturbance, oxygenation, and photolysis [13,14]. This was reflected in the slow decay rate of only −0.22 to −0.30 year^{-1} (20–26% loss over a year) from 1992 to 2001 in Prince William Sound after EVOS [15]. The residual oils of HSOS found in the intertidal mud flat and boulder-armored beach will probably follow similar rates to EVOS.

3.3. Identification of sources

3.3.1. GC/FID chromatogram

For the identification of spill sources, tiered approaches are usually applied [16,17]. The essential components of the tiered approach are GC/FID analysis, GC/MS analysis and diagnostic ratio or statistical analysis for level 1, 2, and 3, respectively. This study also followed oil spill fingerprinting protocols to check the identity of stranded oils with source oils and to discriminate the effects of weathering.

GC/FID provides valuable screening information about the oil source and weathering status. The three cargo oils spilled from the Hebei Spirit showed very similar GC/FID chromatogram pattern. Their normal alkane distribution showed a similar pattern, ranging from n-C8 to n-C35 with n-C11 to n-C15 being the most abundant. However, isoprenoids like pristane and phytane in IHC showed relatively higher peaks than those of UZC and KEC (Fig. 2). This difference was reflected in the diagnostic ratios of pristane to phytane, which clearly differentiate IHC from UZC and KEC (Table 4).

Stranded oil samples showed different chromatograms from those of fresh spill sources, reflecting the compositional changes caused by weathering and different background contamination (Fig. 3). By comparing their GC–FID chromatograms, samples from
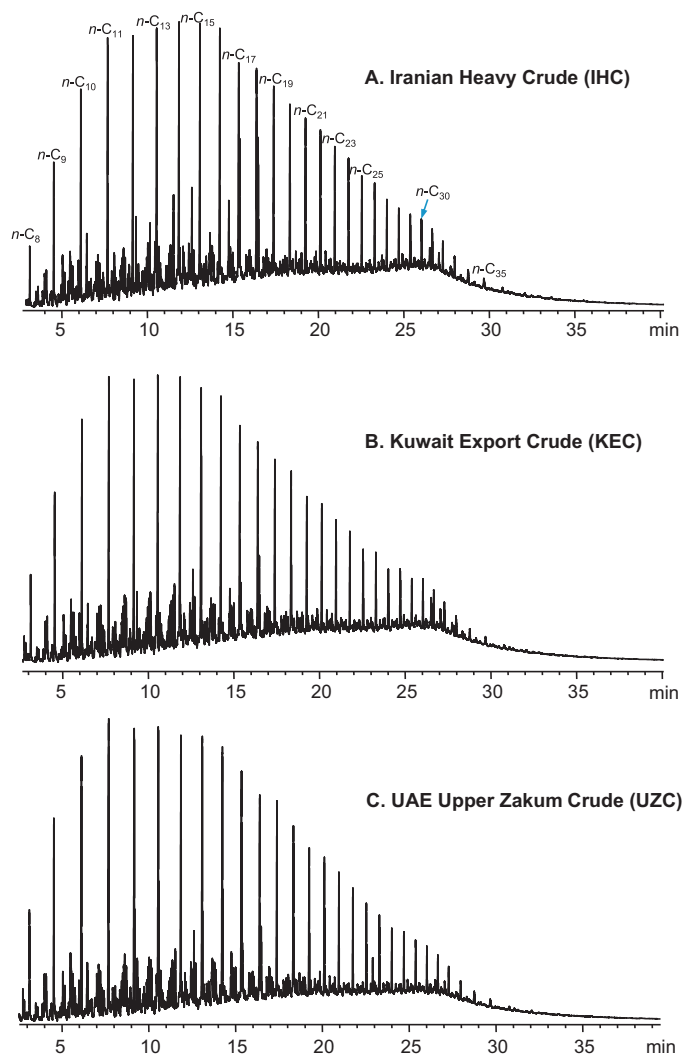

Fig. 2. GC–FID chromatograms of three kinds of Middle East crude oil spilled from HSOS. (A) Iranian Heavy Crude oil (IHC), (B) Kuwait Export Crude oil (KEC) and (C) UAE Upper Zakum Crude oil (UZC).

different source oils could be differentiated. S14-2 was a form of black tar and showed a different alkane distribution pattern. S16-2 showed the normal alkanes in a narrower carbon range with a different UCM hump shape. These features suggest that this oil was spilled from the cargo ship collision accident occurring nearby in August 2008.

3.3.2. Alkane fingerprints

Most of the samples collected during December 2007 to March 2008 were only slightly weathered, with only the light fraction of normal alkanes ranging from n-C8 to n-C13 missing. Samples collected eight to nine months after the spill showed a weathering pattern where significant amounts of light to middle molecular weight normal alkanes were depleted and pristane and phytane became dominant peaks. As weathering processes remove the GC-resolvable fraction, unresolved complex mixtures or "hump" (UCM) occupies the chromatogram overwhelmingly. The pristine/phytane diagnostic ratio was determined. It ranged from 0.57 (KEC) to 0.85 (IHC) for stranded oils collected within three months after the spill. This wide range of pristane/phytane ratio indicates that oils found in the beach are mixtures of at least two cargo oils. Samples collected 8 months after the spill no longer provided useful

Table 4
Selected source diagnostic ratios used for source identification of stranded oils.

Diagnostic ratio	Spill source oil				Stranded oils			Non-match
	IHC	KEC	UZC	Mix[a]	<1 month ($n=11$)	2–3 months ($n=10$)	>8 months ($n=5$)	(S16-2)
Pr/Ph[b]	0.85	0.57	0.74	0.80	0.68 ± 0.10	0.62 ± 0.08	0.44 ± 0.12	0.68
C2D/C2P[c]	2.21	3.32	3.40	2.71	2.49 ± 0.18	2.63 ± 0.45	4.16 ± 1.18	1.05
C3D/C3P[d]	2.86	5.72	4.61	4.12	2.61 ± 0.30	2.94 ± 0.48	4.12 ± 0.69	1.19
4-mD/1-mD[e]	2.16	1.87	1.58	1.84	1.96 ± 0.08	1.95 ± 0.07	1.11 ± 0.58	2.90
2/3-mD/1-mD[f]	1.69	1.52	1.27	1.48	1.56 ± 0.04	1.58 ± 0.06	0.81 ± 0.51	3.23
Ts/Tm[g]	0.51	0.53	1.12	0.51	0.46 ± 0.04	0.49 ± 0.05	0.51 ± 0.09	1.18
Ts/H30[h]	0.16	0.23	0.49	0.15	0.16 ± 0.03	0.27 ± 0.05	0.18 ± 0.05	0.47
H29/H30[i]	1.17	1.74	2.05	1.29	1.32 ± 0.24	2.00 ± 0.32	1.30 ± 0.20	1.32
C28ββ/(C27ββ+C29ββ)[j]	0.42	0.29	0.27	0.37	0.38 ± 0.01	0.37 ± 0.02	0.38 ± 0.01	0.28
C29ββ/(C27~C28ββ)[k]	0.61	0.83	0.85	0.71	0.67 ± 0.02	0.68 ± 0.06	0.67 ± 0.03	0.62

[a] Mixture of IHC, KEC, and UZC according to their spill amount percentage of 42.8, 43.4, and 13.8, respectively.
[b] Ratio of 2,6,10,14-tetramethylpentadecane to 2,6,10,14-tetramethylhexadecane.
[c] Ratio of C2-dibenzothiophene to C2-phenanthrene.
[d] Ratio of C3-dibenzothiophene to C3-phenanthrene.
[e] Ratio of 4-methyldibenzothiophene to 1-methyldibenzothiophene.
[f] Ratio of 2/3-methyldibenzothiophene to 1-methyldibenzothiophene.
[g] Ratio of 18α(H)-22,29,30-trisnorneohopane to 17α(H)-22,29,30-trisnorhopane.
[h] Ratio of 18α(H)-22,29,30-trisnorneohopane to 17α(H), 21β(H)-hopane.
[i] Ratio of 17α(H), 21β(H)-30-norhopane to 17α(H), 22β(H)-hopane.
[j] Ratio of 24-methyl-14β(H),17β(H)-cholestane(20R and 20S) to sum of 14β(H),17β(H)-cholestane(20R and20S) and 24-ethyl-14β(H),17β(H)-cholestane(20R and 20S).
[k] Ratio of 24-ethyl-14β(H),17β(H)-cholestane(20R and 20S) to sum of 14β(H),17β(H)-cholestane(20R and20S), 24-methyl-14β(H),17β(H)-cholestane(20R and 20S) and 24-ethyl-14β(H),17β(H)-cholestane(20R and 20S).
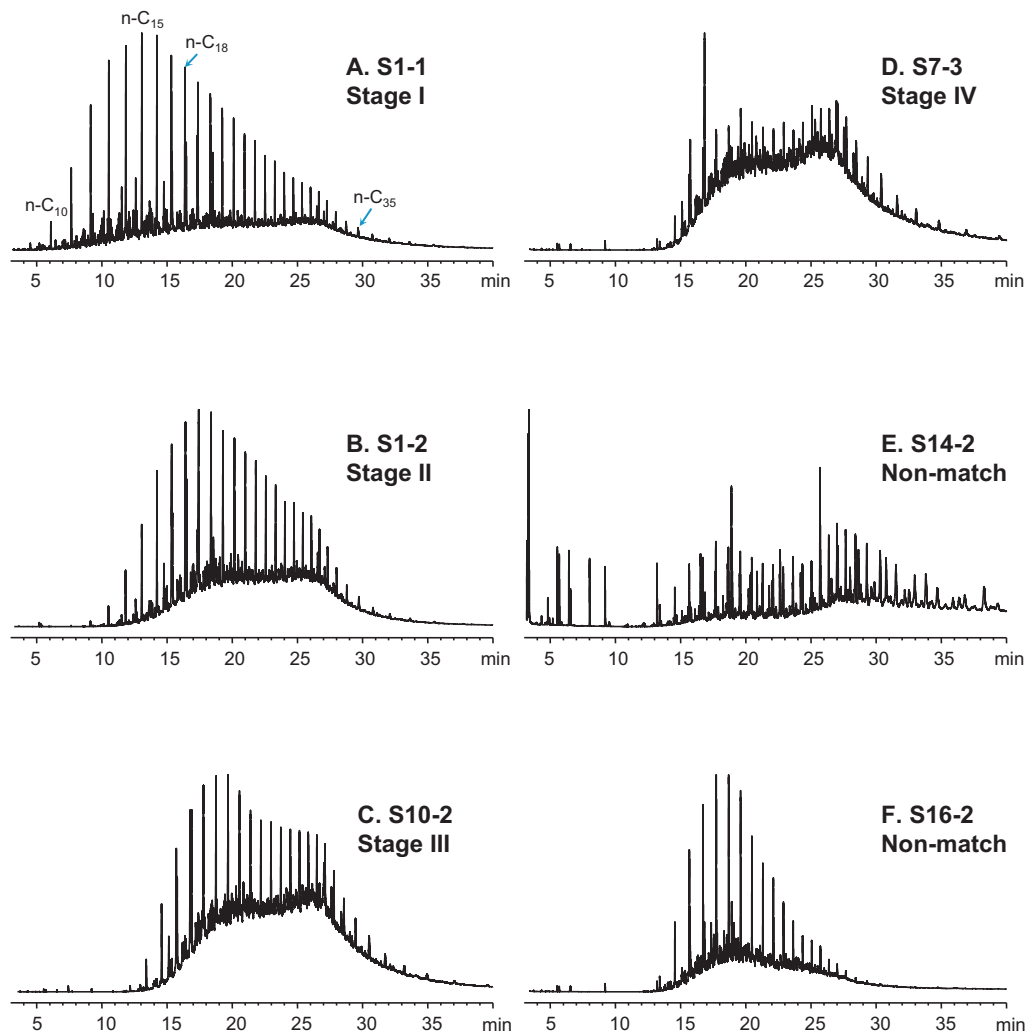

Fig. 3. GC–FID chromatograms of stranded oils according to their weathering stages and sources. (A) S1-1 (Stage I), (B) S1-2 (Stage II), (C) S10-2 (Stage III), (D) S7-3 (Stage IV), (E) S14-2 and (F) S16-2.
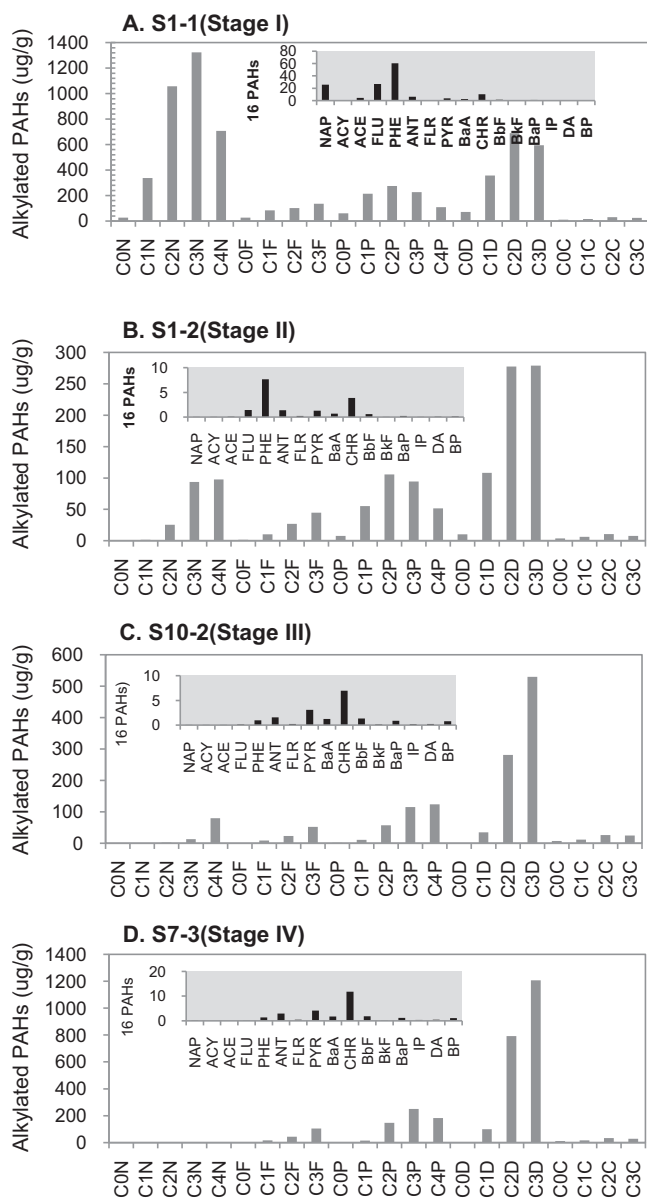
Fig. 4. Profiles of PAHs including 16 EPA PAHs and alkylated PAHs according to their weathering stages. (A) S1-1 (Stage I), (B) S1-2 (Stage II), (C) S10-2 (Stage III) and (D) S7-3 (Stage IV).

Fig. 5. Double ratio plots using alkylated phenanthrenes and dibenzothiophenes. (A) C2D/C2P vs. C3D/C3P, (B) 4-mD/1-mD vs. 2/3-mD/1-mD. Refer to Table 4 for abbreviations.

fingerprinting information from the diagnostic ratio due to weathering effects (Table 4).

3.3.3. PAHs fingerprints

Sum of alkylated PAHs and 16 PAHs (total PAHs) in the three cargo oils were in the range of 4.64–8.50 mg/g, where UZC had the highest, and KEC the lowest concentrations (Table 1). Alkylated PAHs were about 30 times higher than 16 PAHs in these crude oils. Unweathered or slightly weathered oil showed a very similar PAH compound profile, where naphthalenes accounted for more than 56% of total PAHs followed by dibenzothiophenes and phenanthrenes. As weathering proceeded, PAHs were also sequentially degraded according to their aromatic ring number and degree of alkylation (Fig. 4).

The environmental fate of C2- and C3-phenanthrene and dibenzothiophene are known to be similar for light to moderate weathered oils, and their relative distribution (double ratio plot) has been widely used for source identification [18] and source
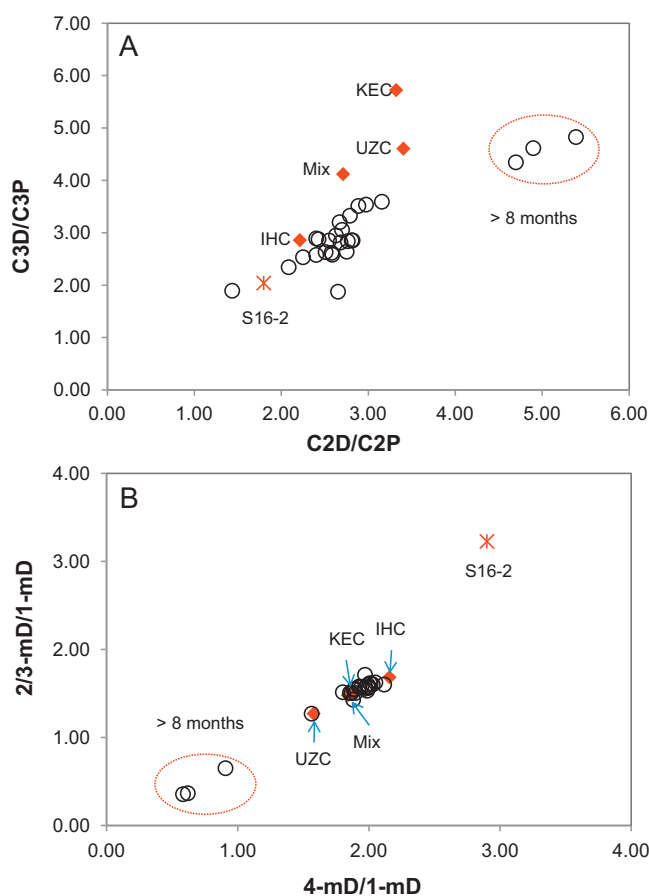
apportionment [19]. Double ratio plot distinguishes samples collected <1 month to 3 months from samples obtained 8 months after the spill easily. This group found a place close to IHC and Mix indicating its close similarity with them (Fig. 5A). This distinction may arise from the fact that short-term weathering generally does not affect diagnostic ratios of target PAHs, but biodegradation, a relatively long-term process can change values of these double ratios [4,20]. Thus it is probable that compositional change imposed by biodegradation distinguishes these groups (Table 4).

Isomeric patterns in C1-dibenzothiophene can also provide distinctive fingerprint information of the oil residue in the early stage of a spill [21]. Plot using ratios of 4-methyldibenzothiophene/1-methyldibenzothiophene and 2/3-methyldibenzothiophene/1-methyldibenzothiophene provides both source and weathering information (Fig. 5B). This plot brings further clarity to the assumption that oil residue after 8 months have gone certain degree of biodegradation, as they were widely separated in the plot. Interestingly, KEC, IHC, UZC and MIX are much closer to samples collected <1 month to 3 months. As in Fig. 5A plot the samples collected 8 months after the spill distinguish itself from others. Here too, biodegradation is a probable cause for this group separation. 4- and 2/3-methyldibenzothiophene are known to be selectively biodegraded faster than 1-methyldibenzothiophene and could be used as a biodegradation marker [20]. Non-matched sample S16-2 is clearly distinguished from spill sources as well. This can further be explained later using weathering categorization using Table 5. In an interesting way, these analyses reveal the deviation of compositional similarity between the stranded oils

Table 5
Weathering indices used for categorizing weathering stages of stranded oils.

Weathering stage	Weathering loss (%)[a]	Evaporation, (C13+C14)/(C25+C26)[b]	Evaporation + dissolution		Biodegradation		Photodegradation Chr/BaA, BaP/BeP[g]
			N/TPAH[c]	(C0N+C1N)/C2N[d]	C18/phy[e]	4-mD/1-mD[f]	
I	28.9	>1.0	>0.5	>0.2	>1.5	>1.5	–
II	37.7	0.1–1.0	0.1–0.5	0.05–0.2	>1.5	>1.5	–
III	47.2	0.01–0.1	0.01–0.1	<0.05	0.5–1.5	<1.0	–
IV	60.3	≤0.01	≤0.01	–	<0.5	<1.0	–

[a] Weathering loss (%) = (1 – ((H0/TPH0)/(H1/TPH1))) × 100; H0 and H1 are the concentration of C30-αβ-hopane in the source mixture oil and weathered samples. Hopane was normalized by TPH concentration.
[b] Ratio of *n*-C13 plus *n*-C14 to *n*-C25 plus *n*-C26 [25].
[c] Ratio of naphthalene to total PAHs [23].
[d] Ratio of C0-naphthalene plus C1-naphthalene to C2-naphthalene [25].
[e] Ratio of *n*-C18 to phytane [23].
[f] Ratio of 4-methyldibenzothiophene to 1-methyldibenzothiophene.
[g] Ratio of chrysene to benz[a]anthracene, ratio of benzo[a]pyrene to benzo[e]pyrene [26].

and spill sources over a period of time when physical process (e.g. evaporation) give way to biological process.

3.3.4. Biomarker fingerprints

Biomarker compounds in the cargo oil were in the range of 532–677 μg/g for total hopanes and 138–330 μg/g for total steranes, respectively. Stranded oils also contain high amounts of biomarkers and their relative ratio to total PAHs increased over time following the spill, reflecting their persistence.

Among hopanes, ratios Ts/Tm and H29/H30 provided distinctive source identification power (for abbreviations of biomarker compounds, refer to Table 4). Similarly, sterane biomarker ratios C28ββ/(C27ββ+C27ββ) and C29ββ/(C27~C28ββ) were very informative for differentiating sources (Table 4). Double ratio plots using these biomarker ratios could definitely identify sources and further define mixing of IHC and KEC (Fig. 6). UZC was clearly distinguished from other sources, due to its relatively high Ts/Tm value. Mixing between IHC and KEC was clear in C28ββ/(C27ββ+C29ββ) vs. C29ββ/(C27~C28ββ) double plot, where IHC and KEC appeared to be the endpoint (Fig. 6B).

As shown in Table 4, the combined ratios of the selected pairs of terpanes and steranes, especially the ratios of Ts/Tm, H29/H30, C28ββ/(C27ββ+C29ββ) and C29ββ/(C27~C28ββ), were apparently independent of weathering effects and useful in identifying spilled oil sources.

As the sizes of the ruptured tank holes were different, IHC was released faster than the other oils in the initial stage of spill [1]. This difference in release rate affected the relative percentage of spilled oil found in each region and confounded their fingerprint identification. Mixtures of IHC, KEC, and UZC were made according to their reported spill volume, 42.8% (IHC), 43.4% (KEC), and 13.8% (UZC), respectively. Source diagnostic ratios were compared with those of spill sources and stranded oils (Table 4). In the double ratio plots using PAHs and biomarkers, this mixture falls among stranded oils, giving evidence that stranded oils were mixtures of the three source oils in varying proportions. Further studies are needed to reveal the mixing rate and final allocation of spill sources.

3.4. Classification of weathering and their implications

3.4.1. Classification of weathering

Petroleum geochemists have developed their own scale for biodegradation of crude oil on a geological timescale in the original petroleum reservoir [22]. However, weathering on an environmental time scale normally does not result in the biodegradation of biomarkers [4]. Categorization into four levels of weathering is used, that is unweathered, slightly weathered, moderately weathered and severely weathered [5,23,24]. Here, we follow the criteria set by Sauer et al. [23] with some modifications.

Weathering characteristics and the progression were determined from the pattern changes in the distributions of saturated hydrocarbon (SHC) and PAH target analytes and weathering ratios like (C13+C14)/(C25+C26), N/TPAH, (C0N+C1N)/C2N, C18/phytane, 4-mD/1-mD, Chr/BaA and BaP/BeP (refer Table 5 for compounds acronyms). Each of the weathering ratios represents evaporation, dissolution, biodegradation and photodegradation, respectively [23,25,26]. Among them, photodegradation does not appear to be a major weathering process. Indices for photodegradation, Chr/BaA and BaP/BeP remained almost unchanged during this study period.
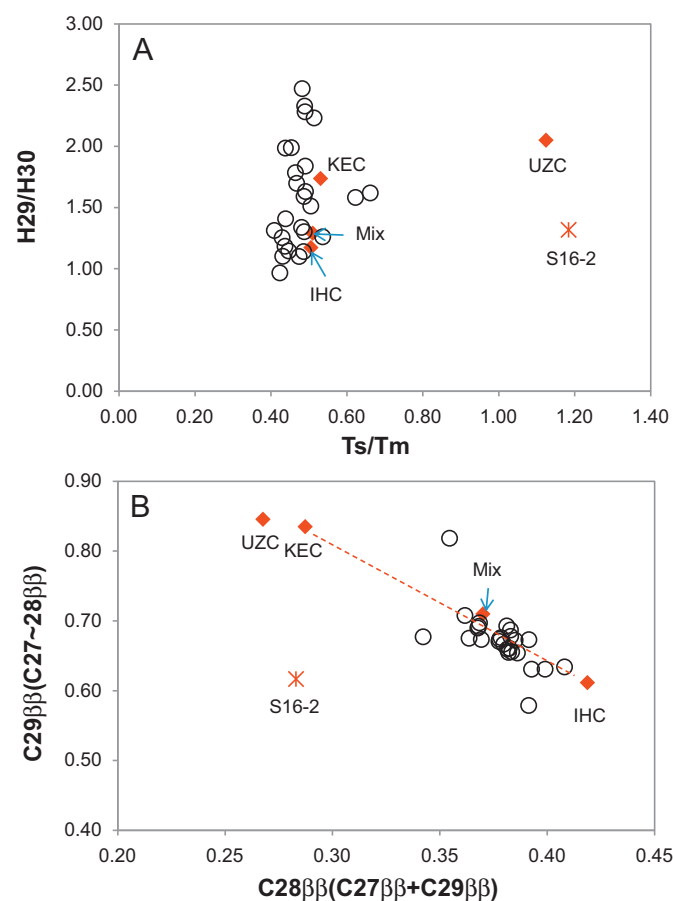

Fig. 6. Double ratio plots using biomarkers. (A) Ts/Tm vs. H29/H30, (B) C28ββ(C27ββ+C29ββ) vs. C29ββ(C27~C28ββ). Refer to Table 4 for abbreviations.

Stage I (initial weathering) represents oil residues for which evaporation was the dominant weathering process. It is characterized by a loss of SHCs up to n-C12, and the parent compounds of the two-ringed PAHs. Weathering indices for evaporation and dissolution in this stage are clearly distinguished from those of fresh oil and stage II oil. Stranded oils found at Taean County within 10 days after the spill are categorized as this group. Average percentage of oil loss was calculated as 28.9%, which is in line with ADIOS2 weathering model's evaporation results, confirming the dominant role of evaporation.

Stage II (moderate weathering) represents oil which has progressively reduced amounts of more volatile SHCs through n-C15 and exhibit loss of the C0-, C1- and C2-alkyl groups of the two- and three-ringed PAHs. The bimodal hump shape of UCM also becomes distinct. Most residual oils found within 3 months after the spill could be categorized into this stage, and average weathering loss was 37.7%. Weathering indices indicate that weathering loss at this stage is mainly due to the mixed effects of evaporation and dissolution.

Stage III (advanced weathering) represents oil in which the saturated hydrocarbon distribution pattern shows reduced SHCs relative to the isoprenoids. The PAH pattern is almost devoid of parent compounds of three ring aromatics and shows significant loss of C1-, C2-phenanthrene and dibenzothiophene. Two residual oil samples collected in summer 2008 (S10-2, S17-2) belong to this weathering stage. Approximately 47.2% of spilled oil hydrocarbon content has been lost by this stage of weathering. The C18/phytane and 4-mD/1-mD ratios clearly demonstrate the effects of biodegradation. This time lag for the initiation of biodegradation compared with other weathering process was also reported at other spills [25,26]. However, the widely used biodegradation indicator C18/phytane could underestimate the magnitude of oil biodegradation due to the fact that the isoprenoids are also biodegradable, even though at slower rates under most environmental conditions [4].

Stage IV (extreme weathering) represents oil which has undergone extensive transformation. The phytane and pristane isoprenoids completely dominate the distribution of SHCs. The PAH alkyl homologues have further decreased with only trace amounts of naphthalene and dominance by alkylated dibenzothiophenes. Residual oils sampled more than 8 months after the spill (S7-3, S15) were categorized as this stage, and average weathering loss was as high as 60.3%. As most identifiable peaks disappear, weathering indices also showed very low values, for example, (C13+C14)/(C25+C26) ratio ranged less than 0.01.

3.4.2. Implication of weathering on fingerprinting

Among various weathering processes, evaporation was the dominant process during the initial stage of the spill. Loss by evaporation was demonstrated by the weathering model and those results were well matched with decay rates and weathering loss. Oils classified as Stage I lost 28.9% of spilled oil which is similar to model results. Stage II oils showed the effects of evaporation and dissolution, with further weathering of 8.8% from the source oil. Oils belonging to these stages were collected within 3 months after the spill, and the half-life of TPH in spilled oil was calculated as 2.6 months, which is consistent with initial and moderate weathering exposure. Stage III and IV samples exhibited the time-lagged effects of biodegradation, which degrade as much as 60.3% in combination with other weathering processes.

Each weathering process has been monitored using compound profiles and weathering indices. Among them, biodegradation caused the most significant effects on the fingerprints of stranded oils. Even well-established double ratios of alkylated phenanthrenes and dibenzothiophenes were slightly changed and complicated the source identification. Only biomarkers could provide defensible source identification fingerprint in the Stage III and IV oils. However, it should be noted that there is no single ratio which can be used to positively identify the source of unknown spilled oil by itself without matching it to known oils [20]. Other diagnostic ratios (such as obtained from n-alkanes and alkylated PAH homologues) remain necessary and useful for oil source identification and characterization.

3.4.3. Implication of weathering on ecotoxicology

Weathering has significant effects on residual oil's ecotoxicology. Persistence of toxic subsurface oil and exposures, even at sublethal levels, could have long-term effects on wildlife [15]. The most important changes observed in the weathered oil in this study are the sequential decrease of the toxic aromatic fraction and increase of UCM. Within the aromatic fraction of the weathered oil, the relative abundance of naphthalenes, fluorenes and phenanthrenes decreased, while those of C2-, C3-dibenzothiophenes, and alkylated chrysenes increased.

As oil weathers the concentration of total aqueous PAH required to cause adverse effects is also lowered, because of proportionate increases in the more hydrophobic PAHs. When the average hydrophobicity increases, an enhancement in bioaccumulation occurs which in turn increase the potential of toxicity. Thus weathered oil does not equate well with decreased toxicity [7]. In addition to non-specific narcotic toxicity, AHR independent cardiac dysfunction, AHR2-dependent developmental toxicity, and hepatic response mediated toxicity have been observed for PAHs common to weathered oil [27–31]. Among the residual oil-related PAHs, the toxicity of 16 PAHs such as phenanthrene, pyrene, and chrysene have been well characterized but not for sulfur containing heterocyclics like dibenzothiophene [32–34]. In this study the portion of dibenzothiophenes to total PAHs increased as the weathering proceed: I (28.9%), II (48.2%), III (62.0%), IV (67.2%). Considering that as much as three times higher levels of dibenzothiophenes to phenanthrenes in the weathered oil, care should be taken to consider the toxicity of dibenzothiophenes. The focus of ecotoxicology studies on weathered oil need to include not only the total amount of residual PAHs, but also the composition [7].

In addition to toxicity of resolved aromatic fractions, unveiling the components of UCM and their potential toxicities is an emerging research field [35–39]. GC separation techniques like GC × GC facilitate an understanding of the sources, weathering, and toxicity of UCM hydrocarbons [37–39]. Among the numerous unknown UCM aromatics, the presence and toxicity of branched alkyl benzenes, branched alkyl indanes and branched alkyl tetralines were revealed in mussel tissue, emphasizing the need for further effort into UCM characterization and toxicity [38]. Residual oils classified as weathering stage III and IV consist of more than 90% UCM, indicating that their contribution to residual toxicity also needs to be included in long-term monitoring studies.

4. Conclusion

Identification of spill sources in stranded oils and characterization of their weathering status is crucial to ecotoxicological study and remediation strategies following a spill. This study is the first attempt at oil spill fingerprinting of the Hebei Spirit oil spill from December 2007. Weathering model results following the spill indicated evaporation as the dominant process, consistent with sequential changes found in the chemical composition over time and the determined half-life of 2.6 months. Tiered approaches using GC–FID and GC–MS analysis successfully identified background contamination and confirmed the identity of stranded oil to spill sources. Weathering status of stranded oil was evaluated using composition profiles of saturated hydrocarbons, polycyclic

aromatic hydrocarbons and various weathering indices. Most samples collected 8 months after the spill were categorized in advanced or extreme weathering stages. Gradual change in hydrocarbon composition in residual oils due to weathering emphasized the need for adaptive ecotoxicological approaches.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.055.

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