



Asphaltene content and composition as a measure of *Deepwater Horizon* oil spill losses within the first 80 days



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ABSTRACT

The composition and content of asphaltenes in spilled and original wellhead oils from the Deepwater Horizon (DWH) incident provide information on the amount of original oil lost and the processes most responsible for the losses within the first 80 days of the active spill. Spilled oils were collected from open waters, coastal waters and coastal sediments during the incident. Asphaltenes are the most refractory component of crude oils but their alteration in the spilled oils during weathering prevents them from being used directly as a conservative component to calculate original oil losses. The alteration is reflected by their increase in oxygen content and depletion in ¹²C. Reconnaissance experiments involving evaporation, photo-oxidation, microbial degradation, dissolution, dispersion and burning indicate that the combined effects of photo-oxidation and evaporation are responsible for these compositional changes. Based on measured losses and altered asphaltenes from these experiments, a mean of 61 ± 3 vol% of the original oil was lost from the surface spilled oils during the incident. This mean percentage of original oil loss is considerably larger than previous estimates of evaporative losses based on only gas chromatography (GC) amenable hydrocarbons (32–50 vol%), and highlights the importance of using asphaltenes, as well as GC amenable parameters in evaluating original oil losses and the processes responsible for the losses.

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1. Introduction

The *Deepwater Horizon* (DWH) incident (April 20 to July 15, 2010) represents the largest oil spill in U.S. waters with an estimated 4.9 million barrels of oil being released from the ruptured Macando-1 wellhead into the Gulf of Mexico (Ramseur, 2010; The Federal Interagency Solutions Group, 2010; Graham et al., 2011). One critical question is where has this spilled oil gone (Lubchenco et al., 2010)? This question becomes more inquiring with the observation that no spilled oil was observed on the open ocean surface 36 days after the wellhead was sealed (Ramseur, 2010). Relevant data have been reported on the fate and source of the spilled oil based on its composition as determined by gas chromatography (GC; Reddy et al., 2012) and its coupling with mass spectrometry (GC-MS; Rosenbauer et al., 2010). However, identifiable GC amenable hydrocarbons account for less than half

of crude oil by mass (Martin et al., 1963; Wang et al., 2003; and Reddy et al., 2012) and as a result, do not always give a complete account of the fate of the spilled oils. Here we employ the non-GC-amenable component in crude oil referred to as asphaltenes. Asphaltenes are the highest molecular weight (500–1000 Da) and most refractory component in crude oils (Mullins, 2010), and they are preferentially concentrated in weathered oil as the more labile lower molecular weight hydrocarbons are lost (Brunnock et al., 1968). The molecular complexity of asphaltenes requires them to be defined operationally as components in crude oil that are soluble in aromatic solvents and insoluble in light alkanes. Asphaltene contents are based on whole-oil mass, and if conservative during weathering, offer a fixed quantity to determine overall losses experienced by spilled oils. The objective of this study is to evaluate the utility of asphaltene content and composition to determine the amount of original oil lost from DWH spilled oil in the first 80 days of the incident.

Various processes collectively weather oil in the oceans. These processes include evaporation, dispersion, microbial degradation, dissolution and photo-oxidation. All of these natural processes

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act collectively on spilled oil to different degrees and rates depending on the character of the original oil, the environmental conditions and duration of exposure. In addition to these natural processes, the DWH spilled oils may have also been subjected to anthropogenic influences including controlled burning (Schaum et al., 2010) and dispersants (Kujawinski et al., 2011). As a result, efforts to evaluate specific processes responsible for given amounts of oil lost are difficult because of overlap in their resulting diagnostic characteristics. This study estimates the collective losses of all the processes and possible anthropogenic influences by comparing asphaltene contents of the original wellhead oil with those of spilled surface-oil samples collected from open waters, coastal waters and coastal sediments during the first 80 days of the incident (Fig. 1 and Table 1). The open-water samples consist of spilled oils floating on the water at distances > 5 km from the coastline. Spilled oils and tars in the coastal-water samples occur floating on waters in marsh areas or immediately offshore from a beach. Sediment samples are oils and tars in direct contact with sediments. Visually, all of the spilled samples appear to be recent occurrences related to the active spill. This is confirmed by comparison of GC–MS analyses of terpane biomarkers in the spilled-oil samples with those in the original wellhead oils. Correlation of 31 identified terpanes in the spilled oils had coefficients of determination (R^2) at or higher than 0.99 (Appendix A) with the wellhead oil. GC analyses of the spilled oils indicate they experienced minimal aerobic microbial degradation with a biodegradation ranking (Peters and Moldowan, 1993) of < 3 based on the presence of C_{20+} n -alkanes and no enhancement in pristane and phytane relative to the n -alkanes (Appendix B). The GC analyses also showed the spilled and original oils contained no detectable Corexit dispersant based on the absence of bis[2-ethylhexyl]sulfosuccinate as described by Place et al. (2010). Although asphaltenes

are the most refractory component in crude oil, they have been shown to be susceptible to some alteration during subsurface and surface oil degradation (Liao et al., 2009; Pesarini et al., 2010). The conservativeness of asphaltenes and whether changes in their composition during oil weathering could be equated to overall oil losses was examined in bench and rooftop experiments conducted on the original wellhead oil.

2. Materials and methods

2.1. Original oil collection

Two original oil samples were collected from a riser insertion tube by TestAmerica on the Discoverer Enterprise drillship and processed and shipped under standard chain of custody protocols. One original oil sample was collected on May 20, 2010 downstream of the separators in 1 l amber glass, narrow neck bottles with no added preservatives. Initially, samples were at elevated temperatures reflecting the subsurface reservoir temperature. The sample was transported at ambient temperature to the Sample Receiving Office at the BP Houma Incident Command Center, Shriever, LA, where it was placed in refrigerated (~ 40 °F; ~ 4.4 °C) storage. The sample used in this study was transferred on July 4, 2010 to a 1 l aluminum container and was maintained in refrigerated storage prior to shipping. It has been reported that the sample may contain some Nalco EC9323A defoamer, methanol, VX9831 oxygen scavenger/catalyst solution and DPnB (i.e., 1-(2-butoxy-1-methylethoxy)-2-propanol), which is a marker used to indicate the presence of Corexit 9500 and 9527 dispersants. Two aliquots of this sample are designated as sample 1 and sample 16. The other original oil sample designated as sample 20 was collected May 21, 2010, and was obtained from B&B Laboratory, College Station, TX.

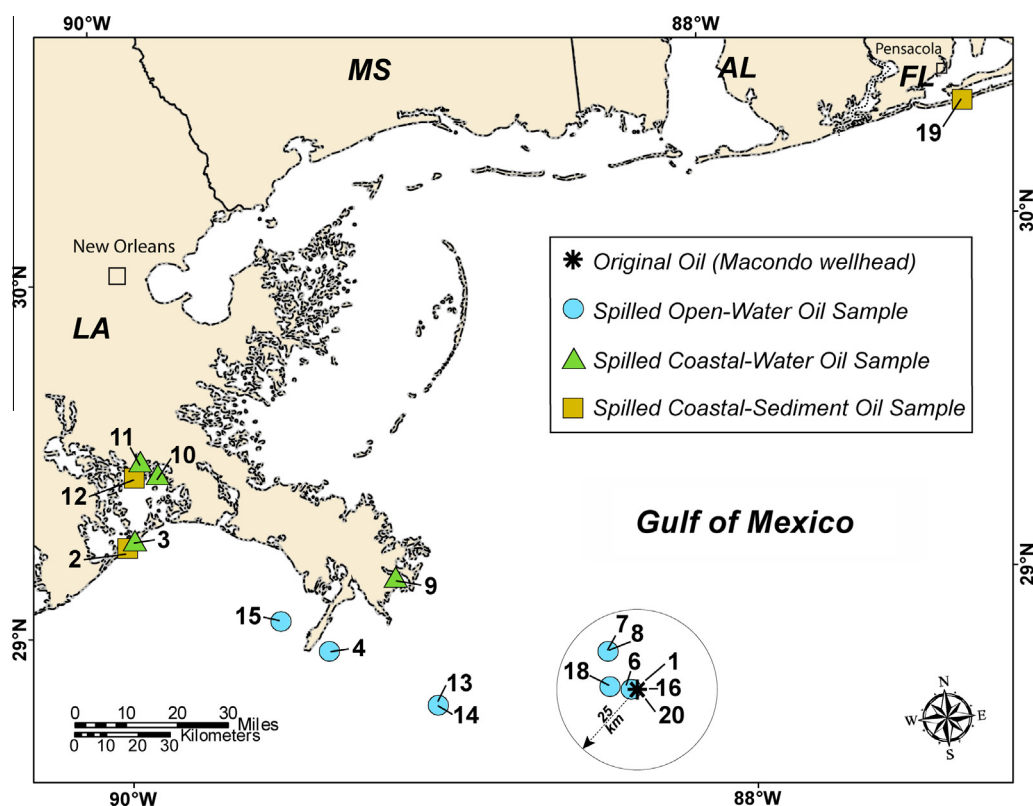


Fig. 1. Map showing the type and location of original oil and spilled oil samples. Sample numbers correspond to those in Table 1. Open-water samples are floating on water more than 5 km from the coast; coastal-water samples are floating on waters within 5 km of the coast; coastal-sediment samples are in contact with coastal sediments. Sample numbers are adjacent to symbols and are described with attributes in Table 1.

Table 1
Description of original (O), spilled (open-water, OW; coastal-water, CW, and coastal-sediment, CS), and experimental (Exp) oil samples with their asphaltene (asph) content, $\delta^{13}\text{C}$ value, oxygen content, and original oil losses in wt% and vol%.

Sample/exp no.	Sample type	Duration (d)	Sample description	Asph (wt% oil)		$\delta^{13}\text{C}_{\text{asph}}$ (‰ VPDB)		Oxygen (wt% asph)		Original oil lost	
				Mean	$\pm(n)$	Mean	$\pm(n)$	Mean	$\pm(n)$	(wt%)	(vol%)
1	O	30	Original wellhead oil	1.0	0.1 (6)	-27.63	0.08 (5)	0.88	0.07 (4)	0.0	0.0
16	O	30	Original wellhead oil	0.9	0.1 (6)	-27.57	0.12 (3)	0.98	0.07 (2)	0.0	0.0
20	O	31	Original wellhead oil	0.9	0.0 (2)	-27.61	0.18 (4)	1.03	-(1)	0.0	0.0
4	OW	17	Floating oil	7.4	-(1)	i.s.		11.36	0.85 (3)	51.6	56.7
6	OW	79	Floating oil	7.6	0.8 (2)	-26.50	0.07 (3)	9.4	0.02 (2)	51.7	56.8
7	OW	79	Floating oil	8.8	-(1)	i.s.		6.47	1.11 (5)	52.4	57.6
8	OW	79	Floating oil	11.1	-(1)	i.s.		8.64	0.72 (5)	53.9	59.2
18	OW	17	Floating oil	7.7	-(1)	-26.29	0.04 (3)	i.s.		51.8	56.9
13	OW	80	Floating emulsion	20.4	0.2 (2)	-26.31	0.05 (7)	13.62	0.05 (2)	59.7	65.6
14	OW	80	Floating emulsion	22.8	0.0 (2)	-26.28	0.05 (3)	14.06	0.15 (2)	61.2	67.3
15	OW	80	Floating tar w/seaweed	14.8	0.2 (2)	-26.31	0.14 (4)	11.97	0.09 (2)	56.2	61.8
3	CW	50	Floating oil	12.6	0.8 (2)	-26.38	0.04 (3)	12.7	0.01 (2)	54.8	60.3
9	CW	78	Heavily oiled vegetation	15.1	0.0 (2)	-26.31	0.12 (6)	13.46	0.00 (2)	56.4	62.0
10	CW	80	Heavily oiled vegetation	17.8	0.2 (2)	-26.43	0.05 (3)	13.13	0.23 (2)	58.1	63.8
11	CW	80	Heavily oiled vegetation	20.1	0.2 (2)	-26.42	0.05 (6)	12.49	0.08 (2)	59.5	65.4
2	CS	50	Tar on top of sand beach	16.0	-(1)	-26.26	0.06 (5)	12.98	0.08 (2)	57.0	62.6
12	CS	80	Oil/tar on marsh sediment	16.5	0.0 (2)	-26.46	0.11 (3)	12.15	0.16 (2)	57.3	62.9
19	CS	67	Oil/tar on sand beach	16.1	-(1)	-26.30	0.03 (3)	i.s.		57.0	62.7
41	Exp	3.22	Evaporation (evap.)	1.6	-(1)	-27.52	0.24 (4)	4.72	0.24 (2)	48.3	53.1
40	Exp	0.98	Photo-oxidation/evap.	5.4	-(1)	-26.34	0.17 (5)	8.97	0.13 (3)	50.1	55.1
44	Exp	1.73	Photo-oxidation/evap.	9.1	-(1)	-26.43	0.11 (6)	11.13	0.11 (3)	52.0	57.1
43	Exp	2.51	Photo-oxidation/evap.	9.8	-(1)	-26.38	0.06 (4)	11.56	0.39 (3)	52.9	58.1
42	Exp	3.22	Photo-oxidation/evap.	12.0	-(1)	-26.30	0.03 (5)	12.97	0.07 (3)	55.2	60.7
37	Exp	0.004	Control burn	1.9	-(1)	-28.91	0.25	1.81	0.06 (3)	50.2	55.2
24	Exp	3.0	Dispersant/dissolution (diss)	0.7	-(1)	-29.03	0.09 (3)	24.65	-(1)	ND	ND
32	Exp	39.0	Biodegradation./diss./evap.	9.8	-(1)	-26.86	0.06	3.72	0.01 (2)	ND	ND

Duration for spilled oils is amount of time from April 20, 2010 to when the samples were collected. Number of replicate analyses denoted as n and, insufficient sample for analysis denoted as i.s. Bold-print values for wt% of original oil lost are calculated from the expression given in Fig. 4a. Vol% of original oil lost is calculated from the expression $\text{vol}\% = 1.099 \text{ wt}\%$ derived from data given in S.L. Ross Environmental Research Ltd. (2010). ND denotes not determined.

This sample is considered pristine in that it contains no additives and is an aliquot of the same sample designated as M-1 in the reconnaissance study by Rosenbauer et al. (2010).

2.2. Spilled oil collection

Oil samples from the ocean surface, marsh areas, and beaches were collected in amber glass vials. All of the ocean and marsh samples included intermixed seawater. Following collection, all environmental oil samples were stored on ice in coolers during transport and refrigerated once in the laboratory. Spilled floating oil and tar on top of beach sand that contained no sediment or vegetation debris (i.e., samples 2, 3, 4, 6, 7, 8 and 18) were centrifuged at 2200 rpm for 10 min in a 7 ml glass vial to separate the spilled oil from water included in the sample. The top oil layer was carefully scraped or transferred by Pasteur pipette into a tared 7 ml vial to determine how much oil was being used for asphaltene isolation.

Oil spill samples containing sediment or plant material (i.e., samples 9, 10, 11, 12, 13, 14, 15 and 19) were transferred into 40 ml centrifuge tubes and filled with ~25–30 ml of chloroform. The tubes were mixed with a vortex mixer for 30 s and then centrifuged at 2200 rpm for 10 min. Heavy particulate matter such as large plant fragments with sand separated to the bottom, while water and less dense plant fragments separated to the top layer above the chloroform extract. The chloroform extract was filtered through 55 mm GF/A Whatman glass microfiber filters to remove additional particulate matter. The remaining particulate matter in the centrifuge was then rinsed 3 more times with 15–20 ml of chloroform and centrifuged and filtered as described above. The filtrate was filtered through a 0.45 μm PTFE syringe filter and collected in a tared 7 ml vial. The amount of spilled oil extracted was determined by evaporation of chloroform with a stream of nitrogen to approximately 0.5 ml and then by CentriVap to a constant weight at room temperature.

The recorded weight of the concentrated spilled oil was used for asphaltene isolation.

2.3. Asphaltene isolation

Fifty to 100 mg of oil or spilled oil samples collected off separated water after centrifuging were placed in a 7 ml glass vial with ~2 ml of *i*-octane. The contents were thoroughly mixed with a vortex mixer at low speed and asphaltenes were allowed to precipitate at room temperature over a 2 h or more duration. For the spilled oils isolated in chloroform, a known volume and concentration (equivalent to 50–100 mg) of sample in chloroform was placed in a glass vial. The volume was then reduced by evaporation to ~1 ml with a stream of nitrogen. An approximately equal volume of *i*-octane was added to the vial and mixed with a vortex mixer at low speed. The volume was again reduced by evaporation to ~1 ml with a stream of nitrogen. This was repeated three times or more until the chloroform was completely displaced by *i*-octane. Asphaltenes were allowed to precipitate at room temperature over at least a 2 h duration. The precipitated asphaltenes were separated from the remaining liquid (i.e., maltene fraction) by first pipetting the liquid to a filter system consisting of a Luer-lock glass syringe (5 ml) with a 0.45 μm PTFE syringe filter (25 mm diameter) vertically mounted. Approximately 1 ml of *i*-octane was added to the asphaltenes remaining in the original vial and transferred to the filter system. This *iso*-octane rinse and filtering was repeated two times. The asphaltenes remaining in the original vial were then dissolved with 3–5 ml of chloroform and transferred to the same filter system and collected in a tared 7 ml vial. This final chloroform rinse and filtering omits any inorganic matter (clay minerals or silt) that may have been present with the asphaltenes. The amount of asphaltene was determined after evaporation of chloroform with a stream of nitrogen to approximately 0.5 ml and then by CentriVap to a constant weight at room temperature.

Iso-octane is used in the above deasphalting procedure because at the lower pressures (83–85 kPa) in the Denver laboratory (1713 MSAL) it is significantly less volatile than *n*-pentane and *n*-hexane. From our experience, iso-octane is also a better displacement solvent for chloroform than *n*-heptane.

2.4. Experiments

The dissolution and dispersion experiment (No. 24) was conducted with 0.95 g of Corexit dispersant, 1.64 g of original oil (sample 1) and 650 ml of artificial seawater (Instant Ocean) in a 1000 ml glass separatory funnel closed with a ground glass stopper. The high ratio of dispersant to oil used in this experiment (0.6) was intended to exaggerate the influence of Corexit on the asphaltenes rather than use the estimated lower ratio of 0.1 to simulate the actual surface spill application (The Federal Interagency Solutions Group, 2010). The closed separatory funnel with contents was agitated in a wrist-action shaker for three days. During the shaking no distinct oil layer was observed, but when the shaking was stopped at the end of the experiment, a distinct oil layer developed on top of the water surface. This oil layer with dissolved Corexit accounted for 70 wt% of the original mixture of oil and Corexit used in the experiment.

The experiment that collectively considered microbial degradation, evaporation and dissolution (No. 32) was conducted under aerobic conditions on 2 ml of original oil (sample 16) with 50 ml of unfiltered Gulf of Mexico seawater in a 250 ml Erlenmeyer flask that was baffled in an orbital shaker for 39 days at room temperatures. No nitrogen or phosphorous supplements were added. The controlled burn experiment (No. 37) was conducted on 5 g of original oil (sample 16) and 50 g of artificial seawater (Instant Ocean) in a 100 ml borosilicate beaker. The beaker was placed inside a 1000 ml borosilicate beaker, which was placed on a top-loading, 0.01 g readability balance with a 2 cm thick Marinite® plate on the balance pan. The oil was ignited under a fume hood and its weight loss monitored by the balance. The burn was stopped by covering the beaker with a Petri cover dish after 5.5 min when 50.2 wt% of the original oil was lost. Once cooled to room temperature, the floating oil was collected and its asphaltenes isolated.

The evaporation and photo-oxidation/evaporation experiments (Nos. 40 through 44) were conducted on the rooftop of Building 20 in the Denver Federal Center over a rain-free 9 d period (May 31 to June 8, 2011). The five 10 cm diameter dishes with 2.5 g of original oil (sample 16) were secured with sheet metal hexagonal washer-head screws to a 1.9 cm thick, 60 × 90 cm plywood board with a white painted surface. Distances between the dishes were 6–8 cm. The board with secured dishes was weighted with an 11.5 kg lead brick and placed on the south side of the rooftop where it was exposed to direct sunlight throughout the day. Four of the oil-bearing dishes were exposed during the day to natural sunlight and covered during the night in case of rain. The total sunlight exposures were 0.98, 1.73, 2.51, and 3.22 days (Table 1; Nos. 40, 44, 43, and 42, respectively). The fifth oil-bearing dish (No. 41) was also placed along with the others during the experiments, but it remained covered with an aluminum foil wrapped glass cover for the full 3.22 day duration. The foil cover omitted sunlight but was not air tight, which allowed evaporation to occur with no accompanying photo-oxidation.

2.5. Asphaltene analyses

The $\delta^{13}\text{C}$ values of asphaltene isolates were determined using an elemental analyzer–isotope ratio mass spectrometer (EA–IRMS). Asphaltene samples and analytical standards were individually weighed (~0.3 mg) into small tin sample cups. Samples were introduced into a Dumas combustion EA via zero-blank

autosampler. The samples were burned at 1030 °C in an oxygen atmosphere; the combustion products were dried using a MgCl_2 trap, then swept into a preparative GC column by carrier helium. Carbon dioxide was separated chromatographically, and final purified CO_2 was passively drawn via open split into the source of a Micromass Optima IRMS for subsequent carbon isotope analysis. The final carbon isotope values represent the average of multiple replicate analyses (generally, $n > 2$) with a standard deviation of better than 0.2‰. All final values are reported relative to the international standard, Vienna Pee Dee Belemnite (VPDB) carbonate. Oxygen content of asphaltenes was determined on an EA using BBOT (2,5-bis[5-tet-butyl-benzoxazol-2-yl]thiophene) and acetanilide as standards.

3. Results and discussion

Asphaltene contents range from 7.4–22.8 wt% of the spilled oils, whereas the original wellhead oils contain only 0.9–1.0 wt% asphaltenes (Table 1). Using these values with the assumption that no alteration to the mass of asphaltenes occurs, results in an unreasonable mass balance indicating 85–95 wt% of the original oil was lost from the spilled oil samples in the first 80 days of the incident. This clearly indicates that asphaltenes are not conservative during weathering. As shown in Fig. 2 and Table 1, compositional changes to the asphaltenes of the spilled oils are most apparent in their elevated oxygen contents and ^{12}C -depleted $\delta^{13}\text{C}$ values. Original wellhead asphaltenes have mean $\delta^{13}\text{C}$ values and oxygen contents of $-27.6 \pm 0.12\text{‰}$ and $0.93 \pm 0.07\text{ wt\%}$, respectively. Asphaltenes of the spilled oils are consistently 1.2‰ depleted in ^{12}C with oxygen contents from 6.5–14.1 wt% (Table 1). Bench and rooftop experiments were conducted to evaluate the processes responsible for these differences and determine whether the altered asphaltenes could still be used to determine original oil losses. These reconnaissance experiments were conducted on aliquots of the original wellhead with the sole intent to simulate the compositions observed in the asphaltenes of the spilled oils. The experiments include dissolution and dispersion (Exp. No. 24), combination of microbial degradation, evaporation and dissolution (Exp. No. 32), controlled

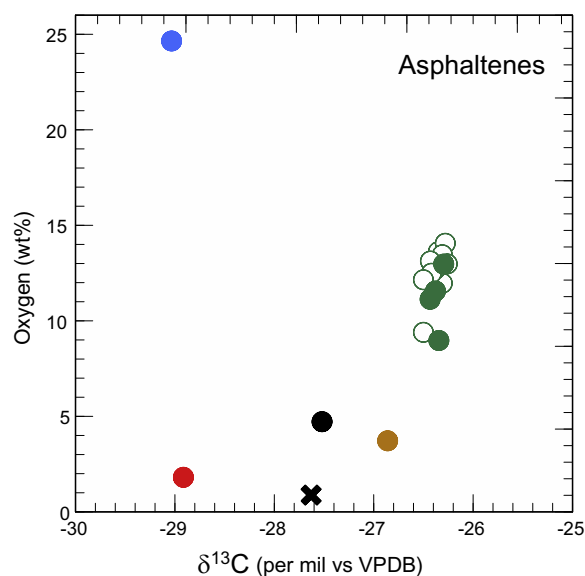


Fig. 2. Plot of asphaltene oxygen content and $\delta^{13}\text{C}$ of original oil (x), spilled oils (○), and experimental oils from evaporation experiment No. 41 (●), photo-oxidation and evaporation experiments Nos. 40–44 (●), controlled burn experiment No. 37 (●), dissolution with dispersant experiment No. 24 (●), and biodegradation/dissolution/evaporation experiment No. 32 (●). Specifics on experiments are given in 2.4 Experiments.

burning (Exp. No. 37), evaporation with no sunlight (Exp. No. 41) and photo-oxidation with evaporation (Exp. Nos. 40, 42–44).

The asphaltene content of the oil recovered from the dissolution and dispersion experiment (Exp. No. 24), as expected, was reduced to 0.7 wt% compared to the original oil because of the addition of Corexit (Table 1). The distinctly different asphaltene oxygen content and $\delta^{13}\text{C}$ value of this floating oil compared to the original and spilled oils indicate that dissolution and dispersion with Corexit are not responsible for the changes observed in the asphaltenes of the spilled oils (Fig. 2). It is also noteworthy, that with the exception of the Corexit compounds, the GC trace of the recovered oil shows no signs of evaporative losses (Appendix C). The experiment combining microbial degradation, evaporation and dissolution (Exp. No. 32) did show a significant increase in the asphaltene content (9.8 wt%), but the oxygen content and $\delta^{13}\text{C}$ values of the asphaltenes are not similar to those from the spilled oils (Fig. 2). The GC trace of the recovered oil shows only *n*-alkane losses up to C_{12} , which is indicative of evaporation and minimal levels of microbial degradation (Appendix C). This is similar to the GC traces of some of the spilled oils (Appendix B). Asphaltene content of the oil recovered from the controlled burn experiment (No. 37) was conservative in that it doubled with a 50 wt% decrease in the original oil (Table 1). However, the oxygen content and $\delta^{13}\text{C}$ value did not simulate those of the asphaltenes of the spilled oils (Fig. 2). The asphaltene content of the evaporation experiment (No. 41; 1.6 wt%) was conservative within the analytical error for a 48.3 wt% oil loss (Table 1), which yields a calculated range of asphaltene contents from 1.5–2.1 wt%. Oxygen content of the recovered asphaltene increased to only about half that observed in asphaltenes from the spilled oils and the $\delta^{13}\text{C}$ value remained unchanged (Fig. 2). Although the previously discussed experiments did not simulate the observed changes in content, oxygen and $\delta^{13}\text{C}$ values of the asphaltenes in the spilled oils, the experiments combining evaporation and photo-oxidation (Exp. Nos. 40 and 42–44) did simulate the observed changes (Fig. 2). In addition to providing similar $\delta^{13}\text{C}$ values and oxygen contents (Fig. 2), the asphaltene

contents of these experiments at 0.98, 1.73, 2.51, and 3.22 days provide a trend that coincides with those of the spilled oils (Fig. 3).

Surface tars and heavy oils exposed to the atmosphere in sandstone outcrops and soils experience an overall increase in oxygen content (Charrié-Duhaut et al., 2000). Sunlight experiments have also shown that photo-oxidation of initially high-asphaltene oils resulted in an increase in asphaltene content from 4 wt% to 7 wt% after 70-h exposures (Garrett et al., 1998). Although these increases are significant, they pale in comparison to the experimental increase from 0.9 wt% to 12 wt% in asphaltene content after 3.22 days in the photo-oxidation/evaporation experiments and the natural increase from 0.9 wt% to 22.8 wt% in asphaltene contents of the DWH oil spill samples (Fig. 3). The specific reactions by which photo-oxidation increases the mass, oxygen and ^{13}C of asphaltenes remain to be determined. However, the high susceptibility of aromatics to the addition of oxygen in photo-oxidation experiments of crude oils (Garrett et al., 1998; Pesarini et al., 2010) suggests that increasing asphaltene mass may be a result of assimilation of oxidized aromatic moieties of the original oil. This is supported, in part by the aromatic fraction of the original oil being depleted in ^{12}C by 1.6‰ (VPDB) relative to the asphaltenes. This general reaction scheme is also in agreement with that proposed by Maki et al. (2001) based on photo-oxidation experiments conducted on devolatilized and biodegraded oil. It is noteworthy that GC–MS biomarker signatures typically used to correlate spilled oils to their source (Rosenbauer et al., 2010) are not affected by photo-oxidation in field studies (Jézéquel et al., 2003). Although compositional changes and increasing mass of asphaltenes can be explained by photo-oxidation, the accompanying reactions responsible for the enhanced oil lost as observed in the experiments (Appendix D) remain to be determined.

The ability of the photo-oxidation/evaporation experiments to simulate increasing asphaltene contents and the accompanying $\delta^{13}\text{C}$ and oxygen compositional changes observed in the DWH spilled oils (Fig. 3) attests to the importance of photo-oxidation in combination with evaporation. Although differences in atmospheric conditions (e.g., ultraviolet radiation, humidity and pressure) between Denver and the Gulf of Mexico excludes applying rates of change, these experimental results do provide a useful relationship between altered asphaltene content and amount of original oil lost, as shown in Fig. 4A. This linear regression includes the collective effects of evaporation and photo-oxidation. Because existing budgets on the fate of the oil are volume based (Ramseur, 2010; The Federal Interagency Solutions Group, 2010), the weight percentages are converted to volume percentages (Table 1) with a linear regression based on evaporative volumes and residual-oil densities presented by S.L. Ross Environmental Research Ltd. (2010). The resulting volume based expression for original oil lost is shown in Fig. 4B with the measured experimental data and the calculated losses for the DWH spilled oils. Within the experimental range of 5.4–12 wt% asphaltene content, the regression indicates that the DWH spilled oils have lost between 56.7 vol% and 59.2 vol% of original oil. Extrapolating the regression beyond the experimental results to DWH spilled oils with as much as 22.8 wt% asphaltenes, yields original oil losses as high as 67.3 vol%. The resulting calculated range of original oil lost in the first 80 days is 56.7–67.3 vol% with a rounded mean of 61 ± 3 vol%. It is noteworthy that differences in the GC amenable hydrocarbons did not suggest this amount or range of losses (Appendix E).

The results in Fig. 4B provide some insights on the range of oil losses in each of the three sampling sites. The open-water spilled oils extend over the full range of losses from 56.7–67.3 vol%. The open-water samples collected within a 25 km radius of the well-head (Nos. 6, 7, 8, 18; Fig. 1) have the lowest oil losses of 56.8–59.2 vol%, irrespective of when they were collected from the time

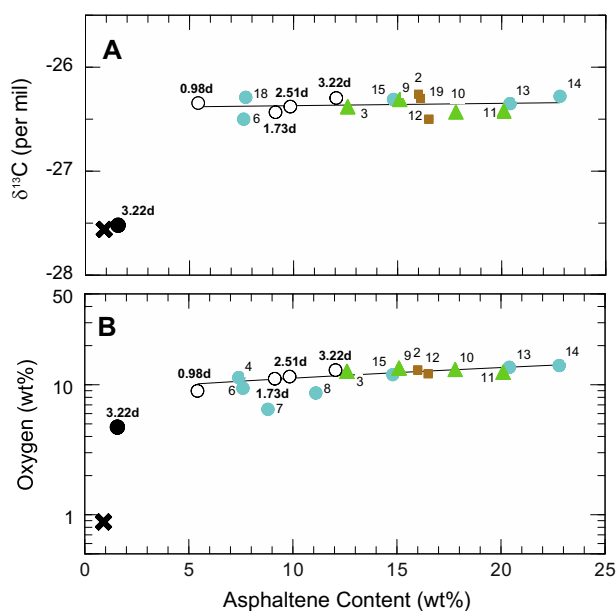


Fig. 3. Asphaltene content of original oil (x), spilled oils in open waters (●), coastal waters (▲), coastal sediments (■), and experimental oils subjected to evaporation (●) and photo-oxidation with evaporation (○) versus asphaltene $\delta^{13}\text{C}$ values (A) and oxygen content (B). Spilled oil sample numbers and duration of experiments in days are adjacent to symbols and are described with attributes in Table 1.

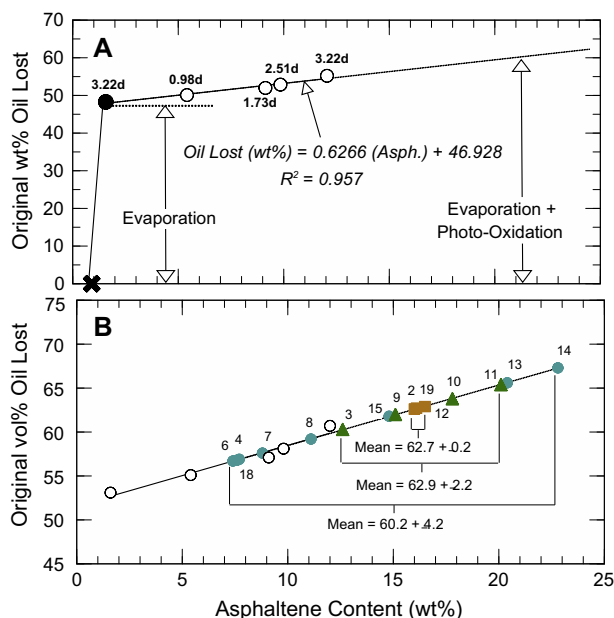


Fig. 4. (A) Relation between asphaltene content and measured wt% original oil lost in evaporation (●) and photo-oxidation with evaporation experiments (○). (B) Measured experimental losses (○) from (A) recalculated as volume% losses of original oil (Table 1) with superimposed calculated vol% original oil lost from DWH spilled oils determined by their asphaltene content using the experimental expression in (A) recalculated as vol% lost. Mean and standard deviation for open-water (●), coastal-water (▲), and coastal-sediment (■) oil samples given in brackets. Spilled sample numbers and duration of experiments in days are respectively given adjacent to symbols and in Table 1.

of the incident (i.e., 17 and 79 days). This would be expected considering their close proximity to the submerged leaking wellhead in which newly discharged oil was continuously coming to the water surface. Compared to the open-water samples, coastal-water spilled oils have a narrower range of oil loss (60.3–65.4 vol%; Fig. 4B). Samples 10 and 11 from marshes at the north end of Barataria Bay have the highest losses (63.8 vol% and 65.4 vol%, respectively) and were collected 80 days into the incident. Coastal-water sample 9, which was also collected in a marsh 80 days into the incident, has a lower oil loss of 62.0 vol%, but is closer to the wellhead source. Sample 3 has the lowest oil loss (i.e., 60.3 wt%) of the coastal-water spilled oils and was collected 50 days into the incident at the mouth of Barataria Bay. The coastal-sediment samples show a consistent 62.7 ± 0.2 vol% oil loss from quartz rich sands of Pensacola, FL (sample 16) to the more feldspar rich sands of Barataria Bay, LA (samples 2 and 12), irrespective of different collection times (Fig. 4B). This may be a result of shielding of the spilled oils from direct atmospheric exposure by sediment, water or weathered crusts. Although consistent explanations, as given above to account for the amount of oil lost in different settings and times can be postulated, they remain equivocal without a known history (i.e., pathway and weather) of the spilled samples. This brings to light the need in future oil spills to establish protocols for collecting samples from designated slicks and monitoring their history and compositional changes as they migrate with time from their source.

The rounded mean of $61 \pm 3\%$ loss of original surface spilled oil in the first 80 days of the incident is considerably larger than the 37–50% range of evaporative losses and the overall 23% evaporative or dissolution losses estimated in the expected case of the Federal Government's Oil Budget (The Federal Interagency Solutions Group, 2010). The specific evaporative percentages for each of the accountable-oil categories in the Federal Government's Oil Budget (The Federal Interagency Solutions Group, 2010) were not

presented for recalculation, but the mean 61% for the losses attributed to evaporation in combination with photo-oxidation definitely improves the budget and can negate the 23 vol% of unaccountable oil categorized as "other." In addition, the mean 61% loss by evaporation combined with photo-oxidation is almost twice that assigned to mean evaporative losses from the surfaced DWH oils (i.e., 31.5 vol%) based on GC amenable hydrocarbons and no consideration of photo-oxidation (Ryerson et al., 2012).

4. Conclusions

Asphaltene content of the DWH spilled oils is not conservative during degradation and cannot be used as a direct measure of oil loss. Relative to the unaltered wellhead oils, the asphaltenes isolated from the DWH spilled oils have a one-order of magnitude increase in oxygen content and $\delta^{13}\text{C}$ values depleted in ^{12}C by $> 1\%$. These differences could not be simulated in laboratory experiments involving burning, dispersion, dissolution, evaporation or biodegradation. However, these compositional differences were simulated in rooftop experiments that involved photo-oxidation and evaporation. These experiments indicated that as much as 61 vol% of the oil was lost during these experiments. Using this experimental relationship that duplicated the observed altered asphaltene compositions, an average of 61 ± 3 vol% of the original oil was lost from the spilled oils within the 80 days of the spill incident. These losses of original oil are significantly higher than those previously estimated (37–50 vol%), and indicate that GC analyses alone do not give a complete or accurate estimate of spilled-oil losses. More research is needed on the specific mechanisms responsible for the enhanced evaporative losses associated with photo-oxidation resulting in asphaltene mass increases and compositional changes for a better understanding of the fate of spilled oils.

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Appendices A, B, C, D, and E. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orggeochem.2014.06.004>.

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