# Recurrent oil sheens at the *Deepwater Horizon* disaster site fingerprinted with synthetic hydrocarbon drilling fluids

## **Supporting Information**

Christoph Aeppli<sup>1</sup>, Christopher M. Reddy<sup>1</sup>\*, Robert K. Nelson<sup>1</sup>, Matthias Y. Kellermann<sup>2</sup>, and David L. Valentine<sup>2</sup>

<sup>1</sup>Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

<sup>2</sup>Department of Earth Science and Marine Science Institute, University of California, Santa Barbara, CA 93106

\*Corresponding author: <u>creddy@whoi.edu</u>; 508-289-2326 (T); 508-457-2164 (F)

16 Pages 2 Tables 10 Figures

### S-I. Supporting Information on Drilling-Mud Samples collected in June 2010

The objective was to analyze the olefin composition of drilling fluids collected from vessels in June 2010 docked in the Gulf of Mexico and compare these results to sheen samples collected near the 2010 *Deepwater Horizon* disaster site in lease block MC252 on October 20 and December 13, 2012. These fluids were received from Alpha Analytical (Mansfield, MA) and according to their chains-of-custody they were associated or planned to be part of the "*Top Kill*" event of late May 2010.

**Sampling**. Six samples were collected from four difference vessels (Table S1). Five of the samples were collected on June 2, 2010 and the sixth on June 26, 2010. All were collected from vessels docked in Port Fourchon, LA. While paperwork stated that all four vessels (*Infant Jesus, Kylie Williams, Carol Chouest*, and *HOS Centerline*) were "*Top Kill*" muds, only the *HOS Centerline* was documented to be involved in "*Top Kill*", as it was the primary vessel for the operation and delivery of the mud. Note, however, that sampling for the *HOS Centerline* (6/26/2010) was one month after "*Top Kill*" (late May 2010). It is unknown if any additional muds were added to the *HOS Center* line in the one month period between "*Top Kill*" and sampling. A thorough review of the Internet and available files did not reveal any evidence that the other three vessels were part of "*Top Kill*".

**Results.** Samples were received in 40-ml clear glass vials about 75% full with complete chains-ofcustody. About half of the volume in each vial was brownish clay settled with an overlying clear liquid. All six samples contained detectable olefins but varied from  $5 \cdot 10^{-6}$  to 18% on a total mass basis via analysis by gas chromatography with flame ionization detection (GC-FID; Figures S6 and S7) and comprehensive two-dimensional gas chromatography with flame ionization detection (GC×GC-FID; Figure S8). (For sample analysis, the vials were shaken/sonicated and a volume of the suspended materials was collected and weighed). These values are lower than expected based on product descriptions for either mixtures prepared from linear alpha olefins (LAOs) or internal olefins (IOs) (expected: 1 to 30%). One possible explanation is that a previous analysis of these samples preferentially removed the liquid portion, presumably enriched with alkenes, or that sampling from the vessel did something similar. Each mud contained alkenes with 14 to 20 carbons with a predominance for even carbon numbers. For  $C_{16}$ ,  $C_{18}$ , and  $C_{20}$ , there was a second, but smaller, cluster of compounds that we suspect are branched alkenes (see later), and perhaps poly alpha olefins (PAOs); we have referred to them as "tails" for each specific carbon number. Remarkably, the bulk composition of alkene classes in these samples was quite similar with  $C_{16}$  as the largest, followed by  $C_{18}$ , and then  $C_{17}$  (Figure S7).

The fluids are composed of internal olefins (IOs) as there are numerous isomers for each carbon number. There are alpha olefins, but they only range from 15 to 25% for  $C_{16}$ ,  $C_{17}$ , and  $C_{18}$ , respectively. (Commercially obtained LAOs from M-I fluids were 95% 1-hexadecene). It is possible that each sample was a mixture of LAO and IO. However, this seems unlikely, as each drilling mixture was too similar considering the wide range of mixtures of LAOs and IOs that could be in a tank. Hence, all of the fluids are near or stock commercial mixtures of IOs.

Hydrogenation of the alkenes in the drilling fluids converts linear alkenes to their respective *n*-alkane and branched alkenes to branched alkanes (Figure S6). For  $C_{16}$  and  $C_{18}$ , the amount of branching was 10 to 20% whereas for  $C_{17}$  it was much lower (0 to 6%). Similar trends were observed in field samples from October 2012 where  $C_{17}$  contained no detectable branching. The reason for this might be different synthesis pathways for various olefins.

**Summary**. Without a more detailed provenance of the drilling fluids in the tanks of these four vessels care must be taken when using any one sample as an endmember. If one endmember was chosen of the six, it would be the *HOS Centerli*ne as it was used during "*Top Kill*" yet sampled a month later. On first inspection, the positive outcome of this study was how remarkably similar the fluids are. They are all IOs with relative compositions of  $49\pm4$ ,  $16\pm4$ , and  $35\pm3\%$  for  $C_{16}$ ,  $C_{17}$ , and  $C_{18}$ , respectively. The "tails" observed in the samples are likely methyl-branched olefins. One important aspect of this study is that the sheen samples are also weathered and hence altering in their relative composition. For example, most field samples have a greater abundance of  $C_{18}$  vs.  $C_{16}$ , presumably resulting from preferential evaporation of  $C_{16}$  compounds at the sea surface (Figure S9). Overall, these samples can be considered "typical" drilling fluids found in vessels in the Gulf of Mexico in the spring/summer of 2010. They are powerful in that they are very similar and may be useful for matching the source oil to the sheens.

#### S-II. Supporting Information for Analytical methods

GC×GC-FID and TOF details. GC×GC-FID analysis was performed on a GC×GC system from Leco, Saint Joseph, Michigan. The first-dimension column oven was programmed to remain isothermal at 60 °C for 10 minutes and then ramped from 60 to 325 °C at 1.25 °C min<sup>-1</sup>. Compounds eluting from the first dimension column (Restek Rtx-1MS column, 60 m length, 0.25 mm I.D., 0.25 µm film thickness) were cryogenically trapped, concentrated, focused and re-injected (modulated) onto a second-dimension column (SGE BPX50, 1.25 m length, 0.10 mm I.D., 0.1 µm film thickness). The modulator cold-jet gas was dry nitrogen, chilled with liquid nitrogen. The thermal modulator hot-jet offset was 15 °C above the temperature of the main GC oven (thermal modulator temperature offset = 15 °C). The hot jet was pulsed for one second every 10 seconds with a 4-second cooling period between stages. The second dimension oven was programmed to remain isothermal at 65 °C for 10 minutes and then ramped from 65 to 330 °C at 1.25 °C min<sup>-1</sup>. The carrier gas was hydrogen at a constant flow rate of 1 mL min<sup>-1</sup>. The FID detector signal was sampled at 100 Hz.

Select samples were analyzed on a GC×GC-time of flight mass spectrometer (GC×GC-TOF) system equipped with a dual stage cryogenic modulator (Leco, Saint Joseph, Michigan). The layout of the system was similar to the GC×GC-FID. The sample was injected in splitless mode and the purge vent was opened at 1 minute. The inlet temperature was 300 °C. The first-dimension column was a nonpolar Restek Rtx-1MS, (60m length, 0.25 mm I.D., 0.25  $\mu$ m film thickness) and second-dimension separations were performed on a 50% phenyl polysilphenylene-siloxane column (SGE BPX50, 1.25 m length, 0.10 mm I.D., 0.1  $\mu$ m film thickness).

The first dimension column oven was programmed to remain isothermal at 50 °C for 0.5 min and ramped from 50 to 115 °C at 30 °C min<sup>-1</sup>. Then the oven remained isothermal at 115 °C for 10 min and then ramped from 115 to 190 °C at 1 °C min<sup>-1</sup>. The thermal modulator hot jet offset was set 15 °C above the temperature of the main GC oven (thermal modulator temperature offset = 15 °C). The hot jet was pulsed for one second every 7.5 seconds with a 2.75 second cooling-period between stages. The second dimension oven was programmed to remain isothermal at 55 °C for 0.5 min and then ramped from 55 to 120 °C at 30 °C min<sup>-1</sup>. The oven remained isothermal at 120 °C for 10 min and then ramped from 120 to 195 °C at 1 °C min<sup>-1</sup>. The carrier gas was helium at a constant flow rate of 1 mL min<sup>-1</sup>. The TOF-MS detector signal was sampled at a data rate of 50 Hz. The transfer line from the second oven to the TOF-MS was deactivated fused silica (0.5 m length, 0.18 mm I.D.), which was held at a constant temperature

of 300 °C. The TOF source temperature was 225 °C, the detector voltage was 1575 Volts, the mass scan range was 40 to 500 amu, and the TOF mass defect was manually set at 111.5 mu/100u (optimized for hexadecenes). The mass spectrometer uses 70 eV electron ionization and operates at a push-pulse rate of 5 kHz, allowing sufficient signal averaging time to ensure good signal-to-noise ratios while still operating at a high enough data acquisition rate to process accurately spectra from the peaks eluting from the second dimension column.

**Comparison of analyzing sheen by GC-FID versus GC**×**GC-FID.** To compare analytical techniques for measuring the total alkene content as well as the relative amounts of  $C_{16}$ ,  $C_{17}$ , and  $C_{18}$  alkenes in oil sheen samples collected, GC-FID and GC×GC-FID were used to analyze 14 samples. The motivation for this comparison was to determine if GC×GC-FID is the superior analytical method compared to GC-FID.

Focusing on the most abundant alkenes ( $C_{16}$ ,  $C_{17}$ , and  $C_{18}$ ), both techniques can detect and measure them based on their order of elution relative to pure standards (Figures 2 and 3 in the main text). These elution windows were additionally confirmed by the disappearance of material when the samples were hydrogenated. The difference between both techniques is the increased resolution afforded by GC×GC. Accuracy is better with GC×GC as hydrogenation shows that no other compounds coeluting in the two-dimensional region of the alkenes (Figure 3 in the main text). Yet following hydrogenation, GC-FID continues to have material in the elution windows (Figure 2 in the main text). Hence, when quantifying alkenes with GC-FID co-eluting material is measured as alkenes, leading to an overestimation of olefins by GC-FID (Figure S10).

Co-eluting material can by corrected by subtracting the olefin retention windows in the GC-FID traces of samples after hydrogenation (i.e., without olefins) from the olefin-containing samples (Figure S10). Such a procedure lead to an under-estimation of olefin content, most likely due to formation of co-eluting saturated compounds during hydrogenation.

Overall, GC×GC-FID provides greater resolution, selectivity, and accuracy than GC-FID for measuring alkene in oil sheen samples. However, GC-FID is a powerful tool for a qualitative (presence/absence) assessment of olefins in petroleum.

#### **III. Supporting Tables and Figures**

**Table S1.** Alkene content of drilling muds suspected to be used in *Top Kill* and *Static Kill*, which were collected (as grabs) from supply vessels near Port Fourchon, LA (see Figures S6 and S7 for GC-FID chromatograms of the drilling-mud extracts).

Alpha ID (Sample ID)	Sampling Date and Time (CST)	Vessel	Latitude / Longitude	Alkenes (% mud) by GC×GCª	Relative amounts of (C <sub>16</sub> /C <sub>17</sub> /C <sub>18</sub> ) by GCxGC <sup>a</sup>	Linear / branched alkenes measured by GC-FID after reduction (%)	% alpha olefins by GCxGC
1009012-01A (GU2909-0602- OTARF 2501) <sup>♭</sup>	6/2/10 15:37	Infant Jesus	29° 07.80′ / -90° 13.06′	0.0003 %	49/15/35	C <sub>16</sub> : 100/0 C <sub>17</sub> : 100/0 C <sub>18</sub> : 92/8	C <sub>16</sub> : 22 C <sub>17</sub> : 16 C <sub>18</sub> : 18
1009012-02A (GU2909-0602- OTARF 2505B) <sup>°</sup>	6/2/10 16:10	Infant Jesus	29° 07.80′ / -90° 13.06′	0.04 %	53/10/37	C <sub>16</sub> : 92/8 C <sub>17</sub> : 98/2 C <sub>18</sub> : 89/11	C <sub>16</sub> : 24 C <sub>17</sub> : 17 C <sub>18</sub> : 23
1009012-03A (GU2909-0602- OTARF 25011) <sup>d</sup>	6/2/10 17:10	Kylie Williams	29° 07.74′ / -90° 13.17′	0.02 %	51/20/29	C <sub>16</sub> : 88/12 C <sub>17</sub> : 98/2 C <sub>18</sub> : 83/17	C <sub>16</sub> : 26 C <sub>17</sub> : 16 C <sub>18</sub> : 23
1009012-04A (GU2909-0602- OTARF 25012) <sup>e</sup>	6/2/10 19:11	Carol Chouest	29° 08.69′ / -90° 12.76′	5·10 <sup>-6</sup> %	45/19/35	NM <sup>f</sup>	C <sub>16</sub> : 24 C <sub>17</sub> : 15 C <sub>18</sub> : 23
1009012-05A (GU2909-0602- OTARF 2527) <sup>g</sup>	6/2/10 19:37	Carol Chouest	29° 08.69′ / -90° 12.76′	2·10 <sup>-5</sup> %	44/17/39	NM	C <sub>16</sub> : 24 C <sub>17</sub> : 23 C <sub>18</sub> : 17
1009012-06A (LAAR38-0626- DMA801) <sup>h</sup>	6/26/10 13:48	HOS Centerline	29° 07.41′ / -90°12.89′	18%	51/16/33	C <sub>16</sub> : 85/15 C <sub>17</sub> : 94/6 C <sub>18</sub> : 80/20	C <sub>16</sub> : 24 C <sub>17</sub> : 25 C <sub>18</sub> : 25

(a) In all samples, C<sub>14</sub> to C<sub>20</sub> alkenes were observed and quantified for the total alkene content. We also calculated the relative distribution of C<sub>16</sub>, C<sub>17</sub>, and C<sub>18</sub> (as the latter are used when comparing to field samples). (b) Rear tank; stirred 30 min / 4 hrs; sampling depth 3'. (c) Composite of front tanks; stirred 30 min / 4 hrs; sampling depth 3'; homogenized in the lab. (d) Separate tanks are noted but no specific tank; T=124°F; tanks stirred 30min / 6 hrs. (e) From L-side port tanks; 50/50 composite of the two chambers; tanks stirred 30/6hr; sample depth 20'. (f) NM=not measured. (g) From R-side port tanks; 50/50 composite of the two chambers; tanks stirred 30 min / 6 hrs; sample depth 20'. (h) Product was *Encore* Synthetic mud (Internal olefin based mixture by Halliburton); 4-hour stir.

**Table S2.** Physical properties of select alkanes and 1-alkenes. Calculated values from the SPARC calculator (version 4.6; http://ibmlc2.chem.uga.edu/sparc/). Compounds are sorted by elution profile on an apolar GC column (such as DB-1 or equivalent).

Name	CAS	Abbrev.	log(K <sub>A-w</sub> ) <sup>(a)</sup>	log(K <sub>o-w</sub> ) <sup>(a)</sup>	<b>p*</b> <sup>(c)</sup>	MP <sup>(d)</sup>	BP (calc) <sup>(e)</sup>
			(-)	(-)	Ра	°C	°C
1-hexadecene	629-73-2	1-C <sub>16</sub> -ene	2.86	9.34	0.09	2.1	285 h (284)
<i>n</i> -hexadecane	544-76-3	<i>n</i> -C <sub>16</sub>	3.04	9.48	0.148	18.1	287 h (287)
1-heptadecene	6765-39-5	1-C17-ene	3.00	9.92	0.083	11.5	300 h (300)
<i>n</i> -heptadecane	629-78-7	<i>n</i> -C <sub>17</sub>	3.18	10.06	0.05	29.6	349 (302)
pristane	1921-70-6	pris	3.91	11.06	0.019	12.1 <sup>(†)</sup>	286 (296) <sup>(†)</sup>
1-octadecene	112-88-9	1-C <sub>18</sub> -ene	3.14	10.50	0.052	18	179 (312)
n-octadecene	593-45-3	<i>n</i> -C <sub>18</sub>	3.32	10.64	0.015	28.2	316 (316)
phytane	638-36-8	phyt	3.97	11.59	0.006	22 <sup>(†)</sup>	301 (301) <sup>(†)</sup>
$17\alpha(H),21\beta(H)$ -hopane	60305-23-9	hopane	3.30	15.91	1.7x10 <sup>-9</sup>	171 <sup>(†)</sup>	424 (410) <sup>(†)</sup>

(a) Logarithm of calculated dimensionless ((mol L<sup>-1</sup>)/(mol L<sup>-1</sup>)) air-water partitioning coefficient. (b) Logarithm of calculated dimensionless octanol-water partitioning coefficient. (c) Calculated vapor pressure. (d) Experimental melting points (MP) form CRC Handbook of Chemistry and Physics, 93<sup>rd</sup> edition (Hanynes *et al.* **2013**, CRC press) unless otherwise noted; (e) Experimental boiling points (BP) from CRC Handbook of Chemistry and Physics unless otherwise noted; calculated values (SPARC calculator) in brackets. (f) Experimental value from EPISuite (U.S. EPA).



**Figure S1.** Spider diagrams for biomarker ratios to fingerprint samples. (a) Biomarker ratios of cofferdam oil, MW, and Alaska North slope oil (reference oil) show a match between cofferdam and MW oil. (b) Biomarker ratios of the sheen samples (here shown are the October samples) match the cofferdam oil.



**Figure S2**. GC-FID chromatograms of (a) MW oil collected in 2010 and (b) cofferdam oil collected in October 2012 by BP.







**Figure S4.** Partial GC×GC-TOF-MS of sheen sample 102012-1. Refer to Figure S5 for the mass spectra of the annotated mass spectra. The data are displayed as a color contour plot, with blue representing low signal, white representing medium signal, and red representing a high signal. In order to visualize the minor peaks, the dynamic range that is plotted is less than the total dynamic range of the sample, with the tops of the tallest peaks chopped off. This produces a larger white area near the center of large peaks.



**Figure S5.** GC×GC-TOF-MS mass spectra from 102012-1 shown in Figure S4. (a) *n*-hexadecane, (b)  $C_{16}$  olefin, (c) *n*-octadecane, and (d)  $C_{18}$  olefin. Refer to Figure S4 for the elution location of each peak, which are labeled according to the same lettering as this figure.



**Figure S6.** Partial GC-FID chromatogram of (a) drilling mud 1009012-06A from *HOS Centerline* with major olefins from  $C_{15}$  to  $C_{18}$  arbitrary annotated **a-d**, and (b) the same sample after hydrogenation. This IO drilling-mud mixture contains internal olefins **b**, **c**, **d**, and alpha-olefins **a**. Note the reduced complexity in the hydrogenated sample. The branched alkanes (most likely methyl-branched), used to calculate the branched alkene content in the drilling mud, eluted before the *n*-alkanes (in this sample only  $C_{16}$  and  $C_{18}$ ).



**Figure S7.** Partial GC-FID chromatogram of extracts of the six drilling-mud grab samples (not hydrogenated), described in Table S1 and Section S-1. The panel titles indicate the sample number and the name of the vessels the samples originated.



**Figure S8**. Partial GC×GC-FID chromatogram of 1009312-01A (*HOS Centerline*) with main olefins from  $C_{15}$  to  $C_{18}$  annotated (same annotation used as in Figure S6). Peak **c** is the alpha isomer (LAO), whereas the other annotated peaks are internal olefins (IOs). The weak peaks around  $C_{16}$  and  $C_{18}$  are most probably methyl-branched olefins, and amount to 17% and 28% of the IOs for  $C_{16}$  and  $C_{18}$ , respectively. Only minor amounts (2.2% of all olefins) of olefins with carbon numbers < 15 or > 18 were observed in all drilling mud samples. Note the different *y*-axis as compared to Figure 3 in the main text due to an optimized temperature program and modulation time for this sample.



**Figure S9**. Distribution of olefins in sheen samples, oiled floating DWH debris, as well as in drillingmud samples from *HOS Centerline* (DM Centerline), *Infant Jesus* (DM I.Jesus), and *Carol Chouest* (DM Chouest a and b) described in Table S1. Shown are relative distribution of (a) total  $C_{16}/C_{17}/C_{18}$ olefins, and (b-d) relative amount of linear  $\alpha$ -isomer (LAO) relative to the internal olefins (IOs).



**Figure S10**. Comparison of olefin quantification by GC-FID and GC×GC (red circles). GC-FID generally overestimates the olefin content. Correcting for co-eluting material in GC-FID by subtracting corresponding the GC-FID traces of samples after hydrogenation (blue circles), leads to an underestimation of actual olefin content.