NewFields

Footprint and Persistence of Synthetic-Base Drilling Mud in Deep-Sea Sediments near the Failed Macondo Well

Scott A. Stout, Ph.D.
NewFields Environmental Forensics Practice, LLC, Rockland, MA
August 2015

Abstract

An unknown volume (perhaps as much as 30,000 barrels) of synthetic-based drilling muds (SBMs) used during the drilling of the failed Macondo well, the blowout, or the failed Top Kill/Junk Shot operation were discharged into the deep-sea.

Chemical analysis of representative SBM samples (6) provided by BP were analyzed and shown to contain prominent C_{15} to C_{18} olefin "clusters" (unsaturated hydrocarbons), dominated by the C_{16} and C_{18} olefins. Other major (non-brine) constituents of the SBM include xantham gum, ethylene glycol, and barium sulfate.

The SBMs' olefin "clusters" – comprised of multiple internal olefins, linear α-olefin (LAO), and methyl-branched olefins – have a distinctive GC/FID "fingerprint" that can be easily identified in deep-sea sediments. GC/FID analysis of >2500 sediments collected in 2010/2011 revealed an ~2.5 mi^2 "footprint" of SBM-impacted surface (0-1 cm) sediments around the Macondo well that extended, at a minimum, up to ~1.5 miles in a southwesterly direction from the Macondo well (Fig. 4). Within this "footprint" SBM was largely unweathered compared to the "fresh" SBM. The SBM was sometimes present from the surface to 5-10 cm deep, indicating significant deposition of SBM occurred. The SBM was found to occur in varying proportions relative to Macondo oil, with some sediments containing "pure" SBM (little/no oil) and *vice versa*.

GC/FID analysis of sediments collected in 2014 still showed (essentially) the same SBM "footprint" that had existed in 2010/2011, indicating SBM has persisted in sediments around the Macondo well for the 5 years since the spill. The SBM still present in 2014 was variably weathered, with some appearing "fresh" and some appearing weathered, apparently biodegraded. In the latter, branched olefins appear preferentially preserved.

Based upon the 5-year persistence in sediments around the well, and SBM's persistence for 10-years in sediments near a former drill site (~38 mi NE of the Macondo well), the SBM released during the *Deepwater Horizon* oil spill is anticipated to remain detectable for many years in sediments within the ~2.5 mi^2 SBM "footprint" (Fig.4).

Introduction

Synthetic-based drilling muds (SBMs) are man-made fluids commonly used in drilling oil and gas wells. SBMs provide lubricity, stability at high temperatures, and borehole stability and can offer some advantage over oil-based (diesel) muds (OBMs), particularly in terms of the potential environmental issues surrounding their accidental or intentional discharge to the environment (Neff et al., 2000).

SBMs are generally comprised of synthetic organic compounds that include linear alpha olefins (LAO), internal olefins (IO), poly alpha olefins (PAO), linear alkyl benzenes (LAB), synthetic paraffins, ethers and esters that are dispersed in a salt brine to form an emulsion. Other ingredients can include emulsifiers, barite, clays, lignite, or lime.

SBM was used in the drilling of the Macondo well prior to the *Deepwater Horizon* (DWH) disaster and oil spill. In addition, BP used SBM in the failed Top Kill operation conducted during the spill (May 26-29, 2010), during which nearly 30,000 bbls of SBM – at times including various bridging materials (e.g., golf balls, cubes, and miscellaneous objects; Junk Shot) – were pumped at rates up to 80 barrels per minute into the failed well in an attempt to stop or reduce the flow of oil and gas (DOE, 2014). After three attempts over three days the Top Kill operation was considered unsuccessful and abandoned. It is unknown what volume of SBM used during the operation was released to the deep-sea. SBM was also used during the Static Kill operation conducted August 3-5, 2010 (after the well was shut in) in an effort to push any remaining oil back into the reservoir.

In this report the chemical composition of the SBMs used by BP are reviewed and their chemical fingerprints are presented. Evidence is presented showing (1) the presence and spatial distribution of SBM in deep-sea sediments around the failed Macondo well in 2010-2011 and (2) the persistence of the SBM in deep-sea sediments around the failed Macondo well in 2014, five years after the spill.

SBM Bulk Composition

BP had MiSWACO (Houston, TX) prepare two formulations of SBM in early May 2010 intended for use in the Top Kill/Junk Shot operation. The general composition of these is provided in Table 2 (MiSWACO, 2010).

The two formulations contained different blends of the same major ingredients that imparted different mud weights in each (14.2 and 16.4 pounds per gallon; Table 2). The major (non-brine) ingredients in each formulation included ethylene glycol (i.e., antifreeze), DUOVIS, and MI BAR. The available product specification sheets for DUOVIS and MI BAR indicate they contain non-dispersible xantham gum (which provides viscosity) and barium sulfate (which increases the density), respectively. Synthetic hydrocarbons (e.g., olefins) are not identified as ingredients in either formulation (despite the fact these are clearly present; see results below).

A calculation of the ethylene glycol concentration in each of the Top Kill formulations (based upon the data contained in Table 2) reveals that the Top Kill SBM formulations 1 and 2 contained 139,000 and 108,000 μg/g (ppm), respectively (13.9 and 10.8 wt%).

Reportedly, 10,000 bbl of each of the two formulations were ordered by BP on May 15-16, 2010 for use during the Top Kill/Junk Shot operation. (This total volume is less than the ~30,000 bbl that was reportedly used; DOE, 2014. The reason for this disparity is unknown.)

The *Encore* mud reportedly had a mud weight of 16.5 ppg (see chain-of-custody document). Other properties obtained from this product's MSDS are summarized in Table 2. This material reportedly contains 10 to 30% of isomerized alpha olefins (the presence of which is confirmed herein; see results below).

Neat SBM Samples and Analyses

The six neat samples of SBMs were provided to the Trustees for study by BP (Table 1). Five of these were characterized as "Top Kill" muds obtained from different sources/vessels approximately 1 week after the Top Kill/Junk Shot operation (Table 1). The sixth sample was identified as an *Encore* drilling mud, which is a product marketed by Halliburton. This sample was collected approximately 1 month after the Top Kill/Junk Shot operation (but prior to the Static Kill operation) from the *HOS Centerline*, a vessel which supplied SBM during both Top Kill/Junk Shot and Static Kill. Therefore, the Encore drilling mud is presumed to represent a sixth sample of Top Kill/Junk Shot SBM.

The samples were shipped from TDI-Brooks Laboratory (College Station, Texas) to Alpha Analytical Laboratory (Mansfield, Massachusetts) under full chain-of-custody on September 20, 2010 and were safely received on September 21, 2010. The samples were analyzed in accordance with the NRDA DWHOS Analytical Quality Assurance Plan (NOAA 2014) via:

(1) *TEM and Saturated Hydrocarbon (SHC) Quantification and Fingerprinting*: a modified EPA Method 8015B was used to determine the concentration of total extractable materials (TEM; C_9-C_{44}) and concentrations of *n*-alkanes (C_9-C_{40}) and selected (C_{15}-C_{20}) acyclic isoprenoids (e.g., pristane and phytane), and simultaneously provide a high resolution gas chromatography-flame ionization detection(GC/FID) fingerprint of the samples. Following solvent extraction with dichloromethane (DCM) the sample extracts were spiked with appropriate internal standards and surrogates and analyzed by GC/FID. There was no silica gel cleanup of the extract performed. The concentrations of target compounds in the dispersants are reported in μg/g and are surrogate corrected.

(2) *PAH, Alkylated PAH and Petroleum Biomarkers:* Semi-volatile compounds in each dispersant were analyzed using GC/MS via a modified EPA Method 8270. This analysis provided the concentration of (1) approximately 80 PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics and (2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic steroids. The concentrations of target compounds in the oils are reported in μg/g and are surrogate corrected.

Results and Discussion

Chemical Character of Top Kill SBMs

Figure 1 shows the GC/FID chromatograms for the six SBMs studied with their TEM and *reported* individual alkane concentrations given in Table 3. It must be noted that the laboratory reported concentrations of individual C_{15} to C_{18} n-alkanes, pristane, and/or phytane in the muds is erroneous and is due to the co-elution of various olefins with these targeted compounds (see below). Although erroneous, the reported detection of elevated n-C_{15} to n-C_{18}, pristane and phytane (in the absence of other oil-derived hydrocarbons) in sediments likely indicates the presence of SBM.

Inspection reveals that there is considerable variability among the SBMs' chromatograms and TEM concentrations. For example, little to no TEM was detected in three of the five samples, and correspondingly, the GC/FID chromatograms for these samples yielded no recognizable fingerprints (Fig. 1A, 1D, 1E). The remaining three SBMs each contained elevated but varying concentrations of TEM and similar GC/FID chromatograms (Fig. 1B, 1C, and 1F). This marked variability among the muds' TEM and chromatograms is attributed to the heterogeneous nature of the muds, i.e., their being largely comprised of inorganic solids (Table 2). It is suspected that sampling of the SBMs from the vessels was unable to obtain homogeneous samples, and that the small aliquots drawn for chemical analysis contained varying amounts of inorganic solids (versus chromatographable liquids), which greatly affected the sample weights and TEM concentrations.

Regardless, the GC/FID chromatograms of the three muds with significant TEM (Fig. 1B, 1C, and 1F) each exhibit similar chromatographic features. Each of these muds is dominated by four clusters of peaks in the C_{15} to C_{18} range (Fig. 1). The peaks in each cluster are comprised of various olefins containing 15 to 18 carbons, as is typical of olefin-based SBMs (Neff et al. 2000; Reddy et al. 2007).

The relative abundances of the C_{15}, C_{16}, C_{17}, and C_{18} clusters tend to vary among the neat SBMs studied (Fig. 1). Although each sample is dominated by the C_{16} and C_{18} clusters (which occur in comparable proportions to one another), the relative abundances of the C_{15} and C_{17} clusters tend to vary. The reason for this variability is uncertain but because these samples were collected from different vessels (Table 1), it is possible that the SBM blends used during the Top Kill operation varied slightly.

Close inspection of the clusters of peaks in one of these muds is shown in Figure 2. There are many peaks present within each cluster, which indicates each cluster likely contains multiple internal olefins (IOs) or mixtures of multiple IOs with the corresponding linear alpha-olefin (LAO) and/or methyl-branched olefins. Recently, Aeppli et al. (2013), who had analyzed aliquots of these same six SBMs using GC x GC, confirmed the presence of multiple IOs, a single LAO, and multiple branched olefins within each cluster as indicated in Figure 2. Notably, minor olefin clusters are also evident around C_{14}, C_{19}, and C_{20} (Fig. 2). Aeppli et al. (2013) also confirmed the absence of n-alkanes, pristane, and phytane among the olefin clusters, which is the basis for considering the reported concentrations of these compounds (Table 2) erroneous.

The concentrations of PAHs detected in the SBMs studied are given in Table 4. Only trace concentrations of mostly low molecular weight (mostly 2-ring) PAHs were detected in each sample (all at concentrations below the reporting limits). In total, the estimated

concentration of PAHs, as represented by TPAH50, ranged from 14.5 to 48.7 $\mu g/g_{mud}$ (Table 4). These concentrations are much lower than were present in the fresh Macondo oil (13,300 $\mu g/g_{oil}$; Stout, 2015) indicating that, on a mass loading basis, the mass of PAHs introduced during Top Kill was minimal compared to the mass of PAHs contributed by ~3.19 million bbls of crude oil. However, because Top Kill mud presumably was deposited directly onto sediment around the well (see below) some exposure to its relatively low concentrations of PAHs seems evident.

Distribution of SBM in Deep-Sea Sediments – 2010/2011

The distinctive GC/FID chromatograms for the SBMs studied (Fig. 1) makes their presence easy to recognize within the GC/FID chromatograms of deep-sea sediments. The C_{15} to C_{18} olefin clusters are not naturally-occurring features of crude oil from the Macondo well or any other GoM crude oil (e.g., seeps). Therefore, the presence of these olefin clusters in deep-sea sediments unequivocally indicates the presence of olefin-based SBM.

In 2010/2011, over 2500 deep-sea sediment samples from 701 cores were collected as part of the NRDA and analyzed using GC/FID. Each of these sediment's GC/FID chromatograms was qualitatively inspected for the presence of the olefin clusters indicative of SBMs. Figure 3 shows four examples of deep-sea sediments collected near the Macondo well in 2011 that contained various proportions of Macondo oil and SBM. In each case, the C_{15} to C_{18} olefin clusters derived from the SBM can be seen to occur in varying proportions relative to n-alkanes and the unresolved complex mixture (UCM "hump") attributable to Macondo crude oil. This variability indicates that SBM was deposited in varying proportions relative to oil, i.e., the hydrocarbons in oil and SBM did not necessarily "travel together" prior to their deposition.

Qualitative review of the GC/FID chromatograms for all deep-sea sediments collected in 2010/2011 revealed that olefin-based SBM was clearly present in 43 surface sediment samples (0-1 cm; Table 5). Thirty-seven of these were present within 1 mile of the well and three additional samples were between 1 mile and 2.5 miles from the well (Fig. 4A). (The three remaining sediments containing SBM were collected 38 miles NE of Macondo at an old drill site; see bottom Table 5 and next section of this report.)

Notably, 37 of the 43 cores collected within 1 mile of the well in 2010/2011 contained SBM, which indicates that SBM was widely deposited within this area. SBM deposition appears to have extended up to ~1.5 miles from the well in a southwesterly direction (Fig. 4A). SBM deposition toward the northeast is also evident, although the continuity of deposition in this direction is uncertain (Fig. 4A). Ignoring the SBM found in the single core >2 miles to the NE, the SBM "footprint" in 2010/2011 can be conservatively depicted to cover approximately 2.5 mi^2 (Fig. 4A).

The character of the SBM throughout the SBM "footprint" was highly consistent with "fresh" SBM (Fig. 2). There were no obvious changes in the olefin cluster "fingerprints" found in the sediments brought about by the transport and deposition of the SBM on the seafloor. This suggests that the olefins in the SBM were not subject to dissolution or biodegradation in the months between being discharged and collected. In other words, the SBM found in 2010/2011 was largely unweathered.

The presence of this 2.5 mi^2 SBM "footprint" is consistent with deposition of unweathered SBM from the Top Kill/Junk Shot operation - although some SBM-

impacted sediments may have resulted from discharges of rock cuttings during the original drilling of the Macondo well or during the initial *Deepwater Horizon* accident and sinking. Some transport of the SBM outside of this approximately 2.5 mi^2 "footprint" is possible but may simply not be recognized upon qualitative inspection of chromatograms. (For example, more specific GC x GC analysis may reveal the presence of low concentrations of olefins when conventional GC cannot; Reddy et al., 2007.) Therefore, the SBM "footprint" qualitatively recognized in 2010-2011 (Fig. 4A) may represent a minimum of the actual seafloor impacted by SBM from the DWH incident. Support for this contention is the presence of SBM in the core ~2.3 mi to the NE of the Macondo well (Fig. 4A),[1] wherein SBM co-occurs with Macondo crude oil.

Many of the 2010-2011 cores collected within surface sediment SBM "footprint" (Fig. 4A, Table 5) also contained SBM at greater depths within the same core. For example, Figure 5 shows the GC/FID chromatograms for samples throughout a core located ~0.6 miles NE. Olefin clusters (indicating the present of SBM) are present throughout the entire length of the 10 cm core. The SBM in this core co-occurs in various proportions with highly-weathered Macondo oil. The presence of Macondo oil and SBM at depths >5 cm testifies to the significant accumulation of SBM in some areas around the wellhead in the course of the *Deepwater Horizon* oil spill.

Notably, SBM was also recognized in some deeper sediments in four cores between approximately 1.5 and 3.5 miles southwest of the wellhead. However, there was no SBM recognized in surface sediments at these locations, which suggests these deeper sediments likely represent SBM discharges from 1999 and 2003 drilling activities (pre-DWH) known to have occurred in this area.[2] (Note that the BOEMRE database confirms that there were no previous drilling activities closer to the Macondo well.) This observation of "old" SBM raises the issue of the SBM's persistence in deep-sea sediments, which is explored in the next section.

Persistence of SBM in Deep-sea Sediments

As noted above, surface sediments in three proximal cores collected in 2011 ~38 miles NE of the Macondo well in the DeSoto Canyon area also contained olefin-based SBM (not shown on Fig. 4).[3] These samples (along with underlying sediments up to 10 cm deep) contained SBM and, given their distance from Macondo, cannot reasonably be attributed to the DWH incident – but rather to a former drill site. Indeed, a review of the BOEMRE well site database shows these three cores are located proximal to an exploration well drilled in November 2001.[4] Therefore, the presence of SBM in these sediments indicates the SBM had persisted in these deep-sea sediments for about 10 years. This, of course, indicates the olefins in SBM are not quickly degraded in (at least some) deep-sea sediments. Thus, one might anticipate that the SBM "footprint" near the failed Macondo well (Fig. 4A) may persist for many years.

In 2014, the persistence of the SBM "footprint" in sediments around the Macondo well was confirmed. At this time over 800 deep-sea sediment samples from 201 cores were

[1] HSW6_FP10188_B0827_S_1485_50_H2_0072
[2] BOEMRE well location database: Well IDs: 608174085602 drilled in 1999 and 608174101801 drilled in 2003.
[3] SB9-65-B0608-S-VK916-HC-3454, SB9-65-B0608-S-VK916-HC-3494, SB9-65-B0608-S-VK916-HC-3534
[4] BOEMRE well location database, Well ID: 608164037600 drilled in 2001.

collected and analyzed, which included a review of the GC/FID chromatograms for the presence of olefin clusters indicative of SBMs. It was determined that 23 of the 24 cores collected within 1.5 mi of the well still contained SBM in surface sediments indicating the persistence of the approximately 2.5 mi^2 SBM "footprint" over the past 5 years (Fig. 4B; Table 5).

A detailed review of the SBM present in the 2014 sediments show a variety of levels of degradation. Some sediments still contained what appears to be "fresh" SBM (Fig. 6B) while other sediments contained weathered, presumably biodegraded, SBM (Fig. 6C). In the latter, it is notable that the numerous C16 and C18 branched olefins appear preferentially preserved, relative to the other olefins. Future study of sediments in the vicinity of the Macondo well should monitor continued weathering of the SBM.

References

Aeppli, Christoph, Christopher M. Reddy, Robert K. Nelson, Matthias Y. Kellerman and David L. Valentine, 2013. "Recurrent oil sheens at the *Deepwater Horizon* disaster site fingerprinted with synthetic hydrocarbon drilling fluids". Environ. Sci. Technol. 47(15): 8211-8219.

Department of Energy, 2014. http://energy.gov/downloads/microsoft-powerpoint-53-item-01-top-kill-operation-status-09-june-1400pptx.

MiSWACO, 2010. BP Maconda (*sic*). Technical services laboratory report, ID Code No. 100513F.001, Lab Master No. 20101479. May 13, 2010. 3 p.

Neff, J. M., S. McKelvie, and R.C. Ayers, Jr., 2000. "Environmental impact of synthetic based drilling fluids". OCS Study MMS 2000-064. www.data.boem.gov/PI/PDFImages/ESPIS/3/3175.pdf

NOAA, 2014. Analytical quality assurance plan, Mississippi Canyon 252 (*Deepwater Horizon*) natural resource damage assessment, Version 4.0. May 30, 2014.

Reddy, Christopher M., Robert K. Nelson, Sean Sylva, Li Xu, Emily A. Peacock, Bhavani Raghuraman, Oliver C. Mullins, 2007. "Identification and quantification of alkene-based drilling fluids in crude oils by comprehensive two-dimensional gas chromatography with flame ionization detection". J. Chromatogr. A, 1148(1): 100-107.

Stout, S.A., 2015. Chemical composition of fresh Macondo crude oil. NewFields Technical Report to the Trustees in support of PDARP.

Table 1: Inventory of synthetic based drilling mud samples analyzed. All vessels used in Top Kill/Junk Shot operation.

Client_ID	Alpha ID	Vessel	Col_Date	Sent_By	Brooks Lab_ID
GU2909-A0602-OTARF2501	1009312-01	Infant Jesus[1]	06/02/10	Entrix: Rob Crotty	DWH1659
GU2909-A0602-OTARF2505B	1009312-02	Infant Jesus[2]	06/02/10	Entrix: Rob Crotty	DWH1664
GU2909-A0602-OTARF2511	1009312-03	Kylie Williams	06/02/10	Entrix: Rob Crotty	DWH1671
GU2909-A0602-OTARF2519	1009312-04	Carol Chouest[3]	06/02/10	Entrix: Rob Crotty	DWH1679
GU2909-A0602-OTARF2527	1009312-05	Carol Chouest[4]	06/02/10	Entrix: Rob Crotty	DWH1687
LAAR38-A0626-DMA801	1009312-06	HOS Centerline[5]	06/26/10	LDEQ: John Vimont	DWH2727

[1] rear tank
[2] front tanks composite
[3] left side port tanks composite
[4] right side port tanks composite
[5] *Encore* SBM

Table 2: General characteristics of Top Kill mud formulations and *Encore* drill mud as reported by manufacturer. ppb-pounds per barrel, ppg-pounds per gallon.

Top Kill Mud (MiSOURCE)	Formulation 1	Formulation 2
Mud Weight, ppg	14.2	16.4
10 ppg brine, bbl	0.632	0.564
Caustic soda, ppb	0.50	0.50
DOUVIS, ppb	1.50	1.25
Ethylene Glycol, ppb	83.0	74.5
MI BAR, ppb	247.29	376.56
Encore Drill Mud (MSDS)	Wt%	
Crystalline silica, quartz	0-1	
Calcium chloride	5-10	
Isomerized alpha olefins	10-30	
Barium sulfate	30-60	

Table 3: Concentrations of target alkanes and total extractable material (TEM) in the Top Kill and Encore drill mud samples studied. Note that the laboratory reported concentrations of individual C15 to C18 n-alkanes, pristane, and/or phytane (greyed) in the muds is erroneous and caused by co-eluting olefins (see text). All concentrations in μg/g (surrogate corrected).

	Top Kill Muds										Encore Drill Mud	
Client ID	GU2909-A0602-OTARF2501		GU2909-A0602-OTARF2505B		GU2909-A0602-OTARF2511		GU2909-A0602-OTARF2519		GU2909-A0602-OTARF2527		LAAR38-A0626-DMA801	
Analytes												
n-Nonane (C9)	9.89	J	44.8	J	16.9	J	19.6	J		U	36.2	J
n-Decane (C10)	14.4	J	66.3	J	23.3	J	22.3	J	16.9	J	52.8	J
n-Undecane (C11)	11.4	J	78.0	J	35.8	J	18.5	J	22.4	J	53.8	J
n-Dodecane (C12)	7.96	J	101	J	55.9	J	16.2	J	13.1	J	89.2	J
n-Tridecane (C13)	5.81	J	92.1	J	45.8	J	11.4	J	9.33	J	73.8	J
2,6,10 Trimethyldodecane (1380)		U		U		U		U		U		U
n-Tetradecane (C14)	3.66	J	248		139	J	7.87	J	5.33	J	300	
2,6,10 Trimethyltridecane (1470)		U		U		U		U		U		U
n-Pentadecane (C15)	32.5	J	1560		1720		25.4	J	27.1	J	4120	
n-Hexadecane (C16)	79.4	J	8670		4320		10.4	J	29.8	J	50900	D
Norpristane (1650)		U		U		U		U		U		U
n-Heptadecane (C17)	24.7	J	1540		1760		5.33	J	12.9	J		U
Pristane	127	J	8020		10900		8.63	J	52.0	J	27100	
n-Octadecane (C18)		U		U	2650		265			U	35100	
Phytane		U		U		U	8.63	J	11.1	J	41100	
n-Nonadecane (C19)		U	184	J	253			U		U	550	
n-Eicosane (C20)		U	301		50.7	J	3.81	J		U	401	
n-Heneicosane (C21)		U	44.6	J		U	2.79	J	2.22	J	34.5	J
n-Docosane (C22)		U	33.8	J		U	2.54	J	2.89	J		U
n-Tricosane (C23)		U	27.8	J		U	9.90	J		U		U
n-Tetracosane (C24)		U	16.1	J		U		U	7.11	J		U
n-Pentacosane (C25)	106	JC	125	JC	101	JC	126	JC	110	JC	121	JC
n-Hexacosane (C26)		U	50.0	J	4.42	J		U		U		U
n-Heptacosane (C27)		U	12.5	J		U		U		U		U
n-Octacosane (C28)		U	21.5	J		U		U		U		U
n-Nonacosane (C29)		U		U	17.5	J		U		U	35.9	J
n-Triacontane (C30)		U	104	J		U		U		U	52.3	J
n-Hentriacontane (C31)		U	161	J	21.5	J		U		U	40.9	J
n-Dotriacontane (C32)		U		U		U		U		U		U
n-Tritriacontane (C33)		U	148	J	17.3	J		U		U	92.8	J
n-Tetratriacontane (C34)		U		U		U		U		U		U
n-Pentatriacontane (C35)		U	57.8	J	9.25	J		U		U	34.3	J
n-Hexatriacontane (C36)		U		U		U		U		U		U
n-Heptatriacontane (C37)		U		U		U		U		U		U
n-Octatriacontane (C38)		U		U		U		U		U		U
n-Nonatriacontane (C39)		U		U		U		U		U		U
n-Tetracontane (C40)		U		U		U		U		U		U
Total Extractable Material(C9-C44)	64800		540000		401000			U		U	1020000	
U - not detected												
J - estimated, conc. Below reporting limit												
C - co-elution												
D - reported from dilution												

Table 4: Concentrations of PAHs in the Top Kill and drill mud samples studied.
Concentrations are in μg/g; surrogate corrected.

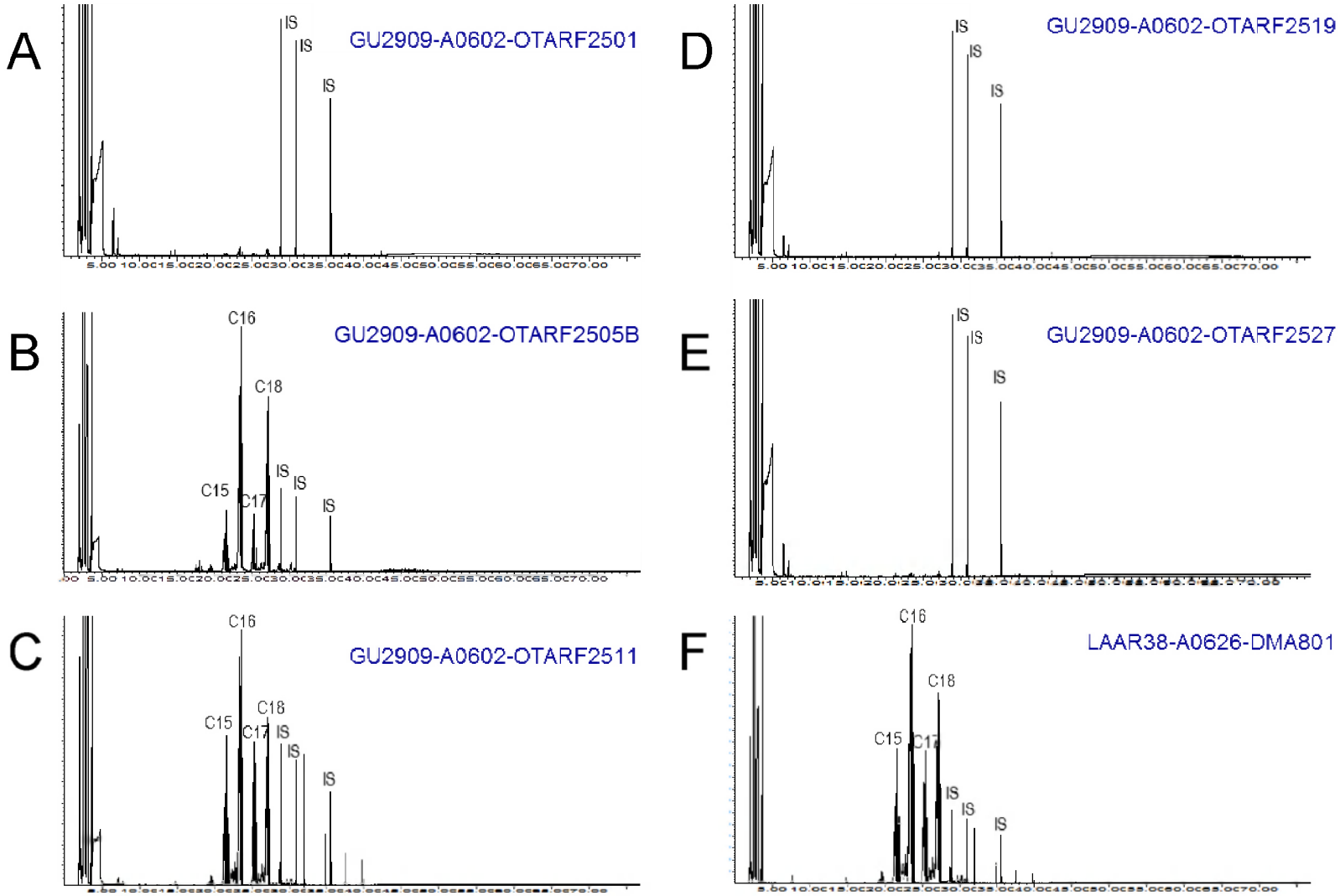
		Top Kill Muds										Encore Drill Mud	
	Client ID	GU2909-A0602-OTARF2501		GU2909-A0602-OTARF2505B		GU2909-A0602-OTARF2511		GU2909-A0602-OTARF2519		GU2909-A0602-OTARF2527		LAAR33-A0626-DMA801	
Abbrev	Analytes												
D0	cis/trans-Decalin		U	0.68	J	1.15	J	0.26	J	0.18	J	0.73	J
D1	C1-Decalins		U	2.45		2.99		1.24	J	0.98	J	2.68	
D2	C2-Decalins		U	4.47		6.64			U		U	6.69	
D3	C3-Decalins		U		U	3.60			U		U		U
D4	C4-Decalins		U		U		U		U		U		U
BT0	Benzothiophene		U		U		U		U		U		U
BT1	C1-Benzo(b)thiophenes		U		U		U		U		U		U
BT2	C2-Benzo(b)thiophenes		U	1.18	J		U		U		U		U
BT3	C3-Benzo(b)thiophenes		U	3.98			U		U		U		U
BT4	C4-Benzo(b)thiophenes		U	3.14			U		U		U		U
N0	Naphthalene	0.53	J	1.21	J	1.30	J	1.69	J	1.29	J	1.10	J
N1	C1-Naphthalenes	0.58	J	2.40		2.54		2.65		1.82	J	1.32	J
N2	C2-Naphthalenes	1.42	J	5.53		6.43		4.66		2.98		4.14	
N3	C3-Naphthalenes	1.33	J	9.14		6.93		4.04		2.89		9.29	
N4	C4-Naphthalenes		U	7.79		6.01			U		U		U
B	Biphenyl	0.51	J	0.66	J	1.20	J	1.25	J	0.87	J	0.68	J
DF	Dibenzofuran		U	2.08		3.42			U		U	8.04	
AY	Acenaphthylene		U		U		U		U		U		U
AE	Acenaphthene		U		U		U	0.22	J	0.22	J		U
F0	Fluorene	0.45	J		U		U	0.51	J	0.41	J		U
F1	C1-Fluorenes	0.63	J		U		U	1.09	J	0.72	J		U
F2	C2-Fluorenes		U		U		U		U		U		U
F3	C3-Fluorenes		U		U		U		U		U		U
A0	Anthracene	0.10	J	0.14	J	0.15	J	0.21	J	0.13	J		U
P0	Phenanthrene	0.67	J	0.81	J	1.21	J	2.20	J	1.39	J	0.68	J
PA1	C1-Phenanthrenes/Anthracenes	0.79	J	1.48	J	1.56	J	1.70	J	1.30	J	1.06	J
PA2	C2-Phenanthrenes/Anthracenes		U	2.39		2.12		2.64		1.63	J	2.39	
PA3	C3-Phenanthrenes/Anthracenes		U	1.83	J		U		U	1.03	J		U
PA4	C4-Phenanthrenes/Anthracenes		U	0.46	J		U		U		U		U
RET	Retene		U	2.10			U		U		U		U
DBT0	Dibenzothiophene	0.14	J		U		U	0.86	J	0.63	J		U
DBT1	C1-Dibenzothiophenes	0.55	J	0.81	J	1.79	J	0.99	J	0.84	J		U
DBT2	C2-Dibenzothiophenes	1.22	J	2.73		1.62	J	1.82	J	1.51	J	1.54	J
DBT3	C3-Dibenzothiophenes		U	3.71			U	1.91	J	1.22	J		U
DBT4	C4-Dibenzothiophenes		U		U		U		U		U		U
BF	Benzo(b)fluorene		U		U		U		U		U		U
FL0	Fluoranthene	0.53	J	0.37	J	0.22	J	1.31	J	0.62	J		U
PY0	Pyrene	0.47	J	0.41	J	0.40	J	1.23	J	0.59	J		U
FP1	C1-Fluoranthenes/Pyrenes	1.17	J	1.23	J	0.80	J	1.62	J	1.00	J		U
FP2	C2-Fluoranthenes/Pyrenes		U		U	0.93	J	2.17	J	1.03	J		U
FP3	C3-Fluoranthenes/Pyrenes		U		U		U		U		U		U
FP4	C4-Fluoranthenes/Pyrenes		U		U		U		U		U		U
NBT0	Naphthobenzothiophenes	0.12	J	0.09	J	0.12	J	0.35	J	0.25	J		U
NBT1	C1-Naphthobenzothiophenes		U		U		U		U		U		U
NBT2	C2-Naphthobenzothiophenes		U		U		U		U		U		U
NBT3	C3-Naphthobenzothiophenes		U		U		U		U		U		U
NBT4	C4-Naphthobenzothiophenes		U		U		U		U		U		U
BA0	Benz[a]anthracene	0.22	J	0.14	J	0.10	J	0.52	J	0.24	J		U
C0	Chrysene/Triphenylene	0.49	J	0.32	J	0.34	J	1.36	J	0.84	J		U
BC1	C1-Chrysenes	0.68	J		U		U	1.64	J	1.00	J		U
BC2	C2-Chrysenes		U		U		U		U		U		U
BC3	C3-Chrysenes		U		U		U		U		U		U
BC4	C4-Chrysenes		U		U		U		U		U		U
BBF	Benzo[b]fluoranthene	0.29	J	0.12	J		U	0.93	J	0.37	J		U
BJKF	Benzo[k]fluoranthene	0.28	J		U		U	0.63	J		U		U
BAF	Benzo[a]fluoranthene		U		U		U		U		U		U
BEP	Benzo[e]pyrene	0.36	J	1.64	J	0.33	J	0.84	J	0.50	J	0.80	J
BAP	Benzo[a]pyrene	0.35	J	1.13	J	0.16	J	1.09	J	0.52	J	0.47	J
PER	Perylene		U	0.78	J		U	0.33	J	0.11	J	0.34	J
IND	Indeno[1,2,3-cd]pyrene	0.24	J		U	0.09	J	0.86	J	0.36	J		U
DA	Dibenz[a,h]anthracene		U	0.13	J		U	0.32	J	0.17	J		U
GHI	Benzo[g,h,i]perylene	0.34	J		U	0.15	J	0.91	J	0.49	J		U
	TPAH50 (N0-GHI, excl. RET & PER)	14.5		48.7		39.9		44.2		28.9		31.5	
	U - not detected												
	J - estimated, conc. Below reporting limit												

Table 5: Inventory of surface sediments (0-1 cm) from 2010-2011 and 2014 containing olefin-based SBM. Locations displayed in Figure 4. Shaded samples not reasonably attributable to DWH, but rather to former drill sites.

2010-2011	
Client ID	**Alpha Lab ID**
HD5_HD5004_A1214_S_BR2_01	1012098-06
HD5_HD5004_A1214_S_GR2_04	1012098-03
HD5_HD5004_A1214_S_PU2_03	1012097-15
HD5_HD5004_A1214_S_YW2_05	1012096-11
HSW2L2_FP0093_B0423_S_50_E2_859	1104258-03
HSW2L2_FP0093A_B0423_S_50_G2_863	1104258-05
HSW2L2_FP0094_B0423_S_50_H2_868	1104258-07
HSW2L2_FP0094_B0423_S_50_I2_869	1108146-17
HSW2L2_FP0095_B0424_S_50_J2_875	1104258-15
HSW2L2_FP0095_B0424_S_50_L2_877	1105067-08
HSW2L2_FP0096_B0424_S_50_N2_885	1104258-09
HSW2L2_FP1088A_B0423_S_50_D2_810	1105066-19
HSW2L2_FP1089_B0423_S_50_G2_817	1105067-01
HSW2L2_FP1090_B0423_S_50_H2_824	1104258-16
HSW2L2_FP1090_B0423_S_50_K2_826	1105067-05
HSW2L2_FP2084_B0422_S_50_F2_773	1108146-08
HSW6_FP10188_B0827_S_1485_50_H2_0072	1201022-18
SB9-65-B0525-S-D038SW-HC-0026	1107040-01
SB9-65-B0525-S-D038SW-HC-0104	1108148-09
SB9-65-B0525-S-D042S-HC-0143	1107040-02
SB9-65-B0525-S-D042S-HC-0182	1108148-03
SB9-65-B0526-S-D040S-HC-0497	1107040-05
SB9-65-B0526-S-D042S-HC-0222	1108148-02
SB9-65-B0526-S-NF006MOD-HC-0379	1107040-04
SB9-65-B0526-S-NF006MOD-HC-0419	1108148-11
SB9-65-B0526-S-NF006MOD-HC-0458	1108148-12
SB9-65-B0527-S-D040S-HC-0536	1108148-14
SB9-65-B0527-S-D040S-HC-0576	1108148-15
SB9-65-B0528-S-ALTNF001-HC-1207	1107040-11
SB9-65-B0528-S-D031S-HC-1087	1107040-10
SB9-65-B0528-S-D031S-HC-1127	1108147-09
SB9-65-B0528-S-D031S-HC-1167	1108147-10
SB9-65-B0528-S-D034S-HC-0969	1107040-09
SB9-65-B0528-S-D034S-HC-1008	1108148-17
SB9-65-B0528-S-D034S-HC-1047	1108148-18
SB9-65-B0529-S-ALTNF001-HC-1246	1108148-05
SB9-65-B0529-S-ALTNF001-HC-1285	1108148-06
SB9-65-B0529-S-LBNL1-HC-1325	1107040-12
SB9-65-B0529-S-LBNL1-HC-1368	1108150-01
SB9-65-B0602-S-LBNL1-HC-1404	1108150-02
SB9-65-B0608-S-VK916-HC-3454*	1107041-08
SB9-65-B0608-S-VK916-HC-3494*	1108136-12
SB9-65-B0608-S-VK916-HC-3534*	1108136-13
*Not Macondo-related	

2014	
RH1-65-E0605-S-LBNL1-HC-1128	1406025-13
RH1-359-E0623-S-MC253-NESW1-HC-3896	1408015-07
RH1-359-E0624-S-21-HC-3967	1408011-09
RH1-359-E0621-S-NF012-HC-3659	1408020-03
RH1-359-E0623-S-MC253-NESW5-HC-3879	1408021-02
RH1-359-E0623-S-NF006MOD-HC-3705	1408019-12
RH1-359-E0623-S-NF006MOD-HC-3826	1408021-19
RH1-359-E0623-S-NF006MOD-HC-3850	1408019-07
RH1-359-E0623-S-NF006MOD-HC-3732	1408019-17
RH1-359-E0623-S-NF006MOD-HC-3789	1408021-14
RH1-359-E0623-S-NF006MOD-HC-3755	1408020-17
RH1-65-E0604-S-D044S-HC-0931	1406031-05
RH1-65-E0605-S-LBNL1-HC-1155	1406025-17
RH1-65-E0603-S-D031S-HC-0616	1406032-13
RH1-65-E0603-S-D031S-HC-0559	1406032-05
RH1-65-E0603-S-D031S-HC-0589	1406032-09
RH1-65-E0605-S-ALTNF001-HC-1043	1406020-01
RH1-65-E0605-S-ALTNF001-HC-1013	1406019-17
RH1-65-E0605-S-ALTNF001-HC-1070	1406020-05
RH1-65-E0603-S-D034S-HC-0643	1406023-09
RH1-65-E0604-S-D040S-HC-0729	1406030-17
RH1-65-E0603-S-D040S-HC-0671	1406030-09
RH1-65-E0603-S-D040S-HC-0702	1406030-13
RH1-65-E0531-S-VK916-HC-0162*	1406028-17
RH1-65-E0601-S-D009S-HC-0246*	1406017-13
RH1-65-E0602-S-MF002-HC-0362*	1406033-01
*Not Macondo-related	

Figure 1: GC/FID chromatograms for the top kill (A through E) and Encore drill mud (F) studied.
C# - olefin clusters; IS – internal standard. The large peak to the far left in each is laboratory solvent.



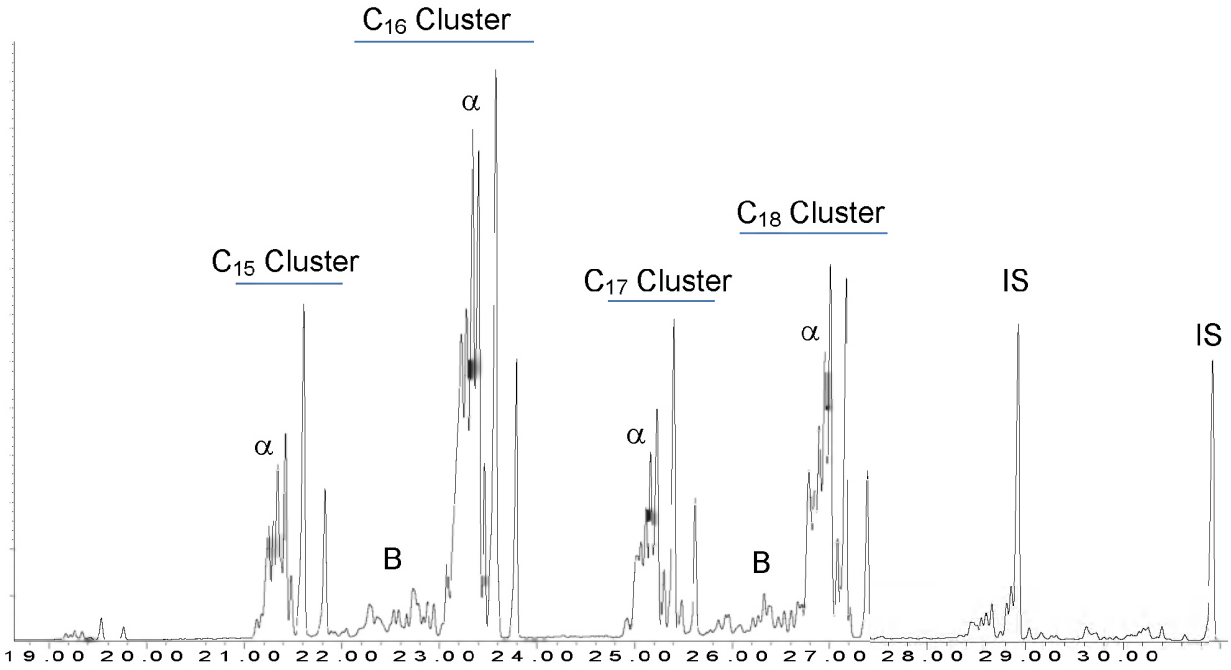


Figure 2: Partial GC/FID chromatogram of Top Kill mud (GU2909-A0602-OTARF2511) showing the olefin clusters around C_{15}, C_{16}, C_{17}, and C_{18}. α - alpha olefins, B – branched olefins, unidentified peaks include various internal olefins. Peak identifications per Aeppli et al. (2013). Note minor clusters around C14, C19, and C20 are also present. IS-internal standard.

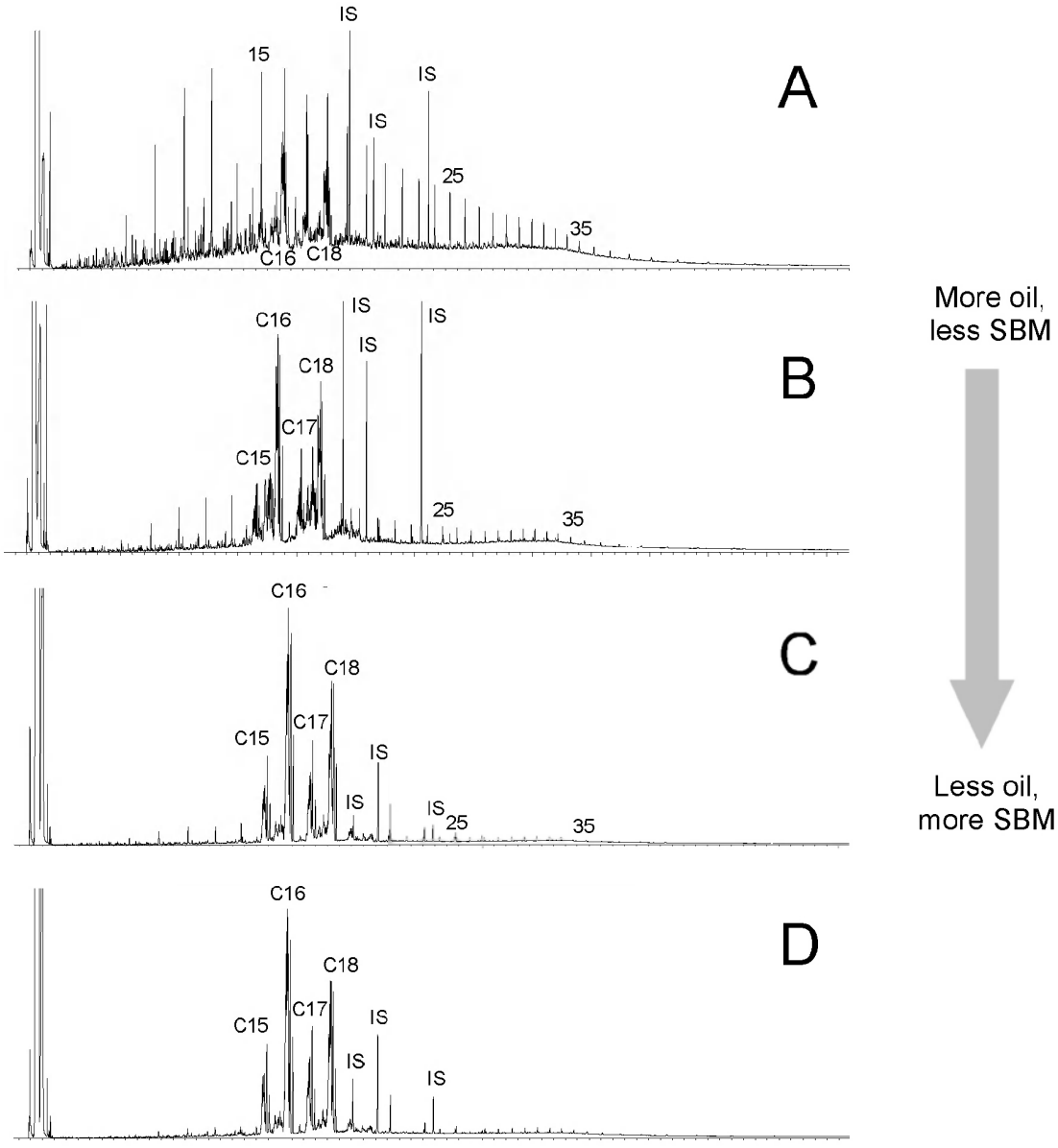


Figure 3: GC/FID chromatograms showing deep-sea sediments containing varying proportions of Macondo oil and olefin-based SBM. (A) SB9—65-B0528-S-D034S-HC-0969, (B) SB9-65-B0528-S-ALTNF001-HC-1007, (C) HSW2L2_ FP0094_B0423_S_50_H2_868,and (D) HSW2L2_ FP1088A_ B0423_S_50_D2_810. #-n-alkane carbon number, C#-olefin cluster, IS-internal standard.

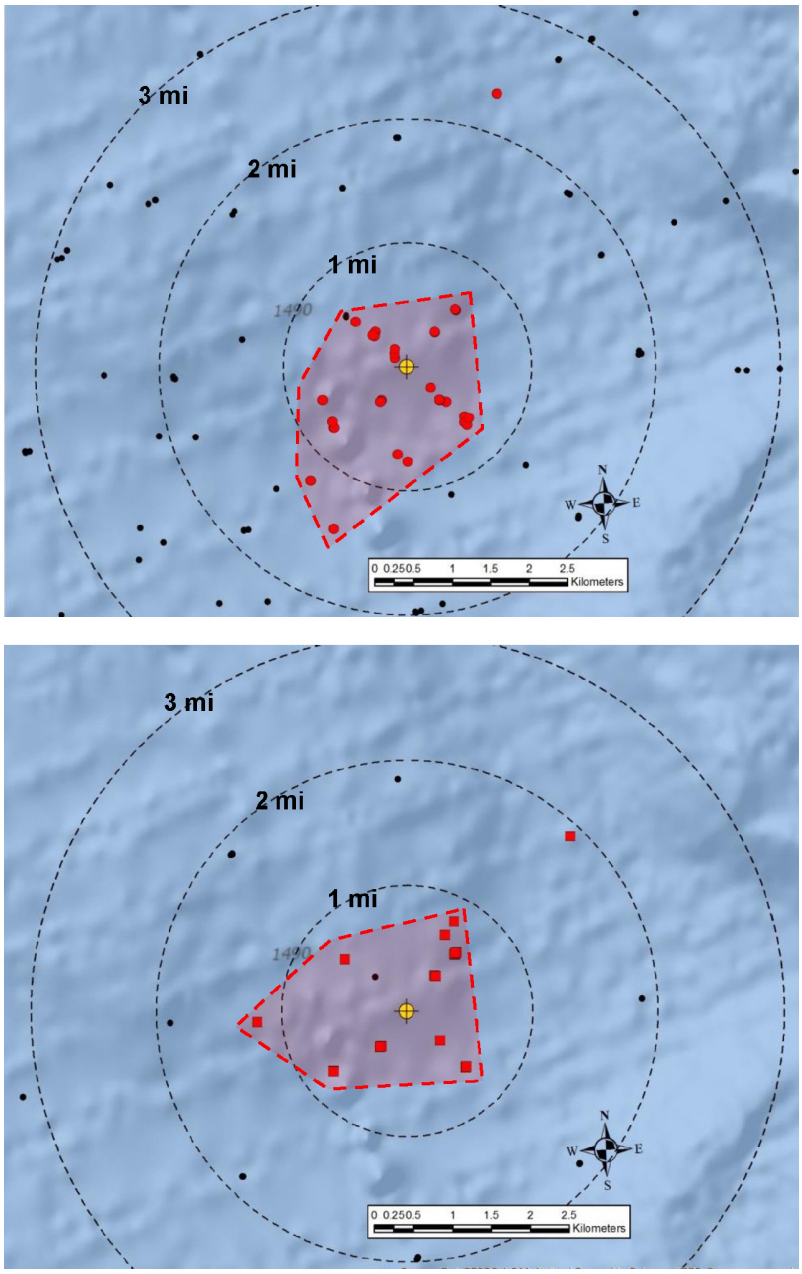


Figure 4: Maps showing the approximate "footprints" of surface (0-1 cm) sediments containing SBM collected in (A) 2010-2011 and (B) 2014. Black dots show all core locations where SBM was not present. Virtually all cores collected within 1 mile of the Macondo well contain SBM in 2010-2011 and 2014. See Table for inventory of cores containing SBM at the surface.

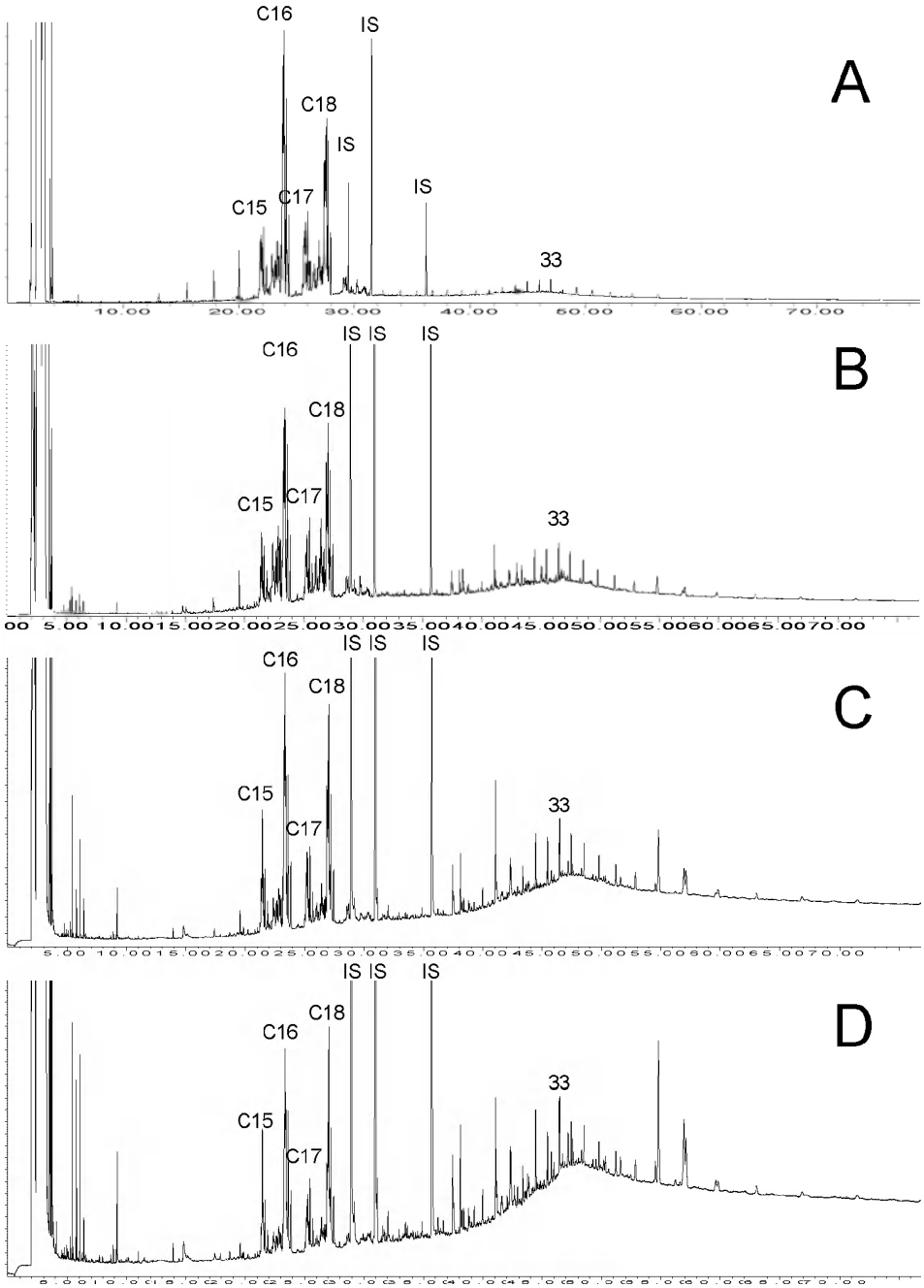


Figure 5: GC/FID chromatograms for sediments in the SB9-65-B026-S-NF006MOD-HC-0458-0461 core (2011) showing the presence of olefin-based SBM in (A) 0-1 cm, (B) 1-3 cm, (C) 3-5 cm, and (D) 5-10 cm intervals. This and other cores with SBM below 5 cm deep near the Macondo well indicate a significant deposition of "sediment" occurred in the area proximal (< 1 mile) to the well site. This core is 0.6 miles NE of wellhead. #-n-alkane carbon number, C#-olefin cluster, IS-internal standard.

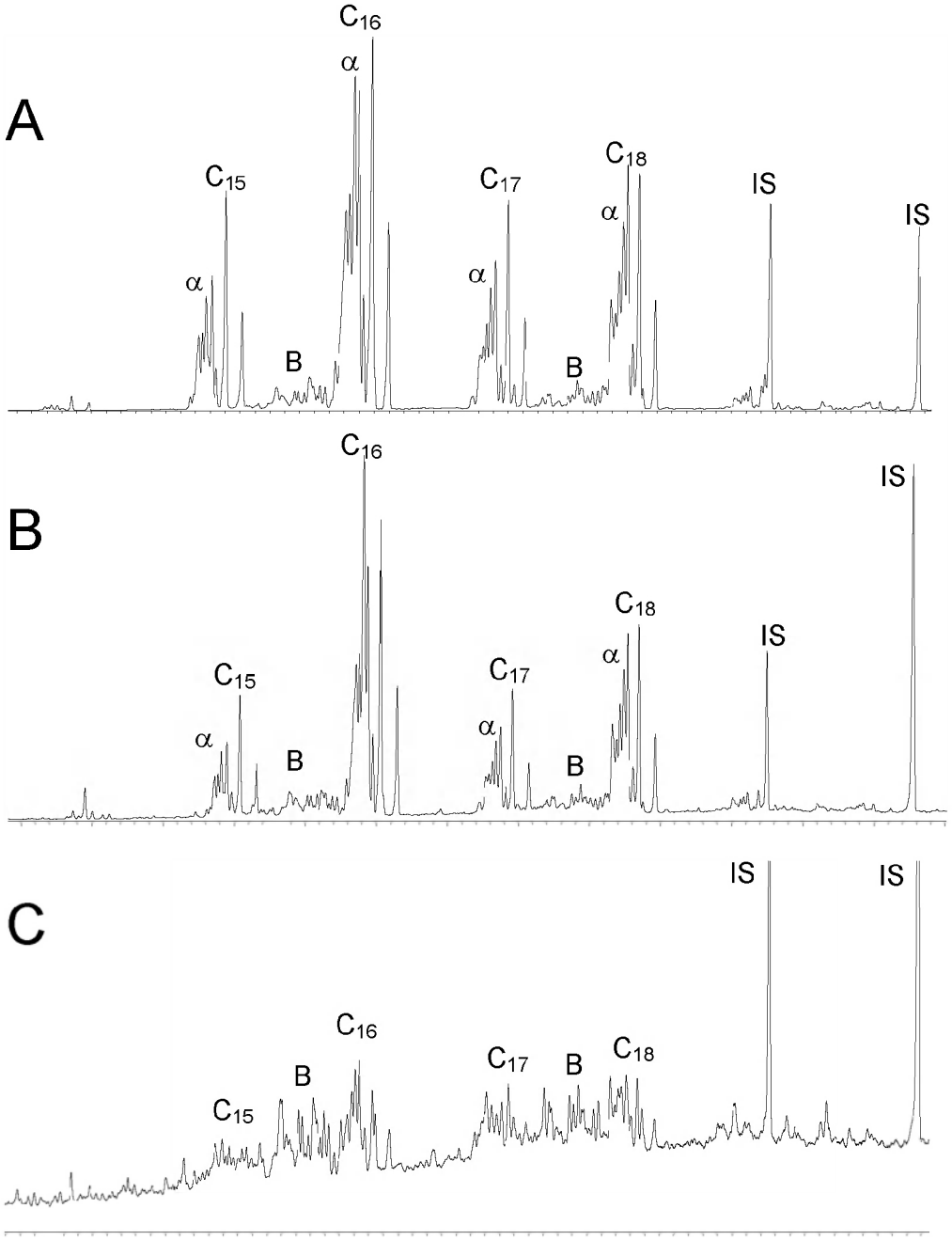


Figure 6: Partial GC/FID chromatogram of (A) "fresh" Top Kill mud (GU2909-A0602-OTARF2511), (B) unweathered SBM in sediment collected in 2014 (3-5 cm; RH1-65-E0603-S-D040S-HC-0673), and (C) weathered SBM in sediment collected in 2014 (1-3 cm; RH1-65-E0604-S-D040S-HC-0730) showing the olefin clusters around C_{15}, C_{16}, C_{17}, and C_{18}. α - alpha olefins, B – branched olefins, unidentified peaks include various internal olefins. Note relative persistence of branched olefins in (C).