INTRODUCTION
An unprecedented volume of crude oil was burned during the Deepwater Horizon oil spill response (Figure 1), with an estimated 220,000-310,000 bbl of surface oil consumed by in-situ burning over a ten-week period in 2010. Most of the resultant burn residue from these large-scale operations sank in the relatively deep waters of the Gulf of Mexico.

In late 2010, the deep-water royal red shrimp fishery operating north of the Macondo wellhead and the primary burn zone encountered tarballs at 200 m (Figure 2). At that time, some of these tarballs were tentatively sourced as Deepwater Horizon in-situ burn residue (Figure 3). This apparent intersection of the fishery with burned oil suggested a need to better understand the characteristics of burned crude oil and the changes that occur to oil during the combustion process.
DEEPWATER HORIZON BURN OPERATIONS
The Deepwater Horizon surface oil was found to readily burn, and a total of 411 individual burns took place during the spill response, with 376 judged to have consumed significant volumes of oil. On June 18, 2010 alone, sixteen in-situ burns took place (U.S. Coast Guard, 2011). Figure 3 shows the locations of in-situ burn operations in the Gulf of Mexico relative to the Louisiana coast and the location of the Macondo wellhead.

While not formally monitored, U.S. Coast Guard and operational workers did observe changes in the physical characteristics of the Macondo oil (also referred to as MC252 oil or Deepwater Horizon oil) once it had been burned: its viscosity and density both appeared to increase. In fact, in-situ burning apparently increased the density of the residual oil to the point where much, if not most, of the post-burn residue was heavier than seawater, resulting in it slowly sinking (Figure 4). A U.S. Coast Guard Gulf Strike Team member who witnessed many of the early burn operations recalled:

The residue definitely did sink, it tended to temporarily float in those strings like...in the photo, and within a few minutes post burn would begin to sink. If you tried to touch it with a pole or other object it began to slowly sink. The consistency was sticky like paste. The residue appeared generally the same regardless of burn duration, with some variation if there was non-petroleum debris in it, it had more visible whitish ash (MSTCS Drew Jaeger, USCG Gulf Strike Team, pers. comm., 27 September 2011).

The tendency of the burn residues to sink rendered them both difficult to remove from the marine environment, and difficult to sample in order to determine physical and chemical changes. When the royal red shrimp fishery encountered what appeared to be burn residue in deep water north of the Macondo wellhead, the need for enhanced in-situ burning physical and chemical fate studies became apparent.
Figure 3. Composite map showing locations of the Macondo wellhead, in-situ burn operations, royal red shrimp trawls with preliminary source identifications, and known hydrocarbon seeps. Numbers in boxes denote approximate tarball counts in each quadrant. Prepared by Bret Magdasy, Genwest Systems.
PROJECT DESCRIPTION AND OVERVIEW OF METHODS

The availability of different sample materials related or presumed to be related to *in-situ* burning during the *Deepwater Horizon* provided the opportunity to study the physical and chemical changes that occur to oil when it is burned at sea. The different sample materials, or matrices, included Macondo source oil; pre-burn oil and post-burn residues from actual *in-situ* burns conducted in May and July, 2010; suspected burn residue collected from deep-water shrimp trawls; before and after samples from laboratory or meso-scale controlled burns of oil at LSU; and a variety of other examples of weathered oil attributed to the *Deepwater Horizon* spill.

Two physical measurements, and chemical analysis by gas chromatography/mass spectrometry with selected ion monitoring (GC/MS-SIM) were used to characterize the samples. Biomarkers were used for source identification. The resulting matrix of oil sample type, and physical and chemical characteristics was then used to infer the changes that occur when crude oil is burned.

Figure 4. *In-situ* burn residue just below the surface of the water following a burn operation for the *Deepwater Horizon* oil spill response, May 2010. U.S. Coast Guard photos, CPO R.J. Schrader.

Density and percent asphaltenes were the physical parameters determined for Macondo source oil; for a similar South Louisiana Crude used in one of the two laboratory burns; and, for samples collected during *in-situ* burn operations. In addition, 55 density and 41 asphaltene content values were measured in other *Deepwater Horizon* oil residue samples collected during the response.\(^1\)

Given the importance of how oil in all its forms behaves on and in the water, density was an obvious physical characteristic to measure.

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\(^1\) Viscosity was acknowledged to be a useful parameter; however, the majority of the residue samples were too viscous for determination of normal fluid flows at environmental temperatures.
Asphaltenes are one of the major components of petroleum, but are chemically complex and not well-defined as a group of compounds. Speight (1980) described them as dark brown to black friable solids that have no definite melting point, instead decomposing upon heating into a carbonaceous residue. Asphaltenic content was determined gravimetrically by dissolving oil residues in hexane and toluene and weighing the insoluble remnant material as asphaltene. This parameter may be less obvious as a key physical characteristic, but Speight (1980) stated that the asphaltic constituents of petroleum exert considerable influence over the physical properties of crude oils.

Target GC/MS-SIM analytes were used to identify petrogenic, biogenic, and pyrogenic hydrocarbons in a variety of sample matrices. The analyte list included commonly-found aromatic hydrocarbons and their alkyl homologs, saturate compounds from C10 to C35, isoprenoids pristane and phytane, and four groups of oil “biomarkers”. The oil biomarkers include the tri- and pentacyclic hopanes, diasteranes and regular steranes, 14β(H)-steranes, and the triaromatic steroids.

Some of these GC/MS data were used to calculate the Fossil Fuel Pollution Index (FFPI) (Boehm and Farrington, 1984) to determine if the PAH signatures in in-situ burn residues changed from a petrogenic (oil-derived) signature to a more pyrogenic (combustion-derived) signature. The original FFPI was modified to incorporate an expanded list of target aromatic compounds. Higher FFPI values (≥0.6) are considered to reflect petrogenic PAH sources, while FFPI < 0.6 indicate pyrogenic-sourced PAHs.

MACONDO SOURCE OIL CHARACTERISTICS

The Macondo crude oil released during the Deepwater Horizon spill was a light, sweet crude, with a density of 0.839 g/cm³ at 15° C. (API gravity 37.2°) (SL Ross Environmental Research, 2010). The fresh oil floated on seawater. In lab studies, the density of the oil increased with increased weathering (evaporation); when the volume of oil was reduced by about 45% through artificial weathering, its density increased to 0.897. As the density of seawater is approximately 1.02, the weathered Macondo oil would have floated in the Gulf of Mexico as well.

The asphaltene content of the fresh Macondo crude oil was measured at 0.8 percent.

The Macondo oil that rose through 1300 m of seawater to the surface of the Gulf would have differed from the fresh oil at depth, in that many of the light hydrocarbons would have dissolved into the water column during the transit of the oil to the surface. Nevertheless, the number of successful in-situ burns showed that oil reaching the surface retained sufficient lighter hydrocarbons to support sustained combustion.

DEEPWATER HORIZON IN-SITU BURN RESIDUE ANALYSIS

A total of 20 actual in-situ burn samples (i.e., collected in the field during Deepwater Horizon response operations) were analyzed. Of the 20, there were 9 sets of paired pre-burn and post-burn samples. The average density of oil before in-situ burning was 0.88 and the average density of samples after in-situ burning was 0.95. The increase in density was significant. The average percent asphaltenes of samples before in-situ burning was 1.9 and the average percent asphaltenes of samples after in-situ burning was 4.8. The percent asphaltenes in post-burn samples collected shortly after burn operations increased; however, the increase was not statistically significant.

Chemical characterization by GC/MS-SIM of Deepwater Horizon oil collected at-sea before and after in-situ burning (Figures 5a & 5b) indicated that there was enhancement of the less-volatile aromatics that are also considered as pyrogenic (e.g., fluoranthene, pyrenes, chrysenes,
benzo(a)pyrene, etc.). With the exception of indeno(1,2,3-cd)pyrene, these compounds were measured in the Macondo oil; however, their concentrations increased after in-situ burning. The average FFPI of the before in-situ burning samples was 0.77 and the average FFPI of the after in-situ burning samples was 0.65. This difference was significant, reflecting the expected shift to more pyrogenic profiles.

**SAMPLES FROM CONTROLLED BURNS OF MACONDO & SOUTH LOUISIANA CRUDE OILS**

Two controlled burns (laboratory and meso-scale) of crude oil were conducted to provide additional empirical information on changes in physical and chemical characteristics that occur in the combustion process. One burn was performed with Macondo source oil; due to the limited amount of the Macondo oil available, the second, larger-scale burn utilized a similar South Louisiana crude.

Samples from the first, smaller-scale controlled burn of Macondo oil exhibited similar chemical characteristics as the in-situ burn samples collected during the response, discussed in the preceding section. There was a significant difference in the FFPI; and there was a significant enhancement in the same pyrogenic PAHs. However, results of the second, larger-scale burn of South Louisiana crude oil were quite different from the first lab burn and actual Deepwater Horizon in-situ burn samples. There were no significant changes in density or percent asphaltenes. There was no enhancement of the pyrogenic PAHs observed in the actual ISB samples and the smaller-scale controlled burn. Only the modified FFPI showed a statistically significant change. The average FFPI before burning was 0.80 and the average FFPI after burning was 0.70. The difference in results may be due to the use of the more generic South Louisiana crude oil instead of Macondo oil.

**ROYAL RED SHRIMP TRAWL TARBALL ANALYSIS**

The last, but very important category of samples, was field-collected tarballs collected by shrimp trawl gear along the 200 m bathymetry line. Following the closure of the royal red shrimp fishery in the Gulf of Mexico due to the trawl encounters with tarballs at depth, NOAA chartered two fishing vessels to sample royal red shrimp in the closed area over three cruises in 2010 and 2011. Samples of shrimp caught during these surveys were assessed for potential oil contamination. Although some of the shrimp were initially judged to be suspect by sensory evaluation, all tissue chemistry results showed no evidence of PAH contamination. The tarballs collected from the shrimp trawls were of particular interest for this study. These tarballs were large, viscous, and dense masses of oily residue encapsulated within a hardened exterior. The tumbling of these tarballs in the trawl nets incorporated shrimp and other trawl debris into the residue (see Figure 2). The physical and chemical properties of the trawl-derived tarballs differed from the other oil matrices analyzed for this study. For example, the average density and percent asphaltenes of the trawl tarballs were significantly different from other Macondo oil-derived tarballs. The average density of the shrimp trawl tarballs was 1.04 g/mL and the average percent asphaltenes was 20%—compared to the density of 0.73 g/mL and percent asphaltenes of 2% for other Macondo tarballs.

While the average density of the shrimp trawl tarballs was not significantly higher than the average density of in-situ burn samples collected after burning, the asphaltenes content was significantly greater than the percent asphaltenes of the in-situ burn samples collected during burn operations as well as other tarballs formed after the Deepwater Horizon incident. This suggests some additional or alternate factor affected these “sunken tarballs” but not those samples taken immediately after in-situ burning at sea or samples in other oil matrices. In the trawl tarball chemistry discussion below, one potential reason for the compositional differences is suggested.
Figure 5a & 5b. Significant enhancement of pyrogenic compounds in oil as a result of in-situ burning, May 2010 (a) and July 2010 (b).

Chemically, all shrimp trawl tarballs (n=26) matched Macondo oil based on the diagnostic biomarker ratio analyses. However, the normal alkane profile of these sunken tarballs (Figure 6b) was significantly different from other Macondo oil tarballs (Figures 6c and 6d). The profile appeared to be unique to trawl tarballs collected at 200 m—but was similar to the normal alkane profile of a simulated distillation\(^2\) of Macondo source oil at 205°C (Figure 6a). The simulated distillation chromatogram, and that for shrimp trawl tarballs appear to reflect a process of thermal fractionation that was absent in most alkane profiles of the in-situ burn oil residues collected after burning. This suggests that thermal fractionation, and combustion, may result in two qualitatively different types of residual materials, and may explain why deep-water tarballs differ from the other oil matrices characterized in this study.

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\(^2\) Simulated distillation is a gas chromatographic technique used to simulate the results of a distillation tower, separating crudes or other multicomponent blends into component fractions by boiling points.
Figures 6 a-d. Normal alkane distribution of (a) the simulated distillation of Macondo oil at 205°C; (b) tarball collected in a royal red shrimp trawl suspected to be from in-situ burning operations; (c) Macondo tarball not associated with in-situ burning; (d) and microbially-weathered Macondo oil.
BIOMARKER RATIO ANALYSIS

An objective of the forensic interpretation of analytical results was to determine if in-situ burn residues had measurable characteristics that could distinguish them from other oil residues/matrices. Some of those characteristics noted in the results included:

- Change (increase) in density and percent asphaltenes (Table 1, below);
- Decrease in FFPI (Table 1, below);
- Enhancement of pyrogenic PAHs (Figure 5);
- Evidence of thermal fractionation in the normal alkane profile (Figure 6).

However, none of these discriminating factors alone could reliably make the distinction among sources. Because of this, the forensic interpretation was expanded to include a statistical analysis of sample matrices (e.g., ISB oil, ISB tarball, oil, other, sediment, or tarball) and sampling locations (e.g., marsh, ocean depth, shore, or water surface) based on the diagnostic biomarker ratio analyses (Meyer et al., 2014; Ramsey et al., 2014). Statistical tests were applied to the sample matrix for each of 15 diagnostic biomarker ratios to determine if any could distinguish between in-situ burn residues and other MC 252 oil residues.

Of the 15 ratios evaluated, 4 showed significant differences between in-situ burn residues and other Macondo oil residues. The analysis showed the diasterane and regular sterane ratio C28 24-methyl-5α(H),14α(H),17α(H), 20R-cholestan / C29 24-ethyl-5α(H),14α(H),17α(H), 20R-cholestan may be useful for distinguishing ISB oil from other oil residues; and, C27 5α(H),14β(H),17β(H)-cholestan (20R+20S) / C28 24-methyl-5α(H),14β(H),17β(H)-cholestan (20R+20S) + C29 24-ethyl-5α(H),14β(H),17β(H)-cholestan (20R+20S) may be useful distinguishing ISB tarballs from other tarballs.

SUMMARY

Table 1 below summarizes values obtained for different oil parameters and oil matrices.

<table>
<thead>
<tr>
<th></th>
<th>Macondo Riser Oil</th>
<th>SLC Pre-Burn</th>
<th>SLC Post-Burn</th>
<th>ISB Oil Pre-Burn</th>
<th>ISB Oil Post-Burn</th>
<th>Shrimp Tarballs</th>
<th>Other Weathered Macondo Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/mL</td>
<td>0.85</td>
<td>0.86</td>
<td>0.84</td>
<td>0.88</td>
<td>0.95</td>
<td>1.04</td>
<td>0.73</td>
</tr>
<tr>
<td>Asphaltene %</td>
<td>0.80</td>
<td>0.68</td>
<td>2.5</td>
<td>1.9</td>
<td>4.8</td>
<td>20</td>
<td>2.0</td>
</tr>
<tr>
<td>FFPI</td>
<td>0.82</td>
<td>0.83</td>
<td>0.70</td>
<td>0.77</td>
<td>0.65</td>
<td>0.62</td>
<td>0.59</td>
</tr>
</tbody>
</table>

The results from this study indicated that no single metric can distinguish in-situ burn residue from all other forms of residual oil. Table 1 shows that increases in percent asphaltene content are indicative of burned oil; but significantly greater asphaltene content of the shrimp trawl tarballs suggests a different mechanism than other burn residues. Comparison of normal alkane profiles, and the similarity between the chromatogram for the trawl tarballs and a simulated 205°C distillation of Macondo oil, support the idea that in-situ burning may result in both combusted oil as well as in-situ fractionation. This would explain the measurably different characteristics of materials that are identified as Deepwater Horizon burn residue. Although FFPI values could identify fresh or less weathered oil, they did not distinguish burn residues from other oil residues.

The majority of residues from the Deepwater Horizon oil spill retained their oil biomarker signatures, making diagnostic ratio analyses possible. The diagnostic ratios were used to:
1) Determine if the oil residue was a match to Macondo source oil; and
2) Determine if there were any differences in the ratios in matching oil residues based on sample matrix and sampling location.

A total of 4 out of the 15 diagnostic biomarker ratios did distinguish in-situ burn residues from the majority of the other residues. Two of these ratios may be useful, respectively, for distinguishing in-situ burn residue from other oil residues, and in-situ burn tarballs from other tarballs.

CONCLUSIONS
The Deepwater Horizon spill experience validated the operational feasibility and practical application of in-situ burning as an open water response method. Like nearly everything else about this incident, the scale of in-situ burn operations was unprecedented: between 28 April and 19 July 2010, 411 individual burns took place, consuming an estimated 220,000-310,000 bbl of oil. This is roughly equivalent to the total oil volume released in the Exxon Valdez spill in 1989.

Implicit in these numbers is the large volume of in-situ burn residue that was generated during the Deepwater Horizon operations. Using the standard in-situ burn efficiency estimates of 90-95 percent, the amount of residue resulting from the operations potentially ranged from 11,000-33,000 bbl. This is a substantial amount of petroleum hydrocarbons introduced into a relatively small portion of the marine environment—although it should be noted that natural seeps contribute an estimated 560,000 to 1.4 million bbl of oil into the waters of the Gulf of Mexico (National Research Council, 2003) each year (note seep locations in Figure 3).

The fate of the burn residue from the Deepwater Horizon in-situ burn operations might never have been known, were it not for the chance encounters of the single deep water fishery operating in the same general area as most of the burn operations (Figure 3). Impacts to the fishery were minimal and it was quickly re-opened after testing and analysis by federal fisheries managers and seafood safety specialists. However, the residue and fishery interactions that occurred in 2010 and 2011 represent a cautionary footnote to large-scale in-situ burn operations that should be factored into tradeoff analysis for future spill responses. Further, the Deepwater Horizon experience suggests a need for additional research into burn residue containment or recovery methods that would reduce or eliminate potential fishery impacts associated with sinking residue. To facilitate this additional research, we recommend incorporation of pre- and post-burn sample collection, archiving, and analysis into operational planning for in-situ burning during actual spill responses.

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