Floating oil-covered debris from Deepwater Horizon: identification and application

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Abstract
The discovery of oiled and non-oiled honeycomb material in the Gulf of Mexico surface waters and along coastal beaches shortly after the explosion of Deepwater Horizon sparked debate about its origin and the oil covering it. We show that the unknown pieces of oiled and non-oiled honeycomb material collected in the Gulf of Mexico were pieces of the riser pipe buoyancy module of Deepwater Horizon. Biomarker ratios confirmed that the oil had originated from the Macondo oil well and had undergone significant weathering. Using the National Oceanic and Atmospheric Administration’s records of the oil spill trajectory at the sea surface, we show that the honeycomb material preceded the front edge of the uncertainty of the oil slick trajectory by several kilometers. We conclude that the observation of debris fields deriving from damaged marine materials may be incorporated into emergency response efforts and forecasting of coastal impacts during future offshore oil spills, and ground truthing predicative models.

Keywords: Deepwater Horizon, Macondo well, Gulf of Mexico, oil spill, floating debris

1. Introduction
Following the explosion of Deepwater Horizon in the Gulf of Mexico on 20 April 2010 and the subsequent release of 170 million gallons of crude oil [1] from the Macondo well, pieces of ‘honeycomb’ material were spotted floating in coastal waters and coming ashore on Gulf coast beaches (figure 1). These buoyant materials preceded the arrival of the oil slick. Floating pieces were as large as 20 cm, while those found floating were up to 3 m. Some were heavily oiled and sticky to the touch, whereas others were not. On closer inspection and dissection, the non-oiled honeycomb substance bore a uniform distribution of black spheres (~1 cm in diameter) embedded in a white porous substrate.

There has been some debate regarding the source of the honeycomb material. Some have suggested that it was biogenic carbonate that was damaged from the explosion [2]. Others suspected that it was foam from the riser pipe or part of a holding tank on Deepwater Horizon [2].

The goals of this study were threefold. First, we aimed to determine the source of the honeycomb material. Second, we wanted to determine whether the oil found on the
coated material came from the Macondo well. Finally, we investigated the migration of the material for its value as a tracer for oil slick movement.

2. Methodology

2.1. Sample collection

Oiled honeycomb material was collected by hand on four separate occasions. On 5 May 2010, two pieces were recovered approximately 50 km south of Dauphin Island, AL (29.77°N, −88.10°W) (figure 2(a)). At this distance from shore, there was a field of approximately 50 pieces of similar material interspersed with sargassum weed over a 10 km east-west line. Winds were light, and glassy sea conditions allowed a ‘halo’ of oil sheen to form around each honeycomb clump floating in the water. Surface water temperatures were ~24°C offshore. These two samples were placed in a bucket, and after about 1.5 h, we noticed the material was oozing a thick, oily material with a petroleum odor.

On 7 May 2010, two additional pieces of material were recovered from the sea surface approximately 40 km south of Dauphin Island, AL (29.89°N, −88.21°W) (figure 2(b)). These samples were also collected in a noticeable accumulation of sargassum weed.

On 19 January 2011 a piece of the material was collected on Elmer’s Beach, Grand Isle, LA (29.17°N, −90.07°W). This sample was non-oiled and contained the characteristic uniform black spheres embedded in a white substrate.

These samples were returned to the Dauphin Island Sea Lab (Dauphin Island, AL), wrapped in aluminum foil, and stored at −20°C until analysis at the Woods Hole Oceanographic Institution (WHOI) in Woods Hole, MA.

On 6 April 2011, several large pieces (1–3 m) of fiberglass-sheathed honeycomb debris were found on the Chandeleur Islands (Breton National Wildlife Refuge, LA). The pieces were covered with small patches of oil and located above tidal zone. The time of arrival of the debris on the islands is not documented. Samples were collected and sent to WHOI for analysis.
2.2. Bulk property analysis of non-oiled honeycomb material

The carbon, hydrogen, and nitrogen content of the white porous material and the black spherical coating was measured by Midwest Microlabs (Indianapolis, IN). The density was measured by a technique modified from Kolb and Kolb (1991) and recently used by Morét-Ferguson to determine the density of plastic materials in surface waters of the Atlantic Ocean [3]. The bulk densities of individual honeycomb pieces vary depending on the quantity and distribution of intact hollow black spheres within the material, as these add significant buoyancy. To test for the presence of carbonates, drops of concentrated hydrochloric acid were dripped onto fragments of the honeycomb material.

2.3. Solvent extraction of materials

The oiled and non-oiled pieces of honeycomb material were extracted with dichloromethane/methanol (90:10) and spiked with an internal standard, n-hexadecane-d_{34}. The extracts were stored until analysis by gas chromatography (GC-FID) and comprehensive two-dimensional gas chromatography with flame ionization detection (GC × GC-FID).

2.4. Analysis of total petroleum hydrocarbons (TPHs)

The GC-FID system was a Hewlett-Packard 5890 Series II gas chromatograph with an FID. Approximately 25 mg of material was spiked with 10 µg of octyl ether (recovery standard). Samples (0.5 µl) were injected cool-on-column and separated on a 100% dimethyl polysiloxane capillary column (Restek Rtx-1, 30 m length, 0.25 mm I.D., 0.25 µm film thickness) with H$_2$ as the carrier gas at a constant flow of 5 ml min$^{-1}$. The GC oven was programmed from 45°C (5 min hold) and ramped at 6°C min$^{-1}$ to 315°C and then at 20°C min$^{-1}$ to 320°C (30 min hold). Using standard baseline subtraction techniques, several regions of the chromatograms were integrated representing n-alkane carbon numbers: C$_{10}$–C$_{25}$, C$_{25}$–C$_{45}$ and C$_{45}$+ [4]. Total petroleum hydrocarbons (TPHs) were quantified by integrating the total area of the FID signal and using response factors determined from n-alkane standards [5]. Individual n-alkanes (n-C$_{10}$ to n-C$_{40}$) and the methyl branched isoprenoid alkanes, pristane and phytane, were measured. Laboratory blanks were free of petroleum hydrocarbons.

2.5. Biomarker analysis

The solvent extracts for biomarkers were analyzed on a GC × GC-FID system equipped with a dual stage cryogenic modulator (Leco, Saint Joseph, MI) installed in an Agilent 7890A gas chromatograph configured with a 7683 series split/splitless auto-injector, two capillary gas chromatography columns, and a FID. Refer to [6, 7] for a more complete discussion on this technique.

Standards used in GC-FID and GC × GC-FID were obtained from Cambridge Isotope Laboratories Inc. (PAHs), Aldrich Chemicals (n-alkanes), Sigma (5β(H)-pregnane; 5α(H)-androstane; 5β(H)-cholestan (Coprostanone), Chiron (17α(H)-22,29,30-trinorhopane; 17α(H),21β(H)-hopane; 24R-ethyl-αββ-20R-cholestan; 24R-ethyl-ααα-20R-cholestan; 17α(H)-Dihopane), and Professor Roger Summons, Massachusetts Institute of Technology (alkylcyclopentanes).

2.6. Analysis of polycyclic aromatic hydrocarbons (PAHs) and high temperature simulated distillation (HTSD)

PAHs were measured by GC with mass spectrometry (GC-MS) by Alpha Analytical (Mansfield, MA) using a modified Environmental Protection Agency method 8270 that targets both parent and alkylated PAHs [8]. HTSD was performed by Triton Analytics Corporation (Houston, TX).

3. Results and discussion

The physical characteristics of the honeycomb material provided invaluable clues on its source. Efforts to remove small pieces for analysis were hindered by the hardness of the material. Since some hypothesized that the white material was coral or other biogenic carbonate structure, we first dripped concentrated hydrochloric acid on the honeycomb material. There was no evolution of carbon dioxide or evidence of bubbling. Elemental analysis (by mass) of the non-oiled material was 64, 8.1 and 0.3% (213:27:1) (white porous material) and 52, 3.9 and 2.3% (22.6:1.7:1) (black material) for carbon, hydrogen and nitrogen, respectively. These ratios are much larger than those of marine biogenic origin [9, 10].

The bulk densities of the non-oiled and oiled material were 0.57 and 0.97 g ml$^{-1}$, respectively. The solvent extract of the non-oiled material was colorless and contained no detectable petroleum hydrocarbons (figure 3). These results indicate that the non-oiled honeycomb pieces were from a hard, buoyant, engineered, non-carbonate material and contained no detectable petroleum hydrocarbons.

During a field study in the Chandeleur Islands (29.97°N, –88.83°W), part of the Breton National Wildlife Refuge, on 6 April 2011, we observed large pieces (1–3 m in length) of the honeycomb material covered with white fiberglass sheathing. There was a visual match between the unknown honeycomb material and this engineered marine material. The manufacturing company and serial number, ‘Cuming Corporation 75-1059’, was legible on one of the pieces of debris. The material was identified as part of a 1000-feet service depth riser pipe buoyancy module that was manufactured for the R&B Falcon (Transocean) Deepwater Horizon. By extension, we conclude the unknown pieces of non-oiled and oiled honeycomb material found floating in the Gulf of Mexico were from one of the riser pipe buoyancy modules of Deepwater Horizon.

To determine the source of oil found on the honeycomb material, we compared the biomarker ratios of the hopanes and steranes to the Macondo well oil [11] (table 1). Biomarker ratios confirmed the Macondo well as the source oil. To highlight the fidelity and similarity of biomarker ratios...
of other oiled samples, we included ratios from samples collected over a one-year period, that were 1 to 230 km from the location of the Deepwater Horizon disaster (table 1).

After determining that the oil on the honeycomb material was from the Macondo well, we compared changes in the abundance and distribution of compounds in the honeycomb oil and the Macondo well oil (figure 3). We analyzed oil found on several samples and all showed similar profiles. Here, we will highlight the analysis of one sample. The oil on the honeycomb material had lost the most volatile and water-soluble petroleum hydrocarbons relative to the Macondo well oil (figure 3). We then compared our results to the analysis of the HTSD of the Macondo well oil. The latter is a gas chromatographic method used to define the boiling distribution of the GC-amenable fraction [12]. For Macondo well oil, we found that, on a non-polar capillary column, 25, 50, 75 and 85% of the mass of the whole oil elutes before the \( n-C_{11} \), \( n-C_{18} \), \( n-C_{30} \) and \( n-C_{40} \) alkanes, respectively (figure 3(c)). Based on these results, we estimate a loss of slightly more than 25% of the initial petroleum hydrocarbons from the honeycomb oil due to evaporation and other processes, within 15 days after the explosion.

Based on the \( n-C_{18} / \text{phytane} \) ratio, an indicator for early biodegradation, and the abundance of other \( n \)-alkanes, there was no evidence of biodegradation [13]. PAH analysis showed a rapid loss of lower molecular weight PAHs, consistent with numerous other studies. To provide a more quantitative assessment of the weathering of the PAHs on the oiled material, we normalized the concentration of each PAH to the concentration of the recalcitrant biomarker 17\( \alpha \)-H, 21\( \beta \)-H-hopane [8, 14], which acts as an internal standard. Briefly, naphthalene, fluorene, phenanthrene and chrysene in the oiled material were depleted relative to Macondo well oil by 98, 72, 43 and 0%, respectively; highlighting the greater susceptibility of smaller two-ring PAHs to weathering than larger five-ring PAHs, which is consistent with other oil spills [5, 8].

The measured densities of 0.57 and 0.97 g ml\(^{-1} \) for the un-oiled and oiled honeycomb, respectively, provided additional information that these materials floated at the sea surface.
surface. Hence, we suspected that the protruding profile of the buoyant material enabled it to traverse the sea surface more rapidly than floating oil, thereby traveling in advance of the oil slick. Floating objects at sea move according to both currents and winds, and the contribution of each factor is described using the leeway or windage. The wind leeway for fresh oil is and winds, and the contribution of each factor is described as shown in Table 2. The forecasts were created using the General NOAA Operational Modeling Environment (GNOME) model that utilized currents, wind velocity and overflight data, as well as satellite imagery, to calculate an estimated oil slick trajectory together with an associated uncertainty [17].

Table 1. Select biomarker ratios to identify the source oil.

<table>
<thead>
<tr>
<th>Biomarker ratio</th>
<th>Macando well oil</th>
<th>Oiled honeycomb material May 2010</th>
<th>Droplet collected May 2010 (210 km away from DWH)</th>
<th>Surface slick collected June 2010 (1 km away from DWH)</th>
<th>Chandeleur Islands collected April 2011 (230 km away from DWH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/C (T + C)</td>
<td>0.56</td>
<td>0.55</td>
<td>0.58</td>
<td>0.58</td>
<td>0.57</td>
</tr>
<tr>
<td>NH/CN</td>
<td>0.51</td>
<td>0.54</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
</tr>
<tr>
<td>C29-Ts/C9</td>
<td>0.46</td>
<td>0.48</td>
<td>0.50</td>
<td>0.50</td>
<td>0.48</td>
</tr>
<tr>
<td>2HH(S)/2HH(S + R)</td>
<td>0.57</td>
<td>0.57</td>
<td>0.58</td>
<td>0.58</td>
<td>0.57</td>
</tr>
<tr>
<td>Tm/Cn</td>
<td>0.17</td>
<td>0.18</td>
<td>0.17</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>H/DiaC27βα (20S)</td>
<td>0.83</td>
<td>0.85</td>
<td>0.85</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>C29αααα (20S)/H</td>
<td>0.32</td>
<td>0.34</td>
<td>0.31</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>C29αβββ β (20S)/DiaC29αα (20S)</td>
<td>0.40</td>
<td>0.41</td>
<td>0.42</td>
<td>0.42</td>
<td>0.40</td>
</tr>
<tr>
<td>DiaC29αα (20R)/DiaC27αα (20S)</td>
<td>0.82</td>
<td>0.83</td>
<td>0.81</td>
<td>0.85</td>
<td>0.82</td>
</tr>
<tr>
<td>C29αββββ (20R)/C29αααα (20R)</td>
<td>0.72</td>
<td>0.74</td>
<td>0.73</td>
<td>0.75</td>
<td>0.72</td>
</tr>
<tr>
<td>C29αβββ steranes/total αββ steranes</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
</tbody>
</table>

a Measured by GC × GC-FID.
b Collected approximately 50 km due south of Dauphin Island, AL at 29.77°N, -88.09°W on 5 May 2010.
c Collected near a patch of marsh as a 2 cm droplet of oil at 29.89°N, -93.44°W on 31 May 2010.
d Collected from a thick layer (2 cm) of oil floating on the surface at 28.74°N, -88.38°W on 20 June 2010.
e Composite sample collected on the Chandeleur Islands, LA 29.95°N, -88.82°W on 6 April 2011.
f Ts/Ts + C = Ratio of 18α(H)-22,29,30-trinorneohopane to the sum of 18α(H)-22,29,30-trinorneohopane and 17α(H)-22,29,30-trinorhopane.
g C29αααα/CH = Ratio of 18α(H),21β(H)-30-norhopane to 17α(H),21β(H)-hopane.
h C29αααα(CH)/NH = Ratio of 18α(H),21β(H)-30-norneohopane to 17α(H),21β(H)-30-norhopane.
i 2HH(S)/2HH(S + R) = Ratio of 17α(H),21β(H)-22S-bishomohopane to the sum of 17α(H),21β(H)-22S-bishomohopane and 17α(H),21β(H)-22R-bishomohopane.
j Tm/Cn = Ratio of 17α(H)-22,29,30-trinorhopane to 17α(H),21β(H)-hopane.
k H/DiaC27βα (20S) = Ratio of 17α(H),21β(H)-hopane to 13β(H),17α(H)-20S-diacholestane.
l C29αααα (20S)/H = Ratio of 24-ethyl-5α(H),14α(H),17α(H)-20S-cholestan to 17α(H),21β(H)-hopane.
m C29αβββ (20S)/DiaC29αα (20S) = Ratio of 5α(H),14β(H),17β(H)-20S-cholestan to 24-ethyl-13β(H),17α(H)-20S-diacholestane.
n DiaC29αα (20R)/DiaC27αα (20S) = Ratio of 24-ethyl-13β(H),17α(H)-20R-diacholestane to 13β(H),17α(H)-20S-diacholestane.
o C27αααα (20R)/C29αααα (20R) = Ratio of 5α(H),14α(H),17α(H)-20R-cholestan to 24-ethyl-5α(H),14α(H),17α(H)-20R-cholestan.
p C29αβββ steranes/total αββ steranes = Ratio of 24-methyl-5α(H),14β(H),17β(H)-20R + 20S-cholestan to all αββ steranes.
4. Summary

After an analysis of the unknown honeycomb material and the subsequent oil found on samples, we are able to identify this material as pieces of the riser pipe buoyancy module of Deepwater Horizon coated with a layer of Macondo well oil. Within 15 days, there was significant weathering of the low molecular weight petroleum components (25% loss of petroleum hydrocarbons when compared with the Macondo well oil) with no significant biodegradation of the crude oil hydrocarbons. Large quantities of the highly buoyant honeycomb material were observed several kilometers outside of the uncertainty of NOAA’s oil trajectory paths. These results provide insights into the fate of debris fields deriving from damaged marine materials and should be incorporated into emergency response efforts and forecasting of coastal impacts during future offshore oil spills.

Acknowledgments

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