Marine Pollution Bulletin 111 (2016) 365–380

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Macondo oil in deep-sea sediments: Part 1 – sub-sea weathering of oil deposited on the seafloor

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ARTICLE INFO

Article history:
Received 14 April 2016
Received in revised form 20 July 2016
Accepted 25 July 2016
Available online 31 July 2016

Keywords:
Deepwater Horizon
Dissolution
Biodegradation
Biomarkers
PAH
Deep-sea plume

ABSTRACT

Chemical analysis of sediment cores collected up to 8 km from the Macondo well in 2010/2011 demonstrates the extent of weathering of the Macondo oil deposited in deep-sea sediments following the Deepwater Horizon disaster. On average, dissolution and biodegradation of the oil on the seafloor increased with distance from the well indicating that weathering occurred rapidly and overwhelmingly during the oil's transport as dispersed oil droplets within the deep-sea plume. Beyond about 5 km from the well, the oil deposited on the seafloor had lost most mass below C_{25}, was relatively enriched in *n*-C_{25} + *n*-alkanes and C_3– and C_4-alkylated benz[*a*]anthracenes/chrysenes, the latter owing to 95% depletion of total PAHs. Biodegradation of C_{28} and C_{29} tricyclic terpanes, C_{34} and C_{35} 17α(H),21β(H)-homohopanes, C_{27} 13β(H),17α(H)-dia and C_{27} 14β(H),17β(H)-steranes and dissolution of C_{26} to C_{28} triaromatic steroids occurred. The results provide a means to distinguish Macondo oil in deep-sea sediments from naturally-occurring seep oils and pervasive ambient background hydrocarbons.

1. Introduction

Crude oil released in the Gulf of Mexico (April 20 to July 15, 2010) from the failed Macondo well at a water depth of ~1500 m following the explosion of the *Deepwater Horizon* (DWH) drill rig experienced a range of environmental fates. Buoyancy forces caused larger droplets of oil to be transported (roughly) vertically through the water column to the sea surface where it formed surface slicks, mousses, and sheens that were spread widely by wind and currents over vast areas of the northern Gulf of Mexico (GoM) during the 87-day spill, before finally dissipating five weeks after the well was capped on July 15 (Ramseur, 2010). Numerous studies showed that most of the surfaced oil (i.e., oil not subjected to *in-situ* burning, chemical dispersion, or mechanical recovery) experienced the typical progression in weathering that predictably altered the chemical and physical properties of the oil (Aeppli et al., 2012, 2014; Liu et al., 2012; Carmichael et al., 2012; Kiruri et al., 2013; Hall et al., 2013; McKenna et al., 2013; Lewan et al., 2014; Ruddy et al., 2014; Daling et al., 2014; Faksness et al., 2015; Stout et al., 2016a). These studies collectively showed that surfaced oil experienced up to 20–25% losses to dissolution of <C8 aliphatics and aromatics during its ascent, with increasing effects of evaporation, continued dissolution, and/or photo-oxidation upon reaching the surface. Biodegradation of surface slicks progressed more slowly – only affecting surfaced oil that stranded along shorelines.

Another fraction of the crude oil released from the failed Macondo well remained within the deep-sea. This subsea oil existed as physically- or chemically-dispersed, neutrally buoyant oil droplets (<50 μm; Lindo-Atichati et al., 2014) that formed as the oil (and gas) was ejected under high pressure and turbulent conditions at the wellhead. The physical atomization of the oil was enhanced or (at least) retained by chemical dispersant injected into the emerging plume (Socolofsky et al., 2011, 2015). The dispersed oil droplets diffused and were advected horizontally within an extensive deep-sea intrusion layer, or "plume", that formed ~200 to 500 m above the wellhead at a water depth of ~1000 to 1300 m (e.g., Camilli et al., 2010; Socolofsky et al., 2011; Atlas and Hazen, 2011; Ryerson et al., 2012; Payne and Driskell, 2015a). Deep water column studies tracked the plume in multiple directions (e.g., Spier et al., 2013; Boehm et al., 2016), but mostly toward the southwest where oil droplets were still recognized ~155 km from the well (Payne and Driskell, 2015a).

Oil droplets within the deep-sea plume did not experience the same types of weathering as was experienced by the surfaced oil because evaporation or photo-oxidation could not affect the subsea oil. However, dissolution and biodegradation undoubtedly altered the subsea oil droplets, the rates of both processes likely accelerated by the small droplet size (i.e., large surface area-to-volume ratio) of the dispersed oil particles within the deep-sea plume (Prince et al., 2013; Driskell and Payne, submitted for publication).

Dissolution of oil within the deep-sea plume is evident from numerous studies that observed elevated concentrations of hydrocarbons in water samples collected between 1000 and 1300 m during or shortly after the spill. These studies measured elevated concentrations of

DOI of original article: http://dx.doi.org/10.1016/j.marpolbul.2016.07.041.
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http://dx.doi.org/10.1016/j.marpolbul.2016.07.036
0025-326X/

BTEX (Hazen et al., 2010), PAHs (Diercks et al., 2010; Boehm et al., 2016), or numerous alkane and aromatic totals (Spier et al., 2013), although none specifically distinguished between hydrocarbons in a dissolved versus particulate phase. Clear evidence that dissolution affected the dispersed oil was obtained through the study of large volume water samples filtered at sea in which the dissolved (<0.7 μm) and particulate phases were analyzed separately using the method of Payne et al. (1999). Specifically, results for paired samples collected from deep-sea plume waters often revealed dissolved and particulate phases that were enriched and depleted, respectively, in the more soluble hydrocarbons (Payne and Driskell, 2015a).

Evidence for biodegradation in the deep-sea plume also exists, and was not unexpected given the presence of indigenous oil-degrading heterotrophic microbes in the deep-sea due to the existence of natural gas and oil seeps throughout the region. Increased microbial cell densities and a widely observed dissolved oxygen (DO) deficit within the deep-sea plume (Hazen et al., 2010) showed that the indigenous deep-sea microbes rapidly responded and completely respired the dissolved gases and partially respired the dispersed oil (Valentine et al., 2010; Kessler et al., 2011; Baelum et al., 2012).

The extent(s) to which dissolution and biodegradation affected the dispersed oil within the deep-sea was only partially represented by the many thousands of water column samples collected from the plume during the spill. This is because quantifying the effects of dissolution and biodegradation of discrete oil droplets within the deep-sea plume was hampered by the difficulty of physically sampling the highly-diluted oil droplets in field-collected grab samples from the water column. However, through multiple mechanisms summarized in the accompanying study (Stout et al., 2016b) at least some of the dispersed oil droplets from the deep-sea plume(s) were deposited on the seafloor within an “oily floc,” where they accumulated and could be more practically sampled.

In the present study, we present results that demonstrate the range to which dissolution and biodegradation affected the Macondo oil present on the seafloor in 2010/2011. We accomplish this by focusing on results obtained from sediment cores collected up to 8 km (5 miles) from the well, which were carefully collected to retain any “oily floc” associated with Macondo oil deposition. The results show that the Macondo oil in deep-sea sediment was dramatically and, on average, progressively weathered with increasing distance from the well up until about 5 to 8 km from well. This indicates (1) the weathering occurred rapidly and overwhelmingly during the oil's transport within the deep-sea plume (and not after its deposition) and (2) after about 8 km of transport the oil droplets in the plume were so severely weathered that the oil carried and deposited in sediments beyond 8 km from the well were universally, severely weathered. Results indicate the physical and chemical dispersion of the oil near the wellhead indeed allowed for dissolution and biodegradation to progress rapidly – but only to a point after which a wax-rich, severely weathered Macondo oil residue with a highly consistent “fingerprint” remained to be deposited in sediments at further distances from the well. The accompanying study (Stout et al., 2016b) uses knowledge gained herein to define the lateral and vertical extent of the “fingerprintable” Macondo oil beyond 8 km from the well with special emphasis on distinguishing it from pervasive background hydrocarbons and localized impacts of oil from the area's natural oil seeps.

2. Samples and methods

2.1. Sediments

Table 1 lists the 15 surveys/cruises from which a total of 2782 sediment samples from 729 cores were collected in 2010/2011 (Fig. 1). All of the sediment samples collected were included either in this study or Stout et al. (2016b). In this study, we focus on cores collected within 8 km (5 miles) of the wellhead (Fig. 1) as these best demonstrate the weathering experienced by the Macondo oil that had accumulated on the seafloor. These cores were collected in four of the cruises indicated, viz., HOS Davis 05, HOS Sweetwater 02 Leg 2, Sarah Bordelon 09, and HOS Sweetwater 6 Leg 1.

Table 1
Inventory of deep-sea sediment samples from 729 cores collected in 2010/2011.

Study ID	Dates	Sediment
2010–2011 surveys[a]		2782
HOS Davis Cruise 03[b]	Sept. 8–28, 2010	142
Pisces Cruise 06	Sept. 25–Oct. 4, 2010	13
Atlantis Cruise	Dec. 4–15, 2010	45
HOS Davis Cruise 05[c]	Dec. 4–18, 2010	190
HOS Sweetwater Cruise 01	Mar. 10–13, 2011	18
HOS Sweetwater Cruise 02	Mar. 23–Apr. 24, 2011	612
Sarah Bordelon Cruise 09	May 23–Jun. 13, 2011	456
HOS Sweetwater Cruise 04	Jul. 14–Aug. 7, 2011	366
HOS Sweetwater Cruise 6 Leg 1	Aug. 24–Sept. 2, 2011	168
Holiday Chouest Cruise 01	Aug. 25–Sept. 13, 2011	112
Holiday Chouest Cruise 02	Sept. 15–30, 2011	84
HOS Sweetwater Cruise 6 Leg 2	Sept. 29–Oct. 21, 2011	414
Holiday Chouest Cruise 03	Oct. 1–25, 2011	162

[a] 47 low resolution cores collected from Nancy Foster Cruises (Jul. 21–30, 2010, Aug. 1–10, 2010), Cape Hatteras Cruise (Sept. 20–Oct. 3, 2010, and Ron Brown Cruise (Oct. 16–Nov. 3, 2010) were excluded.
[b] 4 Low resolution cores ($n = 12$ intervals) were excluded.
[c] 1 Low resolution core ($n = 3$ intervals) was excluded.

Cores considered to be higher resolution were those in which surface sediments were collected in 0 to 0.5, 0 to 1, 0 to 1.5, or 0 to 2 cm intervals. These cores contained between two and seven individual depth intervals that were isolated for study onboard each vessel, which provided a means to compare hydrocarbon profiles within the cores.

Notably, 47 lower resolution cores were collected early in the NRDA assessment during the cruises by the *Nancy Foster*, *Cape Hatteras,* and *Ron Brown* in 2010. As these cores' data became available it was evident that they provided too low a resolution (0–3, 0–5 and 0–10 cm) to unequivocally recognize the impact of the Macondo oil to the surface sediment due to the diluting effect of analyzing broader depth intervals. As the need for higher resolution cores was realized, all sediment cores from subsequent NRDA cruises were collected (1) with caution to preserve and collect any floc layer (see Payne and Driskell, 2015b) and (2) carefully processed at sea shortly after collection to obtain 0 to 0.5, 0 to 1, 0 to 1.5, or 0 to 2 cm intervals for chemical analysis, which allowed better recognition of any impact of Macondo oil to sediments (Table 1).

Additional deep-sea sediment cores collected in September and October 2010 during the response effort (OSAT-1, 2010) were originally evaluated but were also excluded from our assessment. Response cores collected within about 3 km of the wellhead indeed showed the presence of Macondo oil (and synthetic based mud), a conclusion also reached by OSAT-1 (2010). However, cores collected beyond this distance were equivocal with respect to the presence of Macondo oil. This result was attributed to (1) the difficulty of collecting any oily floc that may have been present (e.g., not retained due to bow wake of the sediment samplers) and (2) the relatively low resolution of the cores, wherein the 0–3 cm intervals were homogenized and analyzed, potentially diluting any oily floc in the uppermost core. Both of these shortcomings were explicable at the time these cores were collected because the pervasive existence of the oily floc on the seafloor was not yet recognized.

2.2. Sample preparation

Sediment samples were carefully isolated from cores onboard shortly after collection. Individual core intervals for chemical analysis were placed in glass jars and frozen prior to being shipped cold to Alpha Analytical (Mansfield, Massachusetts) under full chain-of-custody procedures. Upon receipt at the laboratory all samples were stored in the