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Macondo oil in deep-sea sediments: Part 2 — Distribution and distinction from background and natural oil seeps



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1. Introduction

Following explosion of the Deepwater Horizon (DWH) drill rig in the northern Gulf of Mexico (GoM), crude oil released (April 20 to July 15, 2010) from the Macondo well at a water depth of ~1500 m experienced a range of environmental fates. Some fraction of the crude oil released remained in the deep-sea. Early sediment studies confirmed that some oil was directly deposited on the seafloor within ~3 km of the well. aided in part by the oil's co-occurrence with dense synthetic-based drilling mud (SBM; OSAT, 2010). Another fraction of the oil that had remained within the deep-sea was advectively transported horizontally as physically- or chemically-dispersed, neutrally buoyant droplets (<50 µm) within an extensive deep-sea "plume" that formed between ~1000 to 1300 m water depth (Camilli et al., 2010; Hazen 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).

Subsequent studies have shown that some of the oil within the deep-sea plume was ultimately deposited on the seafloor further

ABSTRACT

Following the *Deepwater Horizon* oil spill, the spilled Macondo oil was severely weathered during its transport within the deep-sea plume as discrete particles, which were subsequently deposited on the seafloor. The Macondo oil deposited in deep-sea sediments was distinguished from ambient (background) hydrocarbons and naturally-seeped and genetically-similar oils in the Mississippi Canyon region using a forensic method based upon a systematic, multi-year study of 724 deep-sea sediment cores collected in late 2010 and 2011. The method relied upon: (1) chemical fingerprinting of the distinct features of the wax-rich, severely-weathered Macondo oil; (2) hydrocarbon concentrations, considering a core's proximity to the Macondo well or to known or apparent natural oil seeps, and also vertically within a core; and (3) results from proximal cores and flocculent material from core supernatants and slurp gun filters. The results presented herein establish the geographic extent of "fingerprintable" Macondo oil recognized on the seafloor in 2010/2011.

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than ~3 km from the well (see below). Our accompanying study (Stout and Payne, 2016a) demonstrated the presence of slightly weathered Macondo oil, often in association with synthetic-based drilling mud (SBM), within approximately 1.6 km of the well. In addition, a wax-rich, severely weathered Macondo oil was also found in surface sediments ~5 to 8 km from the well, the degree of weathering of which tended to increase with increasing distance from the well. This weathering trend indicated that the oil had been entrained in the water column upon release. laterally transported within the deep-sea plume, and subsequently deposited on the seafloor. In addition to the direct fallout of oil (and SBM) near the well, the mechanisms by which plume-entrained oil reached the seafloor included: (1) direct impingement of the deep-sea plume onto topographic features within the deep-sea plume's path; and (2) sinking of bacteria-mediated, mucous-rich marine snow particles formed both at the sea surface and within the deep-sea plume itself (see Supplemental information Fig. S-1). As these sinking marine snow particles "scavenged" oil droplets from the deep-sea plume they carried the oil to the seafloor (Passow et al., 2014; Passow, 2012; Hazen et al., 2010; Valentine et al., 2010; Baelum et al., 2012). The latter of these two mechanisms was likely dominant and led to the widespread accumulation of oily flocculant material (known as "floc") on the deep-seafloor (Valentine et al., 2014; Hastings et al., 2015; Chanton et al., 2015; Brooks et al., 2015; Schwing et al., 2015; Romero et al., 2015) and deep-sea corals

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(White et al., 2012; Hsing et al., 2013; Fisher et al., 2014a,b; Brooks et al., 2015). This phenomenon has been referred to as "marine oil snow sedimentation and flocculent accumulation" or MOSSFA (Kinner et al., 2014), the so-called "dirty blizzard" (Schrope, 2013).

The collective results of earlier deep-sea studies provide various means to assess the spatial extent, or "footprint", of the sunken Macondo oil (and floc) on the seafloor, although most of these studies were based upon observations made at only a few locations. Establishing the spatial extent of the Macondo oil on the sea floor was challenged by the fact that some deep-sea sediments in the Mississippi Canyon region contain some low(er) concentrations of pervasive ambient (background) hydrocarbons (Cole et al., 2001; CSA, 2009; Wade et al., 2008; Rowe and Kennicutt, 2009) as well as high(er) concentration of localized hydrocarbons associated with natural oil seeps (e.g., Sassen et al., 1993, 2006; Fugro, 2011; BOEM, 2013; Garcia et al., 2015; Crooke et al. 2015). Boehm and Carragher (2012) suggested that the strong chemical similarities among the Mississippi Canyon family oils, which derive from a common Upper Cretaceous petroleum system (Hood et al., 2002), confound the ability to distinguish spilled Macondo oil from naturallyseeped oil(s) in the environment.

We acknowledge that, despite their acclaimed specificity among different oils, petroleum biomarker ratios alone can sometimes be insufficient for distinguishing between genetically-similar oils, especially in assessing oil within sediments, where interferences can affect chemical fingerprints. However, through our multi-year study of 724 sediment cores collected in late 2010 and 2011, we developed a forensic method capable of distinguishing Macondo oil in deep-sea sediments from sediments containing ambient (background) hydrocarbons and genetically-related, naturally-seeped oils in the Mississippi Canyon region. The method relies in part upon biomarkers, but also upon an understanding (see Stout and Payne, 2016a) of the significant effects of dissolution and biodegradation on the "fingerprint" of the dispersed Macondo oil droplets. Specifically, these physical and biological processes imparted changes to the petroleum constituents of Macondo oil that are recognizable and distinct from seeped oil. In addition, the method relies upon the petroleum fingerprint of core supernatants and floc isolated from the seafloor proximal to sediment cores, as well as vertical and lateral trends in hydrocarbon concentrations to identify the presence of a Macondo oil-bearing floc on the seafloor and distinguish it from sediments containing ambient (background) and seeped hydrocarbons. The results presented herein collectively establish the extent of a "fingerprintable" Macondo oil footprint found on the seafloor in 2010/2011.

2. Method

2.1. Sediment samples

Table 1 lists the 15 surveys/cruises from which a total of 2782 separate sea floor sediment samples from 724 cores were collected in 2010/2011. Fig. 1 shows their locations, which were predominantly collected from locations within approximately 25 km of the well in water depths between 1000 and 2000 m. (Sediment core locations and other sample information are found in Appendix A.) The 6.5 cm (diam.) \times 10 cm cores were considered to be high-resolution because surface sediments were collected from thinly sliced horizontal surface, for purposes of comparison with one or more deeper sections of the cores. Specifically, sediment was sub-sampled from surface sections that were variably 0 to 0.5, 0 to 1, 0 to 1.5, or 0 to 2 cm in depth; and also from one to six deeper intervals up to 10 cm deep. The most cores the deeper sub-samples were from 1 to 3, 3 to 5, and 5 to 10 cm intervals.

The cores were collected to minimize dilution of surface deposited petroleum by preventing mixing with deeper clean sediments, which otherwise effectively lowered concentrations and confounded petroleum fingerprinting. Cores included in this study were collected with the utmost caution to preserve and collect any floc layer (see Payne and Driskell, 2015b) and carefully processed shortly after collection onboard each vessel in order to obtain the high-resolution intervals for chemical analysis discussed above (Table 1).

In contrast, data from additional deep-sea sediment cores collected in September and October 2010 during the response effort and (47 cores) from the Natural Resource Damage Assessment (NRDA) effort (Table 1) were excluded from this assessment because they were collected and homogenized across larger (0 to 3, 0 to 5, or 0 to 10 cm) depth intervals. Although many of these low resolution sediment cores taken from within approximately 3 km of the wellhead indeed showed the presence of Macondo oil (and synthetic based mud) (see OSAT, 2010), cores collected beyond this distance were equivocal with respect to the presence of Macondo oil, due at least in part to the issues identified above.

2.2. Core supernatant samples

On five of the NRDA cruises, the nepheloid layer (i.e., suspended particles in water found above the sediment core top) was carefully poured off, collected, and analyzed as a water sample (Table 1). These samples are referred to herein as *supernatant* samples. There were 442 such samples collected, analyzed and considered herein (Table 1) and their

Table 1

Inventory deep-sea samples evaluated herein from 724 cores collected in 2010/2011.

Study ID	Dates	Sediment 2782	Slurp gun filter 222	Supernatant 442
2010–2011 survey ^a				
HOS Davis Cruise 03	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	Dec. 4–18, 2010	190		34
HOS Sweetwater Cruise 01	Mar. 10-13, 2011	18		
HOS Sweetwater Cruise 02	Mar. 23–Apr. 24, 2011	612	85	168
Sarah Bordelon Cruise 09	May 23–Jun. 13, 2011	456		
HOS Sweetwater Cruise 04	Jul. 14–Aug. 7, 2011	366	58	96
HOS Sweetwater Cruise 6 Leg 1	Aug. 24-Sept. 2, 2011	168	31	43
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	48	101
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.

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