Macondo oil in northern Gulf of Mexico waters – Part 1: Assessments and forensic methods for *Deepwater Horizon* offshore water samples

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ABSTRACT

Forensic chemistry assessments documented the presence of Macondo (MC252) oil from the *Deepwater Horizon* (DWH) spill in offshore water samples collected under Natural Resource Damage Assessment (NRDA) protocols. In ocean depths, oiled water was sampled, observed, photographed, and tracked in dissolved oxygen (DO) and fluorometry profiles. Chemical analyses, sensor records, and observations confirmed the shifting, rising oil plume above the wellhead while smaller, less buoyant droplets were entrapped in a layer at ~1000–1400 m and advected up to 412 km southwest. Near-surface oil samples showed substantial dissolution weathering from oil droplets rising through the water column, as well as enhanced evaporative losses of lighter n-alkanes and aromatic hydrocarbons. Dispersant effects from surface applications and injected at the wellhead were seen in oil profiles as enhanced weathering patterns (increased dissolution), thus implying dispersants were a functionally effective mediation treatment. Forensic assessment methods are detailed in the Supplemental information (SI).

1. Introduction

During the 2010 DWH blowout event, while surface slicks were plainly evident, widely spread, and of great concern, a less visible phenomenon was occurring. Early in the response, remotely-operated-vehicle (ROV) operators monitoring the wellhead reported encountering oil layers, primarily at ~1000 m depth (pers comm, *Skandi Neptune* operators, 2010). Later Operational Science Advisory Team (OSAT), academic, and NRDA sampling efforts confirmed these observations, finding elevated polycyclic aromatic hydrocarbon (PAH) constituents, dispersant indicators, and selected monoaromatic components in the 900–1400 m depth range (Camilli et al., 2010; Payne and Driskell, 2015a). Modeling efforts predicted droplets released from the well's collapsed drill pipe would be trapped at a depth between 1280 and 1310 m, whereas the (larger flow rate) release from the end of the riser would be trapped between 1150 m and 1220 m (Spaulding et al., 2015). While the chemical character of this layer was mostly predictable from similar earlier events (e.g., IXTOC I in 1979), understanding the formation of the deep plume and its protracted extension to the southwest required further observations and insights (Socolofsky et al., 2011; Spaulding et al., 2015; Payne and Driskell, 2015b, 2016).

When oil is released into seawater, its hydrocarbon components partition into dissolved and particulate (oil-droplet) phases (Payne et al., 1984, 1991a, 1991b, 2005; Payne and McNabb Jr., 1984; NRC,

1985, 1989, 2003, 2005; Wolfe et al., 1994; Payne and Driskell, 2003; Reddy et al., 2011; Camilli et al., 2010, 2011; Boehm et al., 2016). In a generally predictable manner, volatile aromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX) plus other alkylated mono-aromatics and lower-molecular-weight PAH all appreciably dissolve in seawater (NRC, 2003, 2005). During the DWH blowout (aka Macondo lease block or MC252), however, the partitioning activities were quite dynamic. Oil droplets and gas bubbles separated in the well's multi-phasic, jetted flow resulted in an almost complete dissolution of lower-molecular-weight aromatics (alkylated benzenes) (Reddy et al., 2011) and aliphatics (at least through heptane, McAuliffe, 1987), plus a more limited dissolution of C_8-C_{13} aliphatics and two- and three-ring aromatics (alkylated naphthalenes, fluorenes, phenanthrenes/anthracenes, and dibenzothiophenes). Similar behavior was observed during the 1979 IXTOC I blowout in the Bay of Campeche, GOM (Payne et al., 1980a, 1980b; Boehm and Fiest, 1982). During the DWH event, volatile gas bubbles were surfacing above the wellhead (pers obs) while evaporated BTEX and lighter PAH were captured in aerial fly-overs (Ryerson et al., 2011).

For traditional damage assessments (including to some extent, the DWH event), whole water total PAH (TPAH) values have been used to estimate toxicity and fate; essentially ignoring known oil-in-water partitioning processes. Partitioning has been reviewed in detail in several National Research Council (1985, 2003, 2005) reports, and

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more recently by Faksness (2007); however, there have been only a few efforts to collect phase-discriminated data in actual oil-spill NRDA efforts. During the DWH event, portable field-filtration equipment built for this task (Payne et al., 1999) was deployed to process selected offshore NRDA water samples (Figs. S- 2and S- 3). Filtering at the time of collection (vs. bench filtering days later), produces complementary dissolved- and particulate-oil phase samples that better reflect the actual environmental conditions. The filtering also uses larger sample volumes (3.5 L versus 1 L) to improve analytic method detection limits. These more detailed, phase-discriminated results dramatically expand the utility of data. From the DWH event, a limited data set from filtered samples provided partitioned source reference samples (Fig. S- 4), which enabled a method to parse out phases in the other non-filtered whole water samples. Subsequent insights into oil fate and transport processes certainly improved forensic assessments but more importantly, provided dissolved-phase concentrations, the component more relevant for toxicological assessments.

Including independent BP and Response cruise efforts and pre- and post-impact, near-shore water samples, over 15,000 samples were collected by local, state, and federal agency representatives for the DWH NRDA. Other researchers utilizing the combined NRDA and BP data sets have reported on the distribution and attenuation of total PAH (TPAH aka TPAH50 as a summation of 50 PAH components) in the water column (Spier et al., 2013; Boehm et al., 2016; Wade et al., 2016). Although admirably comprehensive, in the two more recent studies, the data were largely interpreted by estimating background concentrations and then comparing and delineating average TPAH as functions of time and distance from the wellhead. For both the Boehm and Wade studies, the scope of the spill was defined as the regions where TPAH concentrations exceeded 1 ppb (mostly within 15 to 20 km of the wellhead). Unfortunately, in Wade's comparative tabulation of pre-spill background estimates, many values were from early studies believed to be biased high due to sampling and procedural artifacts (de Lappe et al., 1983) or were constrained by median TPAH concentrations measured in non-representative DWH field blanks with unrelated PAH profiles (e.g., pre-contaminated rinse water with profiles unlike those from environmental samples). Post-spill field results from 2011 (Payne and Driskell, 2015a) suggest these to be overestimates for background (see below). Furthermore, both studies' focus on TPAH averages was biased by both the acknowledged ad hoc nature of the sampling design (implemented primarily for tracking and sampling subsurface oil with no utility as unbiased statistical estimates) and the complexity and heterogeneity of oil in the water column. Specifically, both studies averaged impacted and non-impacted water samples (tabulated by region, date, distance, etc.) and suggested an overall low level and range of impact, e.g., Wade's sample collection maps include efforts beyond the spill's impact region, off Texas and the east coast of Florida. Also, in our opinion, the traditional statistical parameter, TPAH, poorly represents the multi-component, multi-phasic, non-linear nature of oil weathering and ignores current knowledge regarding oil's weathering conversion to unquantified polar compounds (discussed below). Together, the approach, the estimates, and TPAH index create a low-biased impression of the true scale and nature of the spill. Commendably, Spier's study looked at solubility-based groupings of analytes but then censored the data for detection limits, which led, in our opinion, to conclusions of attenuated oil distributions. Likewise, Boehm et al. (2016) acknowledged the multiphasic nature of oil-in-water mixtures but details for quantifying the separate phases were not addressed.

Our approach differs; rather than making generalized assumptions in culling and processing the data, we instead examined each sample's chemical profile and its supporting field data for evidence of MC252 oil ($n = 4189$). There are several approaches to oil-spill forensic assessments of individual samples using various chemistry parameters (PAH, SHC, biomarkers, volatiles, metals, and isotopes), diagnostic ratios, pattern matching, or multivariate analyses, to name a few (many of which are covered in Stout and Wang, 2016). For the DWH spill, only

the traditional suite of PAH, SHC, and sometimes, biomarker data, were available for the Natural Resource Damage Assessment (NRDA). But the abundance of the data enabled developing some novel forensic methods (detailed in SI) and eventually, insights into the behavior and fate of the DWH oil. For this task, additional efforts were made to not only confirm a possible MC252 source but also to deconvolute each sample into its relative dissolved- and particulate-oil-phase PAH components (Payne and Driskell, 2015a, 2015b, 2015c). These forensic assessments were undertaken not to tabulate TPAH/phase levels but rather to create a dataset that could serve as confirmation for a parallel NRDA task, modeling oil's transport, fate, and effects wherein oil is treated as a multi-component material (French-McCay et al., 2015a, 2015b, 2018).

While the scope of this paper summarizes, in a somewhat narrative style, the methods, results and conclusions documenting the DWH exposure, forensic methods and enhanced-dissolution dispersant effects are detailed in the Supplemental Information (SI) and Part 2 of this series, Driskell and Payne (2018b).

2. Methods

2.1. Field methods

The primary offshore sampling challenge for this event was in finding, tracking, and characterizing the entrapped deepwater oil plume (detailed in Payne and Driskell, 2015b, 2016, and White et al., 2016). Consequently, surface samples were a smaller component in the NRDA's offshore sampling (only ~18% of forensically reviewed water samples came from the upper 20 m depths). While surface slicks were of interest, they were forming and transporting in a mostly predictable manner, tracked by remote imaging, oceanographic models, and shoreline surveys. Other than initially documenting near-surface weathering and dissolution processes (Stout et al., 2016a), slicks did not require the effort relative to the oceanographic sampling methods necessary for tracking and sampling the deepwater plume.

Plume tracking at depth required innovative and adaptive efforts. Initially, water collection efforts were focused near the wellhead or within the basin of the blowout (loosely constrained by bathymetry of nearby salt dome features) but sampling moved further afield as knowledge of the deep plume's behavior developed. Field teams eventually evolved highly effective methods for finding and sampling the deepwater oil plume (Payne and Driskell, 2015b, 2016; French-McCay et al., 2015b) using a combination of live CTD, fluorescence, and dissolved oxygen tracking (Fig. 1), and predictive modeling, plus at times, visuals from remotely operated vehicles (ROVs) equipped with a vast array of sensors and closed-circuit TV (Fig. S- 1). The sensor records later provided additional lines of evidence in corroborating forensic chemistry results (Payne and Driskell, 2015c, 2016, 2017).

For the NRDA effort, over 15,000 discrete water samples (including nearshore and QC samples) were collected from numerous vessels-of-opportunity beginning near the wellhead in May 2010 during the initial weeks of the incident and then further afield during the subsequent months and with diminished efforts into fall of 2011. Water was mostly collected by conventional oceanographic methods using Go-Flo® or Niskin bottles (more method details are in SI), preserved in the field after collection by refrigeration or acidification, and later shipped and held refrigerated until extraction at the lab. Fast-runner boats were deployed from Port Fourchon, LA every two-to-three days to offload samples from the larger sampling vessels at sea and deliver them to onshore data/logistics centers where the collected samples were logged into a comprehensive chain-of-custody (COC) database and air-freighted in Blue-Ice® chilled coolers overnight (including Saturday deliveries) to the waiting analytical facilities. Throughout the massive scale of logistical and laboratory efforts, only 217 of 22,039 processed water samples (0.98%) were compromised by exceeding the 14-day maximum hold time specified by the project's Analytical Quality Assurance Plan (AQAP) (NOAA, 2014).