



# 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 monoaromatics 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 multiphase, 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<sub>8</sub>–C<sub>13</sub> 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- 2 and 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).

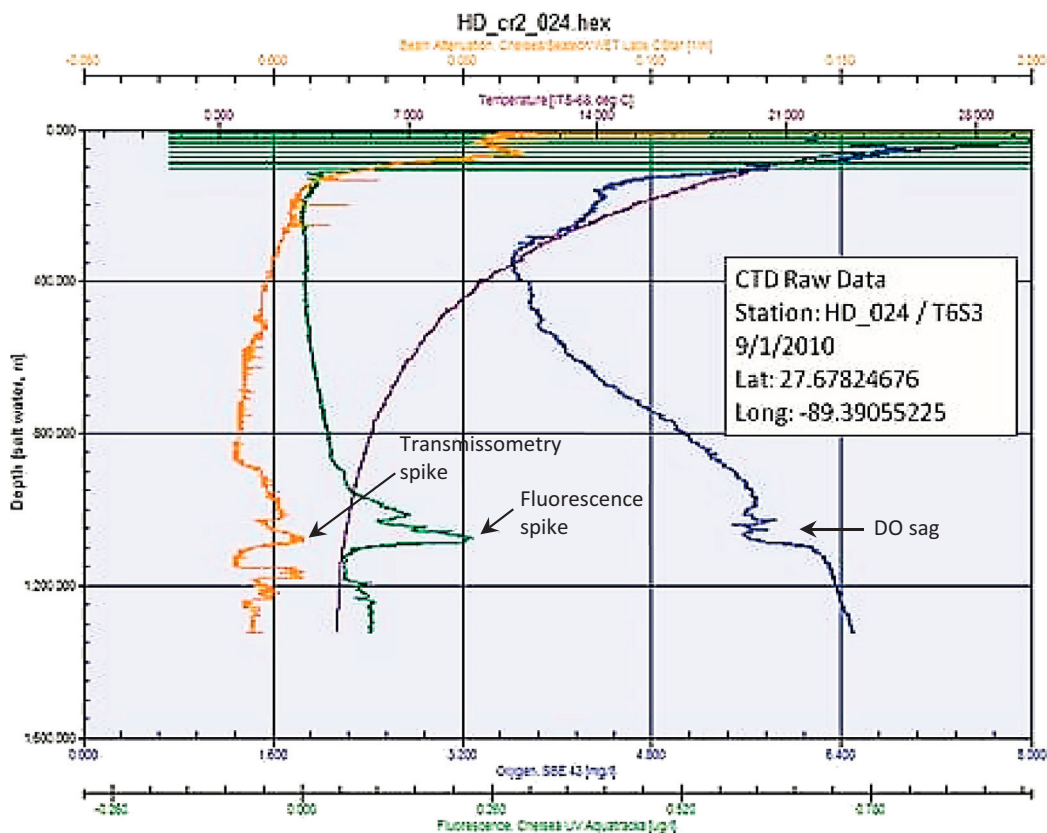


Fig. 1. Field plot showing strong anomalies in dissolved oxygen (blue), fluorescence (green), and transmissometry (orange) live sensor data highlighted the deep subsurface oil plume at 1060 m depth. Samples would ideally be collected at the plume depth and ± 200 m to capture the oil lens and the surrounding water above and below (from Payne and Driskell, 2015b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1  
Forensic matching categories for water samples.

	Category code	Comparable category <sup>a</sup>	Description
Match	1	A	MC252—containing particulate phase oil (with or without extra dissolved)
	2		MC252—dissolved phase only
	3		MC252—phase uncertain, (unresolvably complex)
No match	4	E	Other oil or obvious ship-board contaminants (e.g., hydraulic fluid)
Indeterminate or clean	5	C	Possible MC252—oil-like profile but insufficient to link to MC252
	6		Indeterminate—trace PAH detected but no oil-like profile
	7		No PAH detected or apparent noise (clean)

<sup>a</sup> Non-numeric categories used in other reports for DWH NRDA forensics assessments of oil, tissues and sediment matrices (Stout et al., 2016b).

As mentioned above, for the purpose of assessing phase-partitioning (dissolved vs. particulate oil), on several cruise legs in 2010–11, whole-water samples were vacuumed through 0.7 µm glass-fiber filters immediately upon collection (Figs. S- 2 and S- 3) using a Portable Large Volume Water Sampling System (PLVWSS) (Payne et al., 1999). After filtration, the filters containing the particulate-phase oil were frozen in Certified-Clean glass jars and shipped to Alpha Analytical Laboratories (Mansfield, Massachusetts). The complement 3.5 L dissolved-phase samples were refrigerated in their original, Certified-Clean, one-gallon (3.8 L) amber-glass collection jugs from the PLVWSS and shipped refrigerated to the laboratory for the same analyses.

2.2. Analytical laboratory methods

Nearly all NOAA-NRDA water-column samples discussed in this paper were analyzed by Alpha Analytical Laboratory in Mansfield, MA for detailed hydrocarbon composition in accordance with the AQAP (Stout, 2015a, 2015b). The use of a single laboratory for this effort was critical for developing a quality dataset with known precision,

comparability, accuracy, and completeness to support the multi-year forensics effort (Litman et al., 2018). Analyte lists, methods, and performance requirements were detailed in Stout et al. (2016a) and the AQAP but are also listed in the SI. Analytic methods briefly included:

- Total Extractable Hydrocarbons (TEH) and Saturated Hydrocarbon Compounds (SHC) measured by gas chromatography-flame ionization detector (GC-FID) using a modified EPA Method 8015B.
- PAH, Alkylated PAH, and Petroleum Biomarkers analyzed using Selected Ion Monitoring (SIM) gas chromatography/mass spectrometry (GC/MS) via a modified EPA Method 8270.
- Dispersant components including the surfactant, dioctyl-sulfosuccinate (DOSS), measured by liquid chromatography/mass spectrometry (LC/MS) (Gray et al., 2011, 2014 and Kujawinski et al., 2011) at ALS Kelso (previously CAS in Kelso, WA); while by standard GC/MS methods, Alpha Analytical reported the dispersant indicators, bis (2-ethylhexyl)fumarate, a DOSS-derived GC injection-port breakdown product associated with both Corexit 9527 and 9500, and glycol ethers (GE) common to both dispersants plus 2-butoxyethanol

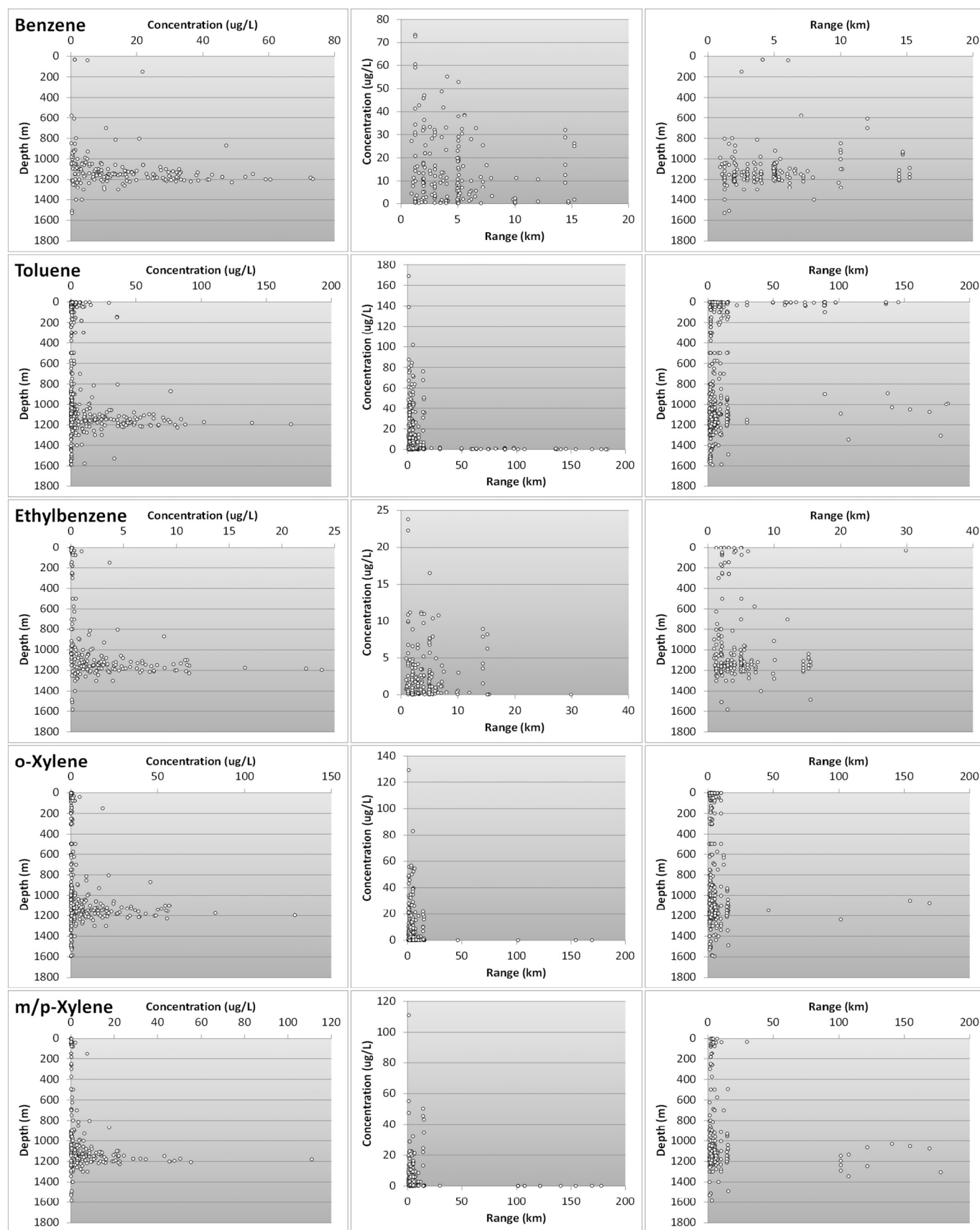


Fig. 2. Distribution of BTEX in forensic-matched (category 1–3) samples by concentration (µg/L), depth (m) and range (km) from wellhead.



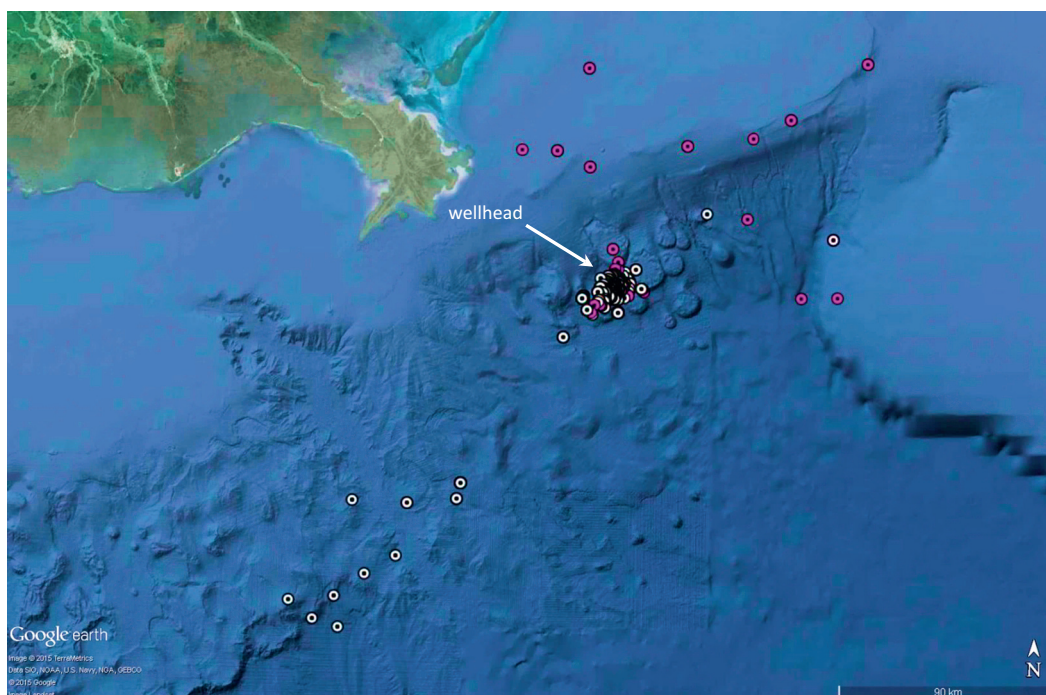


Fig. 3. Distribution of BTEX-containing forensically-matched samples. Red dots are 0–20 m depth, white dots from > 800 m. Farthest surface sample NE at 145 km, deep plume sample SW at 183 km (also see Fig. 2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

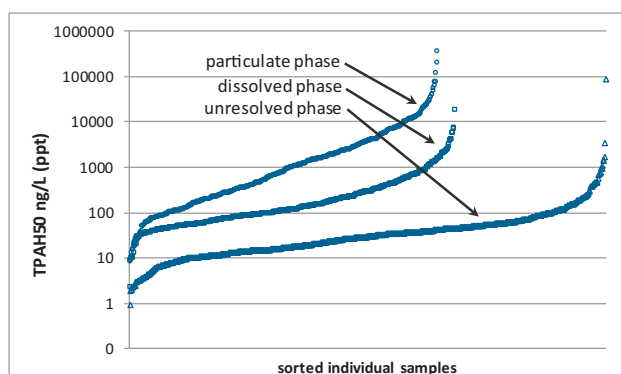


Fig. 4. Sorted TPAH distributions of all MC-252 matched samples (categories 1–3), all depths showing relative range of concentrations.

(a major solvent in Corexit 9527) (Stout, 2015a).

- Volatiles, primarily benzene, toluene, ethylbenzene and xylene(s) (BTEX) plus an expanded list, were analyzed by a purge-and-trap protocol under a modified EPA method 8260.

SHC and volatiles were reported in concentrations of  $\mu\text{g/L}$  (parts per billion, ppb). PAH, biomarkers and dispersant indicators were reported in  $\text{ng/L}$  (parts per trillion, ppt). AQAP Target method detection limits (MDLs) for PAH, biomarkers, volatiles and SHC were 1–5  $\text{ng/L}$ , 10  $\text{ng/L}$ , 0.05–0.5  $\mu\text{g/L}$  and 0.8  $\mu\text{g/L}$ , respectively (see SI tables). Total PAH values were reported as the sum of 50 PAH components (TPAH50), dropping retene (methyl isopropyl phenanthrene also measured as part of C4-phenanthrenes) and perylene (often from background biogenic sources). Dispersant indicators were analyzed at Alpha Analytical without authentic standards and thus reported as semi-quantified estimates. From frozen lab storage, particulate (filter) samples were thawed, macerated, spiked with deuterated recovery standards, and extracted separately from the associated (dissolved) 3.5 L water portion but reported on the associated per-volume basis. Dissolved-phase sample volumes were measured during extraction and later used to

calculate concentrations in both the dissolved and related particulate (filter) samples.

All chemistry data were independently validated by EcoChem (Seattle, WA) as third-party validators where anomalies were investigated, any errors emended, and/or exceedances qualified. Publicly available online data (NOAA ERMA) were reported as surrogate-recovery corrected; however, by preference and strictly for the purpose of forensic analysis, the raw data were used uncorrected for surrogates and uncensored for method detection limits (termed the “forensic dataset”). We are well aware of reviewers' concern for this seemingly naïve practice but have found over years of oil profile analyses that the non-linear distortions in the profile patterns created by molecular-weight-based surrogate-recovery corrections introduce more variance than just using the raw data as generated. As a result, it has been standard practice to use non-surrogate-recovery data in oil-spill fingerprinting studies since the *Exxon Valdez* oil spill in 1989 (Stout and Wang, 2016). Likewise, below-detection-limit or below-reporting-limit data are often found to have profile pattern information useful to the forensic interpretations albeit, sometimes it's just noise. If needed, public data users can recreate the forensic dataset using the surrogate recoveries to back-calculate the raw values.

### 2.3. Forensic matching

For this assessment, only the offshore cruise samples collected in 2010 (5332) were considered, and of those, a total of 4189 were forensically characterized. Traditional ASTM (2000) methods use match, indeterminate, or no-match categories to describe forensic results. For water samples, similar categories were assigned; however, for further understanding the oil's behavior and supporting the needs of fate and transport modeling (French-McCay et al., 2015b), the match category was further subdivided into three phase assignments, i.e., dissolved, particulate, or unresolvable (the last being unparseable phase[s] but matching MC252 oil) (Payne and Driskell, 2015c, 2016). The forensic objective was to assess whether the sample contained MC252 oil and, if possible, to parse out the phase components. Thus, for DWH water samples, seven categories were relevant (Table 1). The first three were

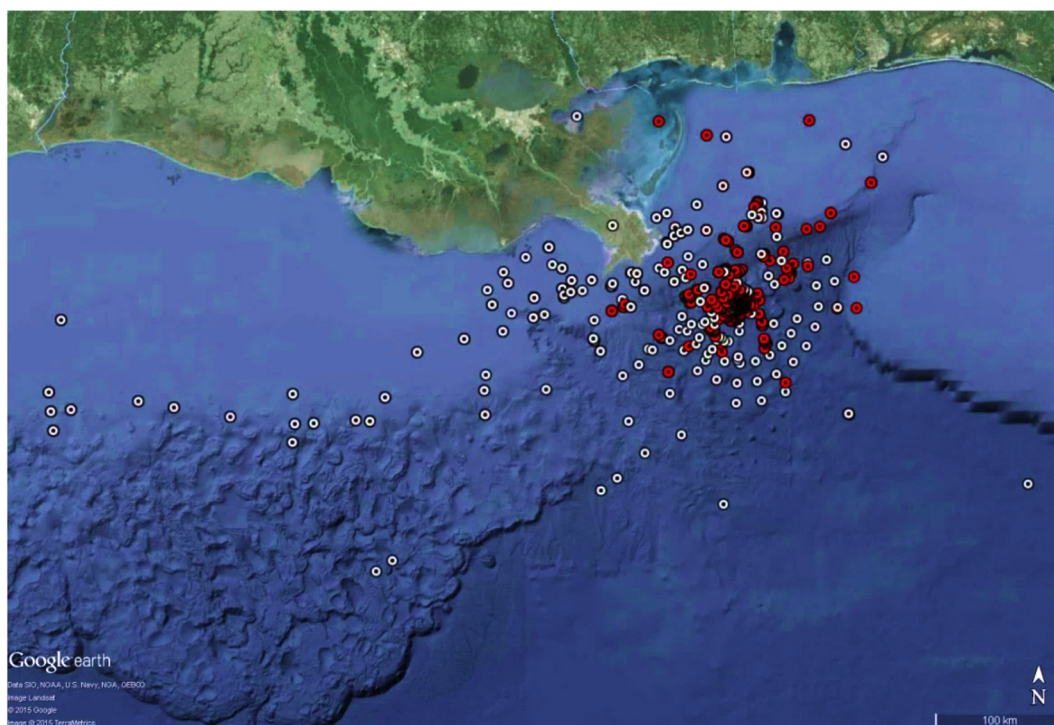


Fig. 5. Near-surface (0–20 m depth) forensic matches (dark) and non-matches (light) ( $n = 359$  and  $331$ , respectively).

considered positive matches, consistent with MC-252 oil but differentiated by phase profiles. The remaining four were non-matching, either another oil, inconclusive, or clean.

The forensic fingerprinting methods are fully described in the Supplemental information (SI) but briefly, the approach for DWH data evolved from our earlier *Cosco Busan* mixing model (Driskell et al., 2010; Driskell and Payne, 2018a). For that event, we developed a parsing, mixing-model approach whereby the reference oil sample (normalized to hopane, chrysene or naphthobenzothiophene) was graphically overlaid on a given field sample profile and then rescaled to tease out any potential source-oil portion and decide whether and how much of the released oil was present in the sample. For this task, the source oil could be statistically weathered to best compare to the stage of weathering seen in the field sample. The weathering model was based upon multiple-regression analyses of each analyte. Multiple lines of evidence were used prior to confirming a match to the source oil. This approach was accepted by both spill Trustees and the Responsible Party (RP) for legal settlement. For the DWH event, rather than statistically weathering the source oil for comparisons, actual weathered-particulate-oil profiles from the field-filtered samples were used for the comparative reference oil (the weathered reference series is posted in Fig. S- 4). Secondly, because most of the deeper offshore water samples were exposed only to simplified weathering factors (i.e., dissolution and biodegradation; no evaporation or photo-oxidation occurred at depth) and not an amalgam of diverse weathered states (typical of surface slicks), it also became possible to parse particulate- and dissolved-phase portions from the remaining majority of the cruise samples, the 1 L unfiltered whole-water samples. The final dataset, including extra details regarding phase state and weathering and sampling metadata, suggested patterns and trends that led to further insights into transport and weathering processes. For example, when first encountered, enhanced dissolution patterns were enigmatic until a correlation with dispersant indicators was noted (See part 2 of this series, Driskell and Payne, 2018b).

### 3. Results

The results for forensic-evaluation end users primarily comprise the spatial distribution of the various phase-characterized categories from MC252 matched samples; cursory map plots are presented to depict a few relevant features. From the profile patterns, trends in dissolution and weathering are discussed along with their context in the DWH scenario; results are noted and interpreted to illustrate transport and fate processes.

BTEX components appeared near the wellhead in gas bubbles, hydrates, and as a mixture of oil-droplet-associated and purely dissolved constituents in the deep samples (Fig. 2 and Socolofsky et al., 2011). Rapid dissolution at depth and resulting loss of buoyancy caused most BTEX to appear with order-of-magnitude higher concentrations than corresponding TPAH at depth in the nearfield. However, benzene, the most volatile and water-soluble BTEX constituent, was largely absent both in the near-surface waters and further from the wellhead (Fig. 2 and Fig. 3). In surface samples, detected BTEX constituents generally appeared within 20 km of the wellhead, thereby suggesting continued dissolution from rising oil droplets as they collected and advected near the surface (Figs. 2 and 3). During the 1979 IXTOC I oil well blowout in Mexico, similar rapid and selective benzene removal (dissolution) from the rising oil plume was reported from a much shallower 60 m ascent (Payne et al., 1980b) (DWH wellhead at 1528). Surfacing DWH oil was subject to additional evaporative losses (Stout et al., 2016a) as directly evidenced in surface oil-sample profiles and the BTEX captured in air samples from above the spill (Ryerson et al., 2011). At depth, benzene could be observed at elevated concentrations ( $\sim 20$ – $40$   $\mu\text{g/L}$ ) out to 15 km, while in comparison, the more persistent toluene occurred at elevated concentrations ( $10$ – $80$   $\mu\text{g/L}$ ) out to 20 km. Remarkably, in the deepwater plume, lower levels of toluene and xylenes were detected associated with forensically matched oil droplets out to 183 km SW of the wellhead (Fig. 3).

Looking at the less volatile hydrocarbons, from 45 cruises, 4189 water samples examined for PAH, SHC, and biomarkers produced 1766 consistent with MC252 profiles (matching categories 1–3) (Table S- 1). Most matching samples had low values of TPAH,  $< 1000$  ng/L (ppt),



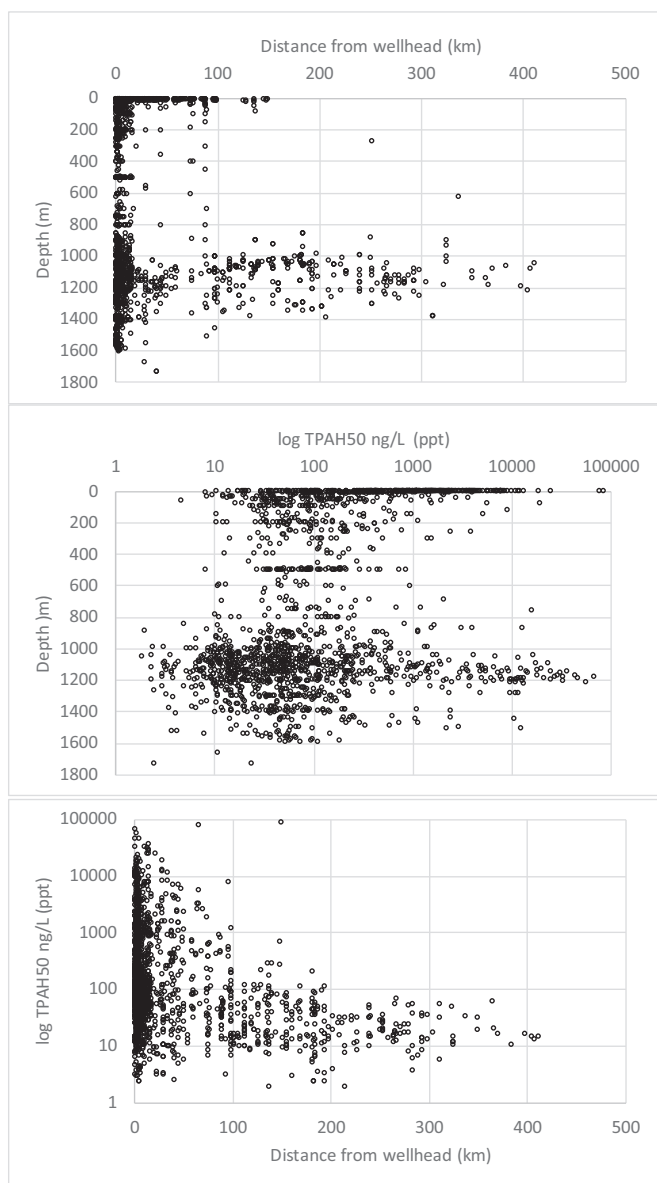


Fig. 6. Distribution and concentration (TPAH50) of water samples forensically matched to MC252 oil (category 1–3,  $n = 1766$ ).

with category medians at 875, 177 and 30 ppt, for particulate-, dissolved-, and unresolved-phase categories (1–3) respectively (Fig. 4). Here, solely for the sake of comparing to other studies, our assessments found DWH BTEX and PAH distributions occurred on a vast spatial and temporal scale where numerous PAH signatures could be spacially and temporally matched to MC252 oil out to 100 km from the wellhead at concentrations up to 1.0 ppb (Wade and Boehm studies suggest 20–25 km) and out to 267 km with at least 0.1 ppb. Again, we emphasize that these values only represent the range of encounters from non-random biased collections, i.e., monitoring near the wellhead combined with plume-tracking efforts rather than using a pre-designed, non-biased sampling scheme.

Because impacts in the near-surface zone of high biological productivity were of significant concern, the shallow water results (0–20 m depth, Fig. 5) are displayed separately from deeper samples showing, within this data set, the extent and distribution of just near-surface matches. The data depict four cruises specifically planned for off-shore, near-surface sampling plus numerous surface and near-surface samples taken during deeper casts on the other NRDA cruises. From 691 forensically assessed, shallow-depth samples, 360 were confirmed as containing MC252 oil. Half of these contained particulate oil droplets,

most with extra dissolved components. Dispersant-mediated effects were apparent in about one-sixth of the profiles, i.e., they showed the diagnostics of enhanced dissolution discussed in Driskell and Payne (2018b). A few anomalously high-concentration samples in the NRDA dataset suggested the inclusion of surface-slick oil. Although cited in other studies as maxima, these were considered to be diluted oil rather than oil suspended in water and thus, as sampling artifacts, they are excluded from results (Fig. 5 depicts water matrices only).

At the entrapped plume depth (~1000–1400 m), field collections followed a sensor trail of particulate-phase (category 1) samples out to 155 km from the wellhead, while dissolved-profile (category 2) samples, typically with dispersant indicators, ranged to 267 km SW from the wellhead, and unresolved-phase (category 3) samples to 412 km from the wellhead (Figs. 6, 7, 8, and Fig. S-5). Dispersant-mediated samples with dispersant-modified, accelerated-dissolution profiles (described in Driskell and Payne, 2018b) extended out to 184 km SW within the deepwater plume and up to 148 km NE in surface waters (< 20 m) atop the shelf (Fig. 9). Non-matching samples were collected out to 530 km along the continental shelf break and 437 km near but outside of the plume track from the wellhead (Fig. S-6). These indeterminate and non-matching category samples (category 5–7) were expected, even desired, as they help to define the plume boundaries (see white-coded samples in Fig. S-5A) and confirm that sampling/procedural artifacts (e.g., equipment contamination, category 4) were not a major problem during the field effort.

In 2011, the year following the blowout, offshore sampling efforts were focused on benthic sampling (unlike the earlier focus on the water column), presuming that most waterborne hydrocarbons would have traveled far afield or settled to the seafloor as marine snow (Payne and Driskell, 2015a; Stout and Payne, 2016; Stout et al., 2016b). At that time, absent the extensive surface oil slicks, the modest number of midwater samples that were acquired ( $n = 55$  from 10 sites within the event basin and ranging from 100 km west to 135 km east of the wellhead) showed no evidence of the deep plume layer. There were no DO anomalies or fluorescent spikes noted; midwater TPAH concentrations were 0–30 ppt and showed only noisy trace patterns with most analytes below method blanks. For aliphatics, TPH ranged from 0 to 1 ppb with patterns dominated by biogenic plant waxes. Dispersant indicators were principally absent or ambiguously close to detection limits.

### 3.1. Forensic interpretations

Knowledge of the initial formation and transport processes of the oil droplets released from the wellhead was critical for understanding the dissolution/weathering behavior of the oil. Conceptually, the blowout was initially envisioned as vertically cone-shaped in the water column forming from the ever-broadening, rising plume of gases and particulate oil droplets jetting from the wellhead. But forensic data suggested there was no semblance of a cone pattern in matched-sample distributions (see depiction of Socolofsky et al., 2011). Rather, in the dynamic environment of ever-shifting currents, the rising plume created a diverse mix of whole-oil particulate droplets each weathered by dissolution processes relative to their size (Spaulding et al., 2015; Payne and Driskell, 2015a) and displaced by the water parcel motions during ascent. Acoustic Doppler Current Profiler (ADCP) data from three locations around the wellhead in May and June 2010 (available at <http://www.ndbc.noaa.gov/>) showed low, time-varying currents (< 5–15 cm/s) in different directions (changing by as much as 180° in < 48 h) between 80 and 1500 m (Kim et al., 2012; French-McCay et al., 2018).

After separation from their buoyant ascending droplets, dissolved hydrocarbons lingered behind in the water column. But rather than being directly advected away from the wellhead, some were instead transported back and forth through the continuously rising droplet plume (Valentine et al., 2012). Specifically, as these dissolved phases' water parcels passed back over the wellhead's rising oil droplets,

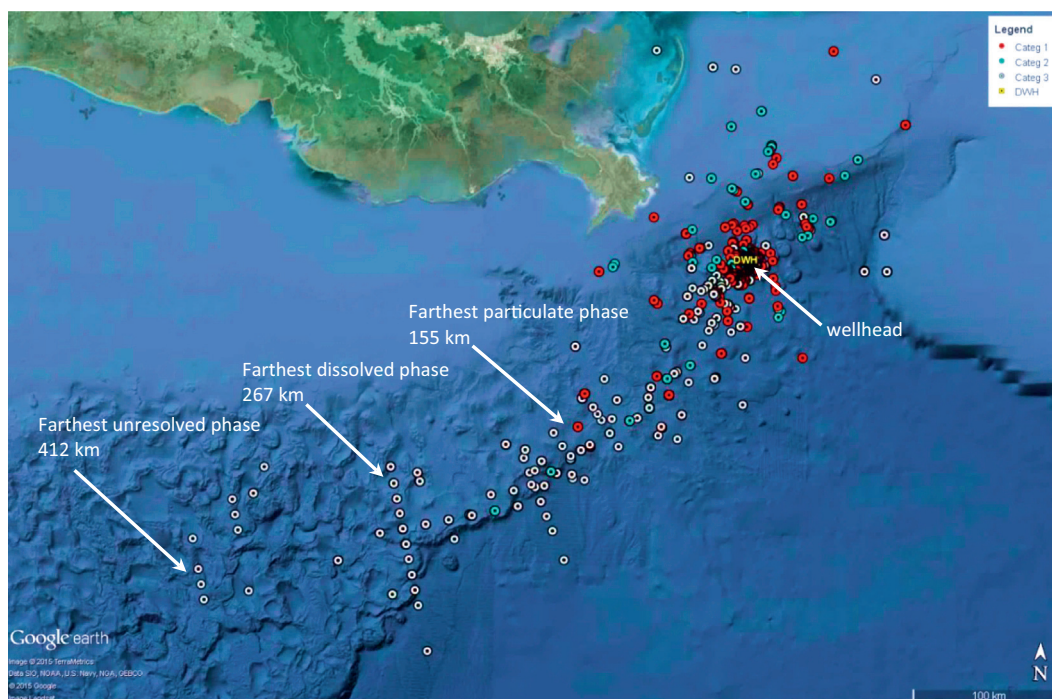


Fig. 7. Distribution of offshore water samples matching MC252 source oil. Matched particulate (Cat. 1; dark), dissolved (Cat. 2; gray), and unresolved phase (Cat. 3; white) samples range to 155, 267, and 412 km from wellhead, respectively. Each location may have collocated samples at multiple depths (see Fig. 6).  $n = 1766$  matches.

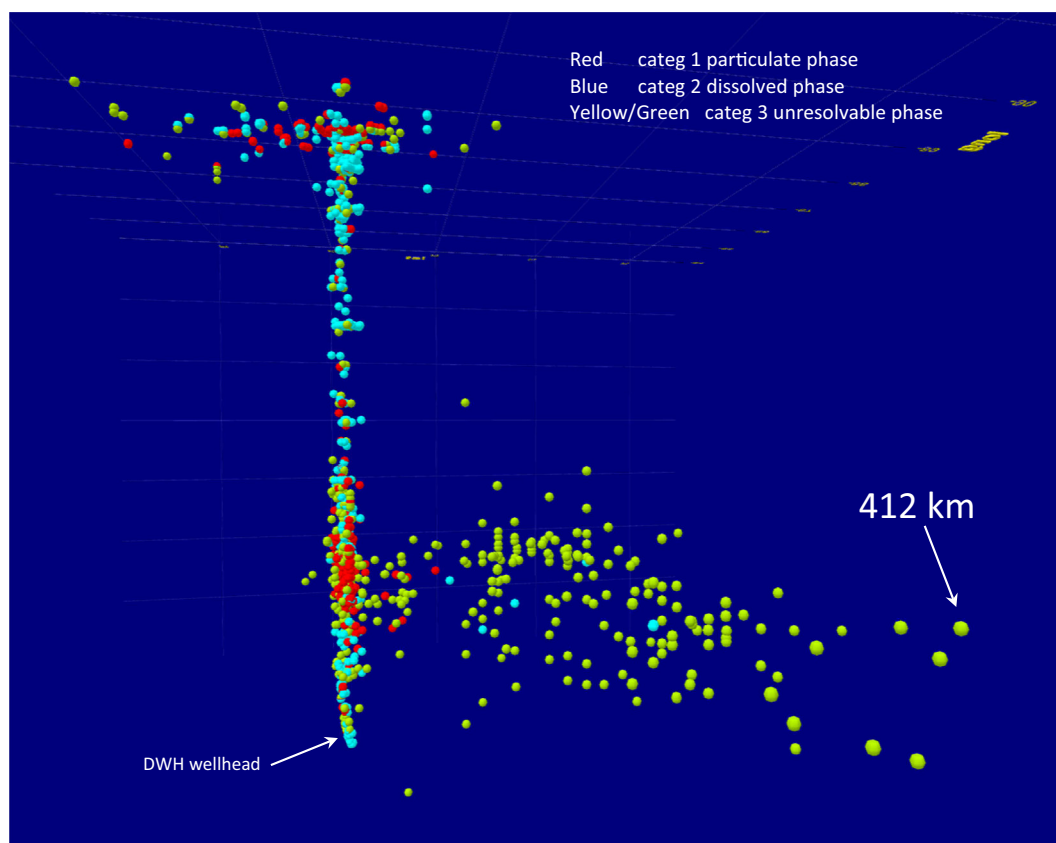


Fig. 8. MC252 matched samples in 3D spatial view at 1000–1400 m plume depth looking east from beyond plume's distal end (also see Fig. S- 5).  
Note to editor – alternative colored image.

additional dissolution from the freshly rising droplets plus the original dissolved components created an enriched profile (Payne and Driskell, 2015a, 2015c, 2016). In the forensic data, these profiles appear as

particulate oil with extra dissolved portions (Fig. S- 7 lower and Fig. S- 12). Eventually, cumulative advective transport carried all the residual waterborne components to the southwest with the droplets and



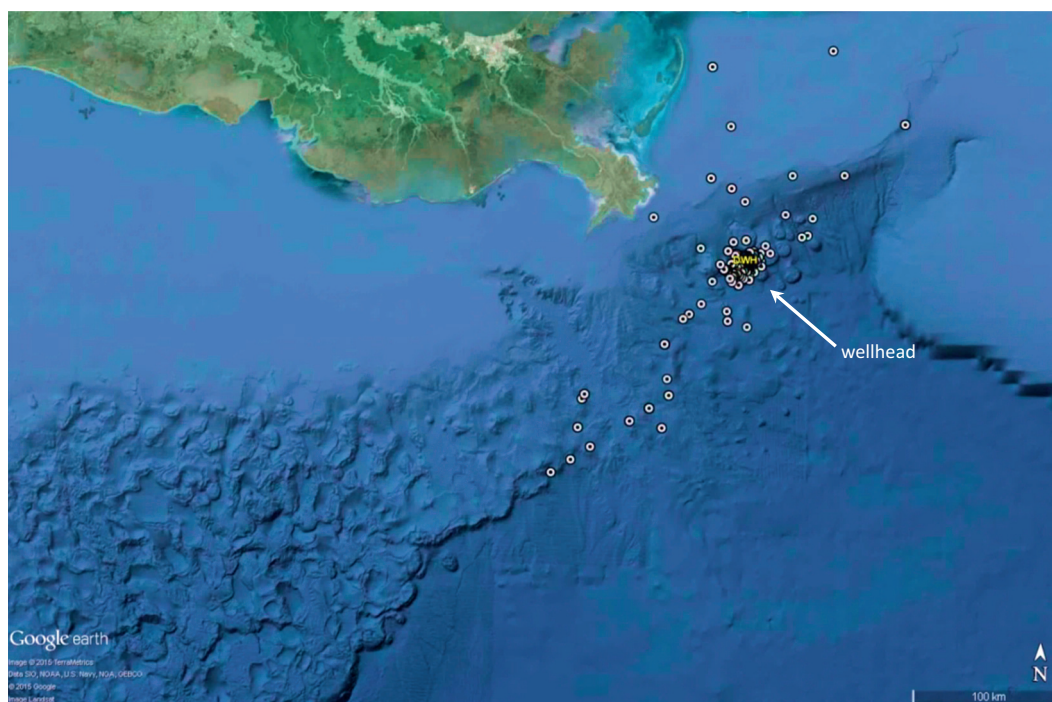


Fig. 9. Distribution of dispersant-mediated samples matching MC252 source oil. Samples southwest of the wellhead were at deep plume depth. Samples on shelf northeast of the wellhead were from < 20 m depth.

dissolved-phase water parcels further subjected to differential diffusion, internal waves, turbulence, basin circulation and tidal currents (Payne and Driskell, 2015a; French-McCay et al., 2015b, 2016, 2018).

Dissolution in oiled-water signatures was evidenced by the weathering of lower-molecular-weight PAH, aliphatics ( $< C_{13}$ ), and BTEX that universally occurred as oil droplets ascended to the surface (Stout et al., 2016a). There was also evidence of photo-degradation and re-entrainment of surfaced oil in near-surface water samples as specifically reflected by the hopane-normalized losses of higher-alkylated (C3- and C4-) chrysenes, fluoranthenes/pyrenes, benz(a)anthracene, and also, the triaromatic steranes (Andersson, 1993; Garrett et al., 1998; Prince et al., 2003; Plata et al., 2008; Aeppli et al., 2014; Radović et al., 2014; Bacosa et al., 2015; Stout et al., 2016a).

From forensic data, surfacing droplets typically became part of a surface slick's amalgam of DWH oil in various weathered states plus any background contamination from vessels' exhaust, deck washes, bilge dumps, dispersant drops, and/or in situ burn operations. Many surface profiles were irresolvably complex in PAH signature but relying more on biomarkers and other lines of evidence, MC252 oil was confirmed in 359 out of 690 near-surface ( $< 20$  m) water samples for at least 100 km in most directions from the wellhead (Fig. 5).

With the requisite amount of wave energy or impacting rainfall (Murphy et al., 2015), surface slicks and sheens can be mechanically broken up and droplets re-entrained in the upper depths (to some degree, down to 10–20 m but more commonly 0–2 m). Data from Special Monitoring of Applied Response Technologies (SMART) fluorescence monitoring (during workable sea states) and surface-focused cruises confirmed enhanced near-surface concentrations. While use of dispersants is still contentious in the spill-response community for other reasons, these findings again demonstrated that surface-applied dispersants were generally effective at creating micro-droplets that would facilitate the dissolution, weathering, and re-entrainment processes (Bejarano et al., 2013; Brandvik et al., 2013, 2014; Davis and Loomis, 2014; Payne and Driskell, 2015d; Boehm et al., 2016; Li et al., 2016; Spaulding et al., 2015, 2017).

In contrast, direct dispersant application at the wellhead was unique; it had not been attempted prior to the *Deepwater Horizon* oil spill,

and thus no data existed on the efficacy or fate of dispersants released in the deep subsurface. From early NRDA and Response data, dispersants were initially observed in plume-depth, whole-water samples but it couldn't be confirmed whether they were simply dissolved in the water or truly associated with the oil droplets (Payne and Beegle-Krause, 2011 and Kujawinski et al., 2011). Later reports of plume-depth, filtered-water NRDA samples having dispersant indicators still associated with the oil-phase droplets (Payne and Driskell, 2015d) finally confirmed their oil-associated functionality in the field. Analyses also showed that dispersants applied directly at the wellhead were active in creating atypical oil-droplet signatures with accelerated loss of the more soluble, lesser alkylated PAH and perhaps delayed biodegradation of SHC (Payne and Driskell, 2015d; Driskell and Payne, 2018b). These mechanistic results showing persisting dispersant attachment to oil droplets and accelerated loss of PAH, together suggest direct wellhead injection was effective for reducing oil-droplet sizes and thus, limiting oil rising to the surface and potentially being transported to shorelines. Others arrive at similar conclusions based on their own approach and evidence (Kujawinski et al., 2011; Spier et al., 2013, and Nagamine, 2014).

Completing the inventory of miscellaneous sample categories, 98 (2.3%) water samples contained an oil that was not matched to MC252 (Table S- 1, Category 4). Of these, 67 were due to hydraulic oil leaked from the ROVs. Fortunately, hydraulic oil reference samples were taken and thus, the contamination was easily spotted (generally from elevated hopane and norhopane levels – see Fig. S- 8). Due to hydraulic oil's refined nature, it often contributed very little to PAH and thus, could usually be confidently deconvoluted or ignored. The remaining 31 non-match samples represented either other obviously-anomalous-but-undiscovered contaminants or were from unknown petrogenic sources.

Unknown sources could include seeps, which were often suggested as potentially major sources of oil contamination in the Gulf (Boehm et al., 2016; Wade et al., 2016). Based on satellite work of MacDonald et al. (2002), the US Geological Survey estimated approximately 350 sheen-forming seeps occur perennially in the northern Gulf of Mexico region (Kvenholden and Cooper, 2003). More recent work by Garcia-Pineda et al. (2015) suggested 1000 geophysical anomalies (potential

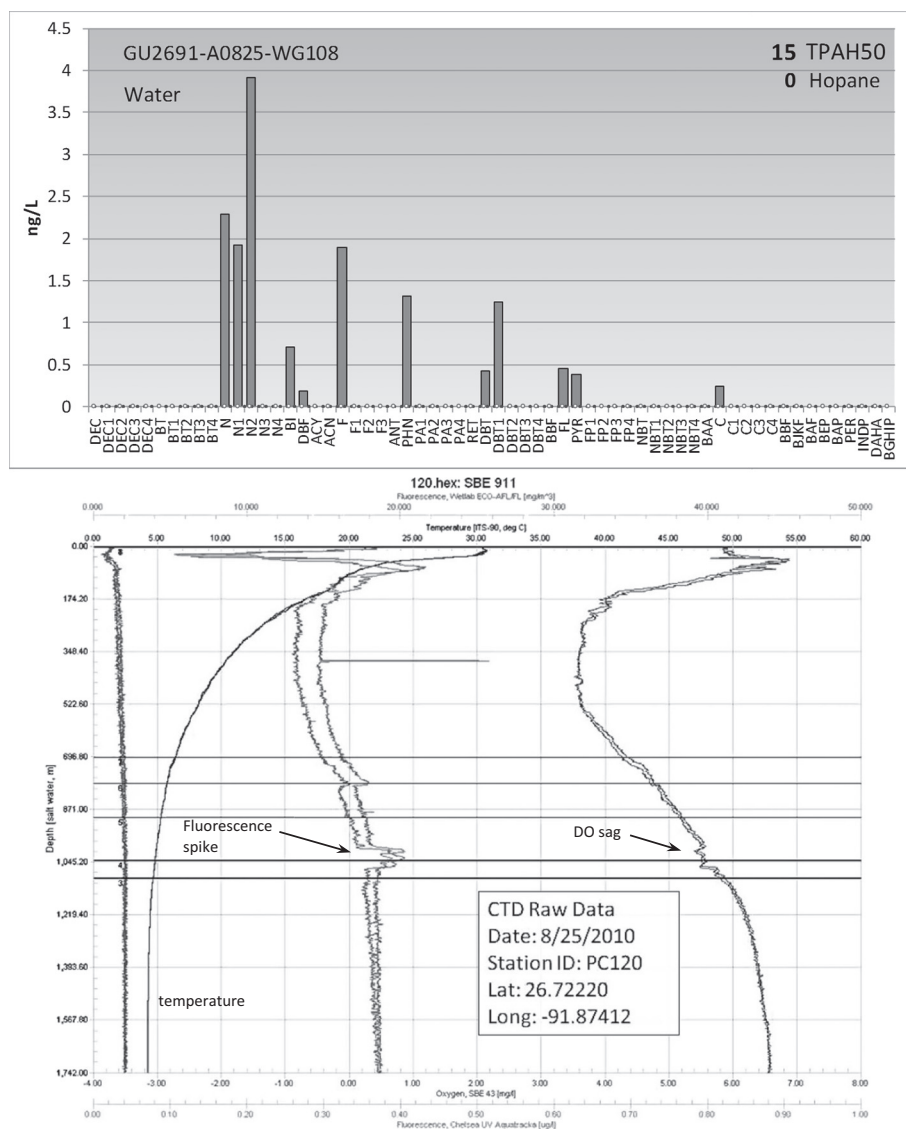


Fig. 10. Trace dissolved PAH pattern (upper plot) from 1000 m depth with fluorescence spike, DO sag (lower plot) and a trace of dispersant indicators (22.5 ng/L, not shown) suggesting the presence of the deepwater plume 412 km from wellhead but without detectible residual PAH components. These data suggest the alkanes and PAH may have been biotically converted to polar components not amenable to GC/FID and SIM GC/MS resolution.

seep formations) but far fewer active oil seeps. Survey work in just the  $50 \times 50$  km Macondo prospect region showed 562 gas plumes detected with 52 various sized slicks appearing over time in synthetic aperture radar (SAR) imagery (Garcia-Pineda et al., 2015). The slicks were intermittent and modest, averaging a total of perhaps  $0.14 \text{ m}^3$  of oil/day (0.91 barrels) with high evaporation rates yielding a proposed 24 h residence/turnover of the sheen hydrocarbons. Following the spill, BP dispatched multiple vessels in 2010 and 2011 to document various aspects of seep chemistry and dynamics. Beneath seep sheens, shallow depth (0–3 m), oiled-water concentrations were within the range of concentrations seen during the spill (excluding the actual surface-slick oil) and were also similar to shallow samples collected at the nearby chronic Taylor Energy sheen site in 2012 (BP, 2014). But seep-oiled water samples from deeper depths, below any surface reinfusion effects, (25–2200 m) were very sparse (only 3 of 296 samples collected on the seep-focused visits by BP cruises) and of low concentration (average 0.24 ppb;  $4\text{--}10 \times$  post-spill background reported by Adhikari et al., 2015). Based solely on these non-extraordinary concentrations from seep-focused sampling plus the sparse detections, we conclude that, despite the impressive tally of documented seeps, the chronic, low-level, sheen-forming, seep inputs to the Gulf of Mexico are dwarfed in

comparison to the prolonged, high-volume (55–60 K bbl/day) release from the 2010 DWH event (McNutt et al., 2011; Spaulding et al., 2015; French-McCay et al., 2016).

The limited 2011 water column data suggest that turnover in the midwater column was complete with a return to absent-to-trace hydrocarbon concentrations without petrogenic signatures. These results helped to further confirm the very low non-spill-impacted “background” concentrations during 2010. From the more extensive sampling of near bottom waters in 2011, there was still an obvious DWH signal present either from floc re-suspension or dissolution processes from oil-contaminated sediments (Stout and Payne, 2016; Stout et al., 2016b; Ziervogel et al., 2016).

### 3.2. TPAH limitations

Total PAH (TPAH), oil's traditional statistical parameter, is oft quoted but poorly represents the multi-component, multi-phasic, non-linear nature of oil weathering when used as a summary proxy for the amount of oil in a sample. In nature, multiple biotic and abiotic processes are constantly and selectively modifying hydrocarbon signatures; a weathered oil droplet, ravaged by dissolution, photooxidation and

microbial attacks, undergoes vast transformations in composition, physical properties and toxicology (Hall et al., 2013; Bacosa et al., 2015). And yet, simply summing the residual PAH components is often the only comparative value presented and thereafter used to evaluate exposures and toxicological effects. For NRDA modelers, tracking individual “pseudo-components” of the oil (BTEX, alkanes and PAH groupings by similar solubilities and vapor pressures) has been a more effective method of assessing transport, fate, and impacts (French-McCay et al., 2015a, 2015b, 2018). Providing forensic phase-discrimination data represents even further progress towards a more realistic depiction of oil fate and behavior.

TPAH values are also biased in the sense that they only represent the detectable GC/MS target analytes, the “quantifiable PAH,” which itself may only represent 1.3–4% of the fresh oil's mass (Camilli et al., 2010; Stout, 2015b). Recent work has shown that the GC/MS view of hydrocarbons in oil, while reliable and prodigiously productive, has constrained our ability to document that weathering processes don't obliterate the oil; it just becomes “transformatively” less visible through our instrumental lens. GC/FID and GC/MS quantification and profiling of aliphatics and PAH only reflect the non-polar target analytes amenable to our instruments and methods (typically reporting ~50 PAH, 55 biomarkers and 34 SHC). Using as alternative method, Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, McKenna et al. (2013) identified > 30,000 hydrocarbon compounds in Macondo oil, while Aeppli et al. (2012), Ruddy et al. (2014) and Radović et al. (2014), among others, documented advanced oxidation states in slicks and stranded tarballs due to photooxidation and shoreline weathering. Although the 2010 NRDA water-column samples have not yet been analyzed using these methods, it is highly likely that some large fraction of the residual deep-plume constituents was microbially converted into similar polar products (Gutierrez et al., 2013a, 2013b; Hall et al., 2013; Gros et al., 2014; Huba and Gardinali, 2016). For example, unquantified polar derivatives would be a logical explanation for the most distant category 3 sample collected 412 km from the wellhead, which held barely a trace of a primarily dissolved-PAH profile but possessed all other indicators of the deepwater plume (fluorescence spike, DO sag, and dispersant indicators) (Fig. 10). Supporting this finding, Du and Kessler (2012) reported a DO anomaly attributed to mass respiration of MC252 oil by microbes extending 505 km SW of the wellhead. Although reported and evaluated only by their low level TPAH values, samples with these trace contaminants (and their unquantified cohorts) probably deserve closer attention and reporting. Beginning with the *Exxon Valdez* oil spill, studies have suggested enhanced low-level toxicity for weathered oil products (Carls et al., 1999; French-McCay et al., 2015a; Morris et al., 2015; Incardona et al., 2004, 2005, 2013, 2015); research regarding toxicity of these polar compounds is ongoing (Overholt et al., 2016; Fingas and Banta, 2016).

#### 4. Conclusions

After forensically examining 4189 offshore water samples from the 2010 NRDA field collections, MC252 oil was detected at depth, further phase- and weathering-state discriminated, and characterized for dispersant effects. Benzene was largely removed by dissolution from rising droplets during ascent but remained at depth out to 15 km while other BTEX components (toluene and xylenes) were detected at depth up to 183 km from the wellhead. Typical of surface oil dynamics, near-surface increases in dissolved and particulate-oil fractions were observed as a result of wind-induced entrainment of surface films and dispersant effects. MC252 oil was identified in deeper water samples as higher-molecular-weight particulate-phase hydrocarbons up to 155 km from the wellhead, and as dissolved-phase as far as 267 km from the wellhead. Furthermore, based primarily on dispersant indicators, fluorescence and DO features, the presence of the plume was detected 412 km SW from the wellhead.

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#### Appendix A. Supplementary information

Supplementary information to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2018.02.055>.

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