Evaluation of Possible Inputs of Oil From the *Deepwater Horizon* Spill to the Loop Current and Associated Eddies in the Gulf of Mexico


The results of the analyses of 282 discreet water samples collected at various depths throughout the water column in the area of the Loop Current and associated eddies in the Gulf of Mexico are reported. No subsurface colored dissolved organic matter fluorescence maximum or oxygen minimum were observed, so samples were collected at standard depths. The concentration of *Deepwater Horizon* (DWH) total oil equivalents (TOE) estimated from total scanning fluorescence (TSF) maximum intensities ranged from less the practical quantitation limit (PQL) of 0.70 to 5.04 μg L⁻¹. The presence of petroleum could not be confirmed in two thirds of the water samples having TOE below the PQL. Forty-eight samples were analyzed by gas chromatography/mass spectrometry for polycyclic aromatic hydrocarbons (PAHs) from primarily samples with higher TOE and from a few samples at the PQ. Of these 48 samples, 35% had PAH concentrations less than or equal to the procedural blank. These concentrations are in the lower range of historical prespill reported results. The oil detected could be from the DWH oil spill as oceanographic currents could have carried the oil from the region of the spill to the sampling sites. If the DWH oil spill was the source of the hydrocarbons detected, the oil would have to have been weathered and greatly diluted by the time it reached these sampling stations. The possibility of other potential sources of oil at the sampling locations cannot be ruled out, including oil from natural seepage, small unrelated discharges, contamination from shipping activities, and atmospheric deposition. Total scanning fluorescence is shown to be a very sensitive indicator of the presence of oil and serves as a valuable screening tool.

1. INTRODUCTION

One of the concerns expressed after the *Deepwater Horizon* (DWH) spill was the possibility of oil reaching the Loop Current and associated eddies in the Gulf of Mexico and subsequent transport to sensitive Florida coastal areas. The purpose of this study was to determine if the higher molecular weight components (C10 to C34) of oil from the DWH oil spill were present in the water column near the Loop Current; if present, were plumes of hydrocarbons at depth apparent, and to compare the concentrations to historical levels. This study excluded gaseous components of the oil, which would have very different long-term fates compared to the components in this study [Camilli et al., 2010; Valentine et al., 2010; Kessler et al., 2011]. In order to investigate DWH oil presence, water samples for petroleum analysis were collected on four legs of scheduled Science Applications International Corporation (SAIC) cruises (Figure 1) aboard the R/V *Pelican*.
Legs 1–3) and R/V Weatherbird II (Leg 4). Leg 1 was from Cocodrie, LA, to St. Petersburg, FL, from 27 June to 5 July 2010. During this leg, 9 conductivity-temperature-depth (CTD) casts and 103 discrete water samples were collected at stations 59, 60, 62, 63, 64, 66, 67, 68, and 71. Leg 2 was from St. Petersburg, FL, to St. Petersburg, FL from 5 July to 13 July 2010. During this leg, 3 CTD casts and 35 discrete water samples were collected at stations 160 (reoccupation of Station 60), 61, and 65. Leg 3 was from St. Petersburg, FL, to Cocodrie, LA, from 13 July to 23 July 2010. During this leg, 7 CTD casts and 84 discrete water samples were collected at stations 51, 53, 54, 55, 56, 57, and 58. Leg 4 was from St. Petersburg, FL, to St. Petersburg, FL, from 24 July to 30 July 2010. During this leg, 5 CTD casts and 60 discrete water samples were collected at stations 69, 72, 73, 74, and 75. Sample station locations are shown in Figure 1.

2. METHODS

Discrete water samples were collected at various depths throughout the water column. The initial sampling strategy was to collect samples coincident with subsurface maximum in the colored dissolved organic matter (CDOM) fluorescence signal or at any subsurface minimum in dissolved oxygen (DO) signal observed in the CTD cast. This was based on the detection of discrete layers of hydrocarbons associated with maximum CDOM fluorescence and reduced oxygen concentrations between 1000 to 1300 m in close proximity to the spill site [Joye et al., 2011]. Neither subsurface CDOM maximum nor DO minimum were observed at any of the sampling stations; consequently, 11 or 12 water samples were spaced throughout the water column at each station. A total of 282 water samples were collected in 1 L certified clean amber bottles and immediately preserved by adding 10 mL of dichloromethane and kept in the dark on the ships. These steps insure that microbial and photochemical degradation of oil components did not occur. Samples were returned to the Geochemical and Environmental Research Group (GERG) at Texas A&M University. Water samples were kept refrigerated (4°C) until extraction. Water samples along with blanks, laboratory spike blanks, and spike blank duplicates were processed following GERG standard operating procedures. The samples (~1 L) were placed in separatory funnels, acidified to a pH of less than 2 with sulfuric acid, surrogate standards added, extracted three times with 60 ml dichloromethane each time, and the dichloromethane extracts combined in 250 ml flat bottom flasks. The combined extract was reduced to 10 mL using a water bath and transferred to 60 mL vials for total scanning fluorescence (TSF) analyses. An aliquot of each sample was momentarily transferred to a precleaned quartz cuvette for fluorescence analysis and returned to the 60 mL vial for subsequent gas chromatographic analysis. Estimates of total oil equivalents (TOE) of DWH oil were based on the TSF maximum intensity (MI) measured at an emission wavelength of 380 nm (excitation at 260 nm) corresponding to the maximum fluorescence intensity from a DWH oil standard reference material obtained from National Institute of Standards and Technology (NIST). This NIST DWH oil was used to construct a calibration curve by determining the MI at seven concentrations (0, 71.68, 143.4, 358.4, 716.8, 1792, and 3584 ng mL⁻¹). The NIST DWH oil was weighed quickly to avoid evaporation and then diluted with dichloromethane to the appropriate concentrations. The linear calibration curve had an R² of 0.9999 (Figure 2). The practical quantitation limit (PQL) for the TSF method (0.70 µg L⁻¹ for a 1 L sample taken to a final volume of 10 mL) is based on the lowest standard concentration other than zero (71.68 ng mL⁻¹) from the calibration curve. All procedural blanks were below the PQL. Samples having a fluorescence maximum intensity greater than the highest standard in the calibration curve were diluted to fall within the calibration range. Sample extracts were reduced in volume to 1 ml, and a subset was analyzed for polycyclic aromatic hydrocarbons (PAHs), the toxic and fluorescent component of oil, by gas chromatography with a mass selective detector [Short et al., 1996]. Forty-eight samples were selected to include mostly samples with higher

Figure 1. Map showing station locations. The diameter of the circles is proportional to the total oil equivalent concentration for each of the water samples collected at the station.
estimated total DWH oil equivalents and also to include procedural blanks and a few samples with concentrations below the PQL.

3. RESULTS AND DISCUSSION

Comparison of water hydrocarbon concentrations in water samples is complicated by different sampling techniques and analytical procedures (e.g., filtered versus unfiltered, fluorescence versus gas chromatography, etc.) as well as nonhomogeneous spatial and temporal distributions. In this study, the concentration of DWH TOE was estimated using TSF compared to the DWH oil (see auxiliary material Table S1). The TOE ranged from less than 0.70 to 5.04 μg L⁻¹. The TOE plotted as a frequency distribution (Figure 3) indicates 66% of the concentrations are below the PQL, a level not significantly different from a procedural blank. The TOE concentrations detected are low compared to concentrations of DWH oil present in subsurface plumes within a few miles of the spill site where concentrations of up to 442 μg L⁻¹ were reported [Diercks et al., 2010; Wade et al., this volume]. The concentrations reported here are also low compared to total hydrocarbon concentration reported for a water sample from 2 m below the surface from the Ixtoc oil spill of 7010 μg L⁻¹ [Boehm et al., 1982]. The concentrations of TOE of each sample at each station are shown in Figure 1. The diameter of each circle is proportional to TOE; a dot for a concentration of 1 μg L⁻¹ is shown in the key for Figure 1.

Concentrations in this study are in the lower range of those reported in the 1970s. For example, historical surface concentrations of approximately 1 μg L⁻¹ from the Gulf of Mexico and Caribbean Sea [Parker et al., 1972] are reported. Concentrations in the North Atlantic along shipping lanes ranged from 1 to 50 μg L⁻¹ [Brown and Huffman, 1976]. Dissolved hydrocarbon concentrations reported from locations close to our sampling sites at depths of 1 m below the surface to 500 m ranged from trace (~1 μg L⁻¹) to 75 μg L⁻¹ with the highest concentrations occurring in the Florida Strait [Hilfe and Calder, 1974] where no consistent concentration trend with depth (data shown in Figure 1) was noted. The lack of any subsurface maximum is similar to the results of this study. A study of hydrocarbon concentrations in water samples from the surface microlayer and near surface (~20–30 cm below the surface) from the Sargasso Sea found oil concentrations that ranged from 13 to 259 μg L⁻¹ in unfiltered water samples; this oil was thought to be the result of the presence of small tar particles from tanker operations [Wade and Quinn, 1975]. Pelagic tar is a historic source of hydrocarbons to the study area as documented by detection at concentrations substantially higher than reported in other coastal areas in the world [Van Vleet et al., 1984]. It was estimated that 10% to 50% of the tar was transported to the Gulf of Mexico from the Caribbean by the Gulf Loop Current, and half was the result of tanker wall washing operations, a practice which has since been discontinued [Van Vleet et al., 1984]. It is also important from a historical perspective to note that reports of subsurface hydrocarbon plumes have been reported prior to the DWH spill. In 1978, a layer of water at a depth of 200 m was discovered in the southwest North Atlantic and eastern Caribbean [Harvey et al., 1979] with concentrations ranging from 3000 to 12000 μg L⁻¹. The oil-rich layer had a spatial extent of over 800
nautical miles and an estimated total mass of more than 1 megaton [Harvey et al., 1979]. The initial and subsequent analyses suggest this plume originated as a massive oil seep from the Venezuelan shelf at a depth of 200 m [Harvey et al., 1979; Requejo and Boehm, 1985].

The highest concentrations present during Summer 2010 in the vicinity of the Loop Current are two orders of magnitude lower than the highest concentration measured in the DWH subsurface plume [Wade et al., this volume] and a factor of 30 lower than concentrations reported in the 1970s from a location in the vicinity of our sampling sites. They are also significantly lower compared to data reported from the Ixtok oil spill.

The total PAH reported here are the sum of 45 individual PAH compounds and groups of alkylated PAH. The PAH detected in these samples were naphthalene, alkylated naphthalenes (C1 to C4), biphenyl, phenanthrene, fluoranthene, pyrene, chrysene, fluorne, and alkylated fluorenes (C1 to C4). The total PAH concentration detected in the water samples ranged from 0.70 to 160 ng L$^{-1}$. The frequency distribution (Figure 4) indicates 35% of the samples analyzed for PAH were at or below the concentration found in a procedural blank (5 ng L$^{-1}$). Many of the higher PAH

![Cumulative Percentage](Image)

**Figure 4.** Frequency distribution for polycyclic aromatic hydrocarbon (PAH) concentration for 48 water samples.

![Concentration Total PAH (ng/mL)](Image)

**Figure 5.** Distribution of PAH in DWH oil from NIST (filled bars) and a sample from this study (unfilled bars).
concentrations were found in samples collected at Stations 74 and 75. The PAH detected were predominantly naphthalene and alkylated naphthalenes (Figure 5). These are also the predominant PAH components present in the NIST DWH oil standard as well as among the most water-soluble PAHs [Wade et al., this volume]. The naphthalene distribution of the NIST DWH oil is what is normally found for petroleum from this area of the Gulf of Mexico with a predominance of the alkylated naphthalenes (e.g., C1, C2, C3, and C4) compared to the parent naphthalene (Figure 5). The distribution for the naphthalenes from a representative station, P69 (300 m), has a similar distribution for the naphthalenes but with maximum percentage for C2 naphthalenes compared to maximum percentage for C1 for the DWH oil (Figure 5). The comparison of other PAH distributions for P69 (300 m) and the DWH oil are not similar. For example, major components of P69 (300 m) are phenanthrene and fluoranthene and pyrene. These only represent minor percentages of the DWH oil. These differences could be due to changes in the distribution resulting from differential weathering (e.g., dissolution, biodegradation, photodegradation, evaporation) and/or different input sources. The total PAH concentration for 48 water samples was not directly related to the TOE concentration (Figure 6, $R^2 = 0.05$). When only the 27 samples having PAH concentrations greater than 20 ng L$^{-1}$ are considered, the $R^2 = 0.45$ (Figure 6). Samples taken from areas near the DWH spill did have good correlations between PAH and TPH [Wade et al., this volume]. Low concentrations present in the samples for both TOE and PAH, possible “weathering” of the DWH oil, or inputs of oil from other sources may contribute to the low $R^2$ value. These concentrations of TOE either at the surface or at depth (Figure 7) suggest major inputs of oil from surface slicks, or subsurface oil plumes were not encountered at these locations as were observed by research conducted near the DWH spill. The CTD data collected coincident with the discrete water samples support this conclusion with no CDOM fluorescence maximum or oxygen minimum. It should be noted that the TSF and PAH analyses are more sensitive by a factor of ~100 compared to the CDOM data and therefore could measure oil not detectable by the in situ CDOM fluorometer.

Our results do not rule out the possibility that these low concentrations of oil are from weathered DWH oil from the spill site. There are oceanic processes that may have caused oil from the spill to be transported to the sampling locations by ocean currents. The currents in the region south of the DWH site are controlled in part by the Loop Current, large warm core eddies (WCE), and smaller cyclonic eddies (CE). At the onset of the spill the Loop Current extended to 27° N on 30 April 2010 as shown in Figure 8a [Leben et al., 2002; R. R. Leben, Real-time altimetry project, Gulf of Mexico near real-time altimeter viewer, maps, Colorado Center for Astrodynamics Research, University of Colorado, Boulder, 2010, available at http://argo.colorado.edu/~realtime/gsfc_gom-real-time_ssh/, hereinafter referred to as Leben, online maps, 2010]. A cyclonic eddy (CE) north of the Loop Current may have advected small amounts of oil to the south and the east where some of it may have entered the Loop Current. By 30 May the Loop Current was in the final phases

**Figure 6.** Total oil equivalent concentration versus PAH for 48 water samples (see text for description of two lines).

**Figure 7.** Total oil equivalent concentration plotted versus water depth for all samples.
of shedding a WCE as seen in satellite altimetry (Figure 8b). Figure 9 shows contours of sea surface elevations on 1 June 2010. The averages of TOE values for each of the stations are shown in Figure 9 as green diamonds that show the average concentration of all samples at each location with the size of the diamond proportional to concentration. Higher values generally fall on the periphery of the WCE. The cyclonic eddy to the north of the WCE (marked L in Figure 9) intensified and could have carried trace amounts of oil to the south and east along 27°N. This physical process is suggested by the relatively higher TOE concentrations at Stations 62 and 66 (Figure 1). By June 30 (Figure 8c), the WCE and the CE aligned to provide a pathway that could be responsible for the elevated TOE concentrations detected at Stations 74 and 75. By July 30 (Figure 8d), the ring was almost completely detached. We estimate travel times for a parcel of water around this eddy to be several days to a few weeks depending on depth.

This proposed pathway is supported by 3 day oil trajectory forecasts made by four different numerical ocean current models [Liu et al., this volume]. Virtual drifters placed in these models at different depths for forecasts initiated on 12 June 2010 show that oil could have reached our stations P66, P74, P75, P73, and P79 along a clockwise path around the outside of the Loop Current eddy centered at about 25.5°N 87.5°W (Marked H in Figure 9).
There are also abundant natural seeps in the area that could be the source of some of this oil. Figure 9 shows small brown circles at the locations of known natural seeps in the area (I. MacDonald, personal communication, 2011). Also shown are 10 km by 10 km squares near our sampling locations where satellite imagery showed surface slicks greater than 0.6% of the time [Garcia-Pineda et al., 2010; I. MacDonald, personal communication, 2011]. Stations further from known seep sites had higher concentrations and stations closer to known seep sites had lower concentrations.

4. CONCLUSIONS

Trace concentrations of oil were detected at some sampling stations at various depths. These concentrations are low compared to historical data dating back to the 1970s from locations close to our sampling sites, to the subsurface plume associated with the DWH spill, to the Ixtox spill, and to a historic oil-rich plume in the North Atlantic and Eastern Caribbean. The oil detected could be from the DWH oil spill as oceanographic currents could have carried the oil from the region of the spill to the vicinity of the Loop Current. If the DWH oil spill was the source of the hydrocarbons detected, the oil would have been weathered and greatly diluted by the time it reached these sampling stations. One cannot rule out the possibility of other potential sources of oil at the sampling locations including oil from natural seepage, small unrelated discharges, contamination from shipping activities, and atmospheric deposition. Additional studies at these locations would provide information on these other potential sources.
sources. They could also investigate why stations further from known seep sites had higher concentrations, while stations closer to known seep sites had lower concentrations. These studies should include sampling larger volumes of water to enable more reliable determination of hydrocarbon fingerprints at these low concentrations. Background data on hydrocarbon concentrations/fingerprints would be invaluable to document sources such as natural seepage events and place any future spills threat to the Florida Coast as the result of oil being entrained in the Loop Current in context. Total scanning fluorescence was shown to be a very sensitive indicator of the presence of oil and serves as a valuable screening tool for selected more sophisticated analyses.

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