Analyses of Water Samples From the *Deepwater Horizon* Oil Spill: Documentation of the Subsurface Plume

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Surface and subsurface water samples were collected in the vicinity of the *Deepwater* Horizon (DWH) wellhead in the Gulf of Mexico. Samples were extracted with dichloromethane and analyzed for a toxic component, polycyclic aromatic hydrocarbons (PAHs), using total scanning fluorescence (TSF) and by gas chromatography/mass spectrometry (GC/MS). An aliquot of fresh, floating oil from a surface sample was used as a DWH oil reference standard. Twelve of 19 samples collected from 24 May 2010 to 6 June 2010 on the R/V *Walton Smith* cruise contained TSF maximum intensities above background ($0.7 \ \mu g \ L^{-1}$ based on 1 L sample size). These 12 samples had total petroleum hydrocarbon (TPH) concentrations as measured by quantitative gas chromatography flame ionization detector (FID) ranging from 2 to $442 \ \mu g \ L^{-1}$. Quantitative GC/MS analysis of these 12 samples resulted in total PAH concentrations ranging from 0.01 to $59 \ \mu g \ L^{-1}$. Low molecular weight, more water-soluble naphthalene and alkylated naphthalene dominated the PAH composition patterns for 11 of the 12 water samples. Sample 12 exhibited substantially reduced concentrations of naphthalenes relative to other PAH compounds. The total PAH concentrations were positively correlated ($R^2 = 0.80$) with the TSF maximum intensity (MI). TSF is a simple, rapid technique providing an accurate prediction of the amount of PAH present in a sample. TSF-derived estimates of the relative contribution of PAH present in the oil provided evidence that PAH represented ~10% of the higher molecular weight TPH. The subsurface oil plume was confirmed by the analyses of discrete water samples for TSF, TPH, and PAH.

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1. INTRODUCTION

The *Deepwater Horizon* (DWH) spill was unique as gas, oil, and dispersants were all released at a depth of approximately 1500 m. This mixture resulted in significant dispersion of the liquid oil at depth. The purpose of this study was to determine whether the higher molecular weight components (nC10 to nC34) of the oil from the DWH oil spill were present in samples from the subsurface plume. Gaseous components of the oil are outside the scope of this work as they have very different long-term fates compared to the components examined in this study [*Camilli et al.*, 2010; *Valentine et al.*, 2010; *Kessler et al.*, 2011; *Joye et al.*, 2011].

A cruise of opportunity 3 weeks after the spill on the R/V *Pelican* detected subsurface maxima of fluorescence (using a color dissolved organic matter (CDOM) fluorometer) that were thought to represent subsurface oil plumes [*Diercks et al.*, 2010; *Joye et al.*, 2011]. The components of oil responsible for its fluorescent properties and toxicity [*Barron et al.*, 2003; *Yamada et al.*, 2003] are the polycyclic aromatic hydrocarbons. In order to confirm that these subsurface fluorescence maxima were due to the presence of oil, water samples were collected in the plumes and analyzed for polycyclic aromatic hydrocarbons (PAHs). In addition, a sample of oil collected from a surface slick in the vicinity of the wellhead was analyzed for total scanning fluorescence (TSF), PAH, and total petroleum hydrocarbon (TPH) to document the oil signature of plume using relatively unweathered and undispersed surface oil.

2. METHODS

Water samples were processed as previously described [*Wade et al.*, this volume]. Briefly, samples (~0.4 to 1 L) were placed in separatory funnels, acidified to a pH of less than 2 with sulfuric acid, aliphatic surrogate standards added, extracted with dichloromethane, and the dichloromethane extracts combined in a 250 mL flat bottom flasks. The sample extracts were reduced in volume and solvent exchanged to hexane. The sample extracts along with procedural blanks were then analyzed by TSF. Samples were diluted, when necessary, to minimize quenching effects. Estimates of total oil equivalents of DWH oil were based on the maximum intensity (MI) measured at an excitation wavelength of 260 nm and an emission wavelength of 370 nm corresponding to MI from a sample of DWH oil obtained with a bucket from the sea surface near the spill. The practical quantitation limit (PQL) for the TSF method was estimated at 0.70 µg L^{-1} for a 1 L sample [*Wade et al.*, this volume]. All procedural blanks were below the PQL. Sample extracts were reduced in volume to 1 mL and analyzed for TPH by gas chromatography (GC) with a flame ionization detector (GC/FID) and PAHs by GC with a mass selective detector [*Short et al.*, 1996].

3. RESULTS AND DISCUSSION

The TSF plot for DWH oil collected from the water surface is provided in Figure 1. We found a strong relationship between MI and the total PAH concentration (range from 0.1 to 59 µg L^{-1}) from GC/mass spectrometry (MS) (Figure 2). The correlation (R^2 of 0.80) is expected as the PAHs are the fluorescent components of oil. TPH concentrations ranged from 2 to 422 µg L^{-1}. TPH and TSF MI were also strongly correlated with an R^2 of 0.80 (Figure 3). There was a strong correlation between PAH and TPH with an R^2 of 0.73 (Figure 4). These results indicate fluorometry is an excellent means to screen samples for the presence of oil. Using high MI values to select impacted samples, more sophisticated
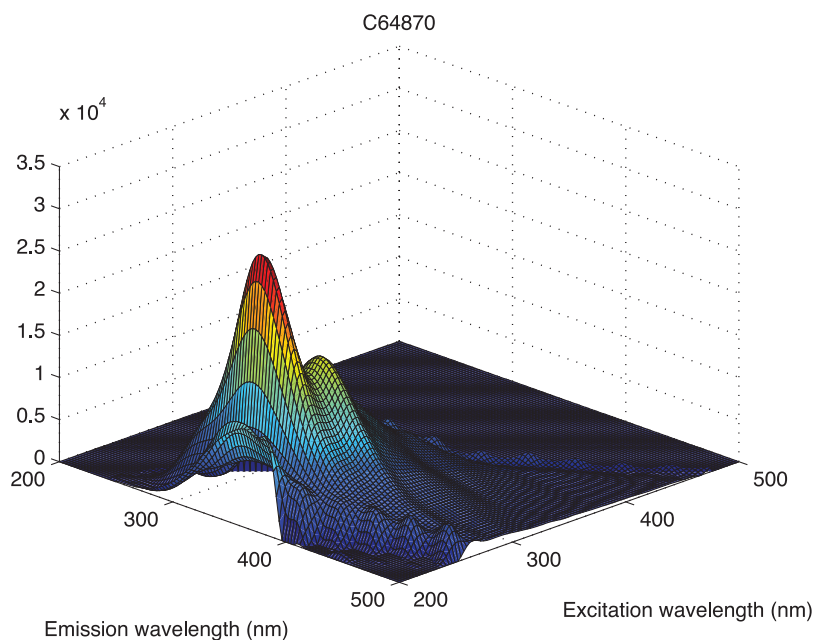

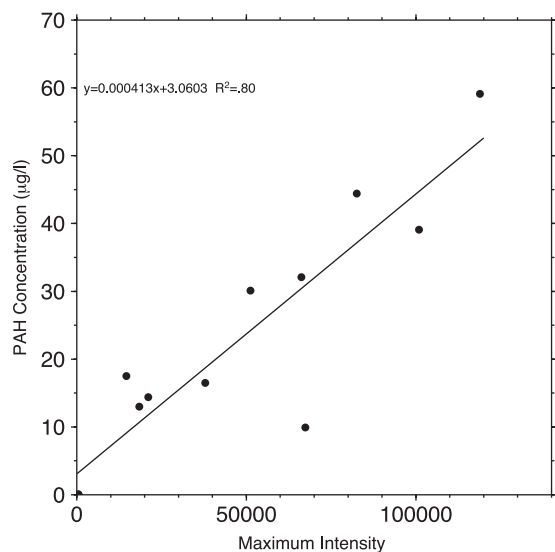**Figure 1.** Total scanning fluorescence (TSF) fingerprint of fresh *Deepwater Horizon* surface oil.

Figure 2. TSF maximum intensity (MI) versus total polycyclic aromatic hydrocarbon (PAH) concentrations.

Figure 4. Total PAH concentrations versus total TPH concentrations.

analyses can be employed in a more cost-effective manner to determine compositional information that can indicate a source of the oil. The distribution of nC10 to nC35 n-alkanes, pristane, and phytane are typical of a freshly oiled pattern/fingerprint. Examples for a sample collected 1.2 miles (1.93 km) from the blowout site at a depth of 1240 m (Station 6) and 3.4 miles (5.47 km) from the blowout site at a depth of 900 m (Station 4) are provided in Figure 5. The TPH concentration at the near site (Station 6) and the distant site (Station 4) were 442 and 232 μg L^{-1}, respectively. The
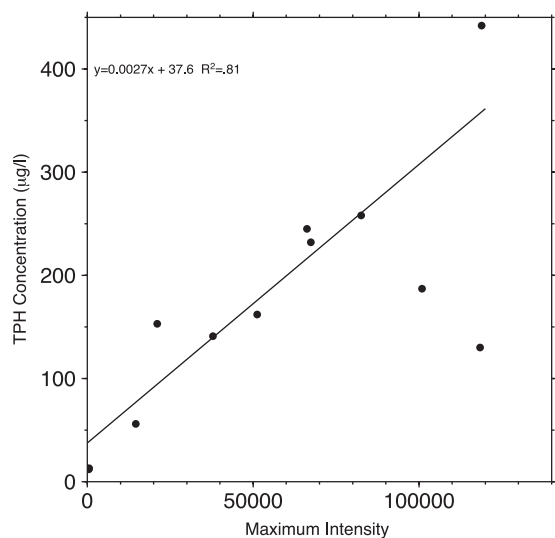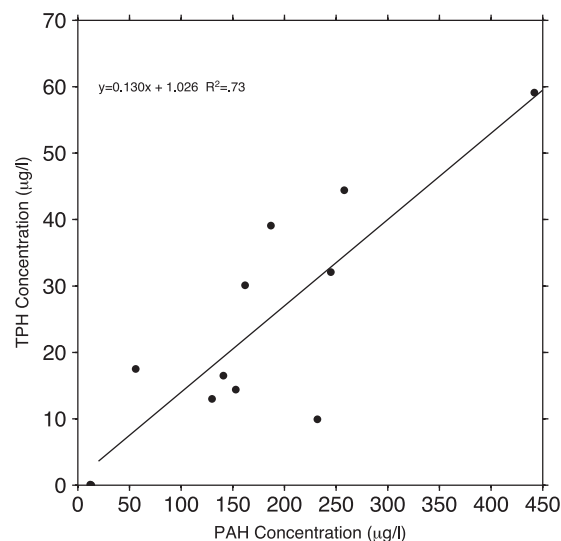

Figure 3. TSF MI versus total TPH concentrations.

dominant n-alkane in the near station was nC14, while the highest for the more distant station was nC17. This pattern was consistent with preferential loss of lower molecular weight, more water soluble n-alkanes from the plume with time, using distance as a surrogate. The average odd n-alkane to even n-alkane ratio for samples with TPH concentrations over 130 μg L^{-1} was 1.06, which is in good agreement with that of oil collected from the surface in the vicinity of the spill (1.05). A ratio near 1 is a good indicator of fresh oil [*Stout et al.*, 2003]. The ratio slightly above 1 in these samples suggested the presence of lower molecular weight n-alkanes nC11, nC13, nC15, and nC17, which are components common to both oil and marine phytoplankton. The average (for samples with TPH greater than 130 μg L^{-1}) pristane/nC17 ratio was 0.60 and phytane/nC18 ratio was 0.54. The pristane/nC17 ratio and phytane/nC18 ratio of oil collected from the surface in the vicinity of the spill were 0.58 and 0.46, respectively. The average ratios are very close to those of the surface oil suggesting little biodegradation of the n-alkanes in samples with concentrations greater than 130 μg L^{-1}. The distribution of PAH in the water samples at near and distant stations with total PAH concentrations of 59 and 9.9 μg L^{-1}, respectively, are provided in Figure 6. The PAH distributions were markedly different at these two sites with the total naphthalenes (naphthalene + C1 + C2 + C3 +C4) in the near sample location accounting for 83.6% and only 56.2 % of the total PAH at the more distant station. The percentages of the total PAH to TPH were 13.3% and 4.5% for the near and distant stations, respectively, indicating a preferential loss of lower molecular weight, more water-soluble PAH.
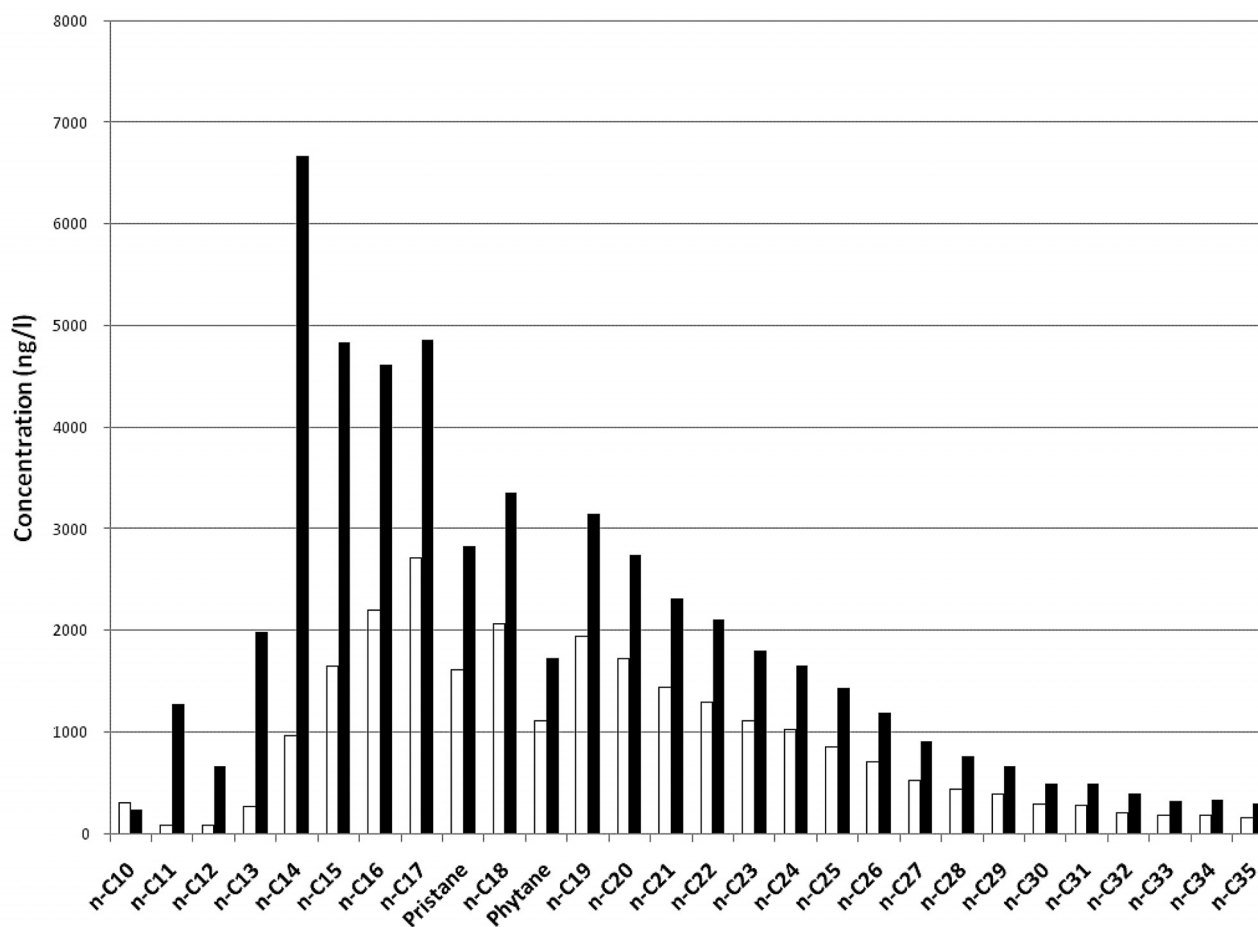
Figure 5. Aliphatic hydrocarbon distribution: Station 6 (solid bars) and Station 4 (open bars).

Natural petroleum seepage into the Gulf of Mexico is a widespread phenomenon and a significant source of hydrocarbons into the marine environment [*Kennicutt et al.*, 1988a, 1988b]. There is a linkage of sea slicks and tar balls with the subterranean reservoir oil based on the distributions of PAH and biomarkers in the northern Gulf of Mexico [*Kennicutt et al.*, 1988a]. Hydrocarbon concentrations from the Gulf of Mexico and adjacent areas from the near surface and subsurface have been summarized [*Wade et al.*, this volume]. Dissolved hydrocarbon concentrations near the Loop Current at depths of 1 m below the surface to 500 m ranged from 1 to 75 μg L^{-1} [*Iliffe and Calder*, 1974]. A recent study of 282 water samples collected in the vicinity of the Loop Current [*Wade et al.*, this volume] at various depths in the water column reported hydrocarbon concentrations ranging from 0.70 to 160 μg L^{-1}. Neither of these studies documented a subsurface plume. The concentration range from this study for total hydrocarbon concentrations was from 2 to 442 μg L^{-1}. The highest concentration reported

here is substantially lower compared to the 7010 μg L^{-1} reported for samples collected 2 m below the surface from the Ixtox oil spill [*Boehm et al.*, 1982]. Concentrations reported here were also low compared to reports of a subsurface plume at a depth of 200 m in the southwest North Atlantic and eastern Caribbean [*Harvey et al.*, 1979] with concentrations ranging from 3000 to 12,000 μg L^{-1}. The source of this plume was attributed to a massive oil seep from the Venezuelan shelf at a depth of 200 m [*Requejo and Boehm*, 1985]. The concentrations in the plume reached almost 30 times the highest concentrations found in this study. The ephemeral nature of these natural seeps is evidenced by their inability to detect this plume 11 months later [*Harvey et al.*, 1979].

4. CONCLUSIONS

These analyses confirm the presence of subsurface plumes of oil (the higher molecular weight components) near the
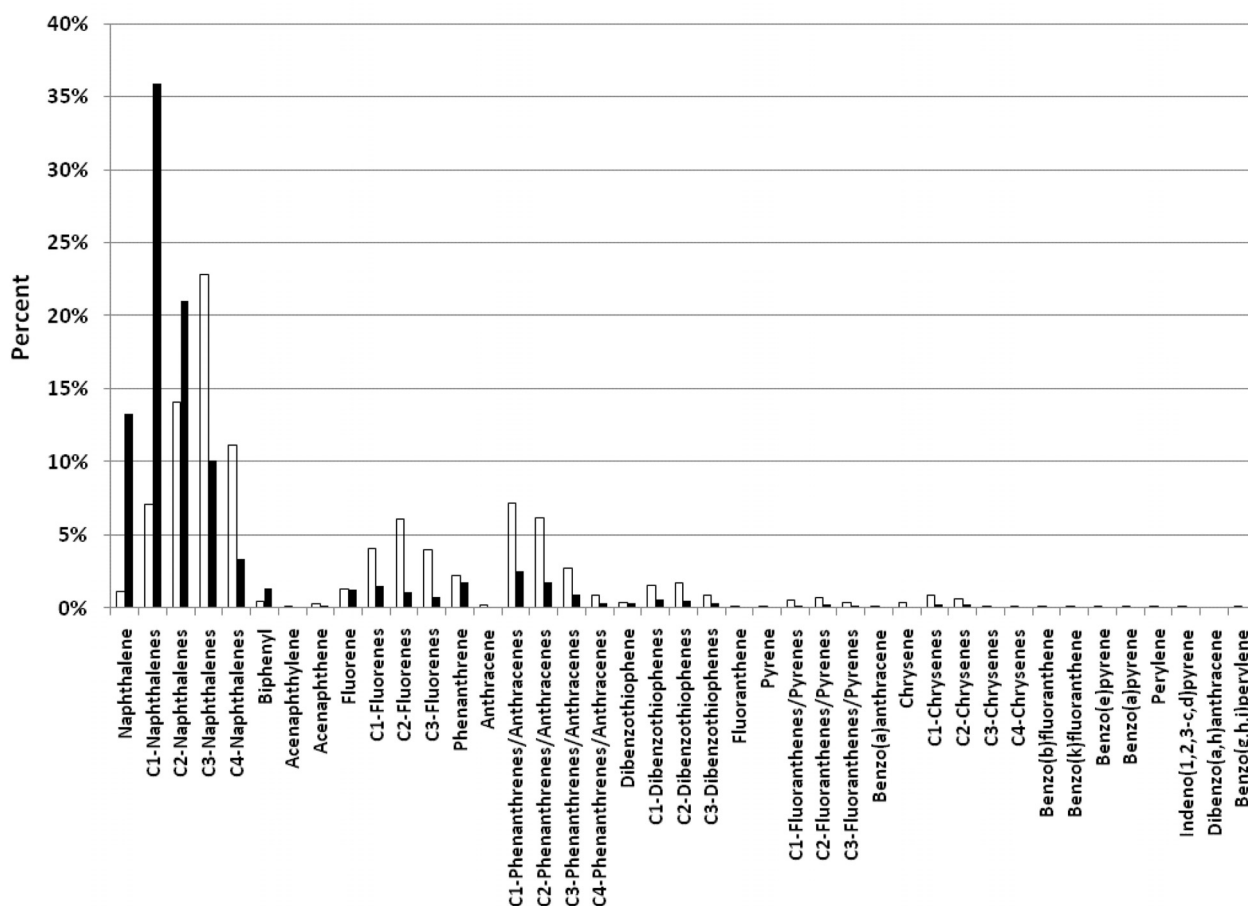
Figure 6. PAH percent distribution: Station 6 (solid bars) and Station 4 (open bars).

DWH wellhead. Extraction techniques used in this study provide measurements of both dissolved and particulate oil (samples were unfiltered). If only dissolved hydrocarbons had been measured, the reported concentrations may have been lower. The detected oil lost some of the lower molecular weight components suggesting preferential dissolution or biodegradation of the lower molecular weight, more water-soluble components. Biodegradation processes did not modify the n-alkanes in subsurface samples based on the ratios of odd to even n-alkanes, pristane/nC17, and phytane/nC18. How the use of dispersants affected these processes cannot be determined from our data. The results of our analyses confirm that CDOM fluorometers are a valuable tool in detecting subsurface oil. TSF is an effective method for rapid screening of samples to estimate oil concentrations. Additional analysis by more sophisticated techniques (e.g., TPH, PAH, biomarkers, etc.) is required to adequately fingerprint the oil to a specific source or to document its weathering history. Based on historical data, it is unlikely that high concentrations of DWH oil would presently be detectable in the water column near the

spill, but that hypothesis needs to be tested. The collection of larger-volume water samples would also be prudent in order to have prespill background data on hydrocarbons.

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