

Tracking Hydrocarbon Plume Transport and Biodegradation at *Deepwater Horizon*

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The *Deepwater Horizon* blowout is the largest offshore oil spill in history. We present results from a subsurface hydrocarbon survey using an autonomous underwater vehicle and a ship-cabled sampler. Our findings indicate the presence of a continuous plume over 35 km in length, at approximately 1100 m depth that persisted for months without substantial biodegradation. Samples collected from within the plume reveal monoaromatic petroleum hydrocarbon concentrations in excess of 50 $\mu\text{g L}^{-1}$. These data indicate that monoaromatic input to this plume was at least 5500 kg day⁻¹, which is more than double the total source rate of all natural seeps of the monoaromatic petroleum hydrocarbons in the northern Gulf of Mexico. Dissolved oxygen concentrations suggest that microbial respiration rates within the plume were not appreciably more than 1 $\mu\text{M O}_2$ day⁻¹.

The *Deepwater Horizon* blowout at the MC 252 Macondo well site released over four million barrels (636 million liters) of oil into the Gulf of Mexico (1). Its scale and source depth, at 1500 m below the sea surface, represent a relatively uninvestigated category of oil spill. The mechanisms of plume formation are complex due to numerous factors including the interplay of gas and oil in multiphase flow, preferential solubility of each oil constituent, and potential gas hydrate formation (2). Consequently, deep water oil spills are difficult to model and plume dynamics remain challenging to predict (2–4). Many deepwater models include the Gulf of Mexico in their spill scenarios (4–6).

We initially observed a subsurface layer of oil between 1030 and 1300 m depth during a United States Coast Guard authorized flow assessment effort at the well site in late May and early June 2010 (fig. S1). To further characterize any resultant plume stemming from the *Deepwater Horizon* blowout, we performed a ten-day subsurface sampling effort, including three long range surveys from 19 to 28 June 2010 using the National Deep Submergence Facility's autonomous underwater vehicle (AUV) *Sentry* (fig. S7) and a cable-lowered sample collection rosette (fig. S2), each equipped

with a *TETHYS* in situ membrane inlet mass spectrometer (7, 8). *Sentry* was chosen for these operations based on this vehicle class's demonstrated utility in characterizing deep ocean hydrothermal vents (9) and cold-seeps (10). Sampling utilized an iterative approach of in-situ sensing and automated data analysis to identify select petroleum hydrocarbons and any associated oxygen anomalies. The three *Sentry* surveys, all conducted between 23 and 27 June 2010 at depths in excess of 1000 m, operated for 64 hours to cover a linear distance of 235 km. During these deployments, *Sentry*'s mass spectrometer recorded over 3500 discrete sample measurements, simultaneously tracking ten independent chemical parameters in real-time. Another 2300 sample measurements were recorded by mass spectrometry during rosette profiling. These mass spectrometers have previously been used for analyzing naturally occurring oil seeps off the coast of California and the Gulf of Mexico (11, 12), tracking subsurface oil leaks from blowout preventers damaged by hurricanes in the Gulf of Mexico (13), and for mapping deep-ocean hydrates in real-time (10).

Mass spectrometric and fluorescence data, recorded during vertical profiling with the ship's sampling rosette approximately 4 km from the leak source, confirmed the presence of a large plume at approximately 1000 to 1200 m depth, as well as a more diffuse plume existing between 50 and 500 m depth (Fig. 1). We operationally define a plume as a discrete spatial interval with hydrocarbon signals or signal surrogates (i.e., colored dissolved organic matter or aromatic hydrocarbon fluorescence) more than two standard deviations above the root-mean-square baseline variability.

Mass spectra indicate a heterogeneous hydrocarbon mixture changing in composition as a function of depth (Fig. 2); for example, ion peaks associated with aromatic hydrocarbons such as benzene and toluene (i.e., m/z 78 and 91, respectively) are present at 1160 m, but greatly attenuated at 10 m depth. This difference in composition may be the result of preferential solubility during upward hydrocarbon migration through the water column, or ventilation. These

data suggest that the aromatic hydrocarbons, often associated with adverse biological effects, may be in greater abundance at depth. The sharp decrease of methane and light volatile hydrocarbon fractions in the interval between 30 m depth and the surface implies substantial rates of loss to the atmosphere.

The subsurface plume's lateral direction was then constrained via a continuous rosette casting technique at a constant radius of approximately 5 km from the well site in a circular arc spanning over 300 degrees (except in the NNE due to surface oil collection activity and poor air quality). Based on mass spectra and aromatic fluorometer data, the strongest hydrocarbon readings were encountered at approximately 1100 m depth WSW of the well site, as well as a weaker signal NE of the well site (Fig. 3A).

The first long-range *Sentry* survey, conducted as an ENE radial projection from the source at three separate depth intervals (1000, 1150, and 1300 m), did not encounter petroleum hydrocarbons significantly above background levels. The second survey, carried out as a constant 1120 m depth "zig-zag" pattern SW of the leak source, reported elevated petroleum hydrocarbons from its mass spectrometer on each segment of the survey (fig. S8). The third survey extended this pattern further to the southwest. Approximately 27 km from the source petroleum hydrocarbon values rapidly diminished at this 1120 m survey depth. Using its dynamic re-tasking capability, *Sentry* executed track lines at differing depths until it identified a hydrocarbon maximum at 1160 m. The dive track continued at this modified depth until the survey's conclusion at 35 km from the source. Further AUV operations were discontinued because of deteriorating sea state generated by Hurricane Alex.

The second and third *Sentry* dives transited across horizontal plume anomalies during each of the mission track lines. These data, combined with the rosette profiling data indicate a continuous, neutrally buoyant plume as much as 200 m high and in certain areas over 2 km in width, moving along a southwestern trend for a distance of more than 35 km from its source (Fig. 3A). Water velocity data gathered by *Sentry*'s Doppler velocity log during dives two and three measured a SW trending current at 1100 m depth averaging 7.8 cm s^{-1} at 247 degrees from true north (fig. S9). The plume's horizontal stability and limited cross sectional increase as a function of distance from the well site suggest Lagrangian transport. Its track is coincident with water current direction at this depth, indicative of topographically controlled transport (14) along an isodepth at the continental slope. Mass spectrometer indicator ions for dissolved methane exhibited limited amplitude decrease along the plume track during *Sentry* dives, with the local maxima encountered at 35 km from the source only 53% less than the maxima encountered at 5.8 km from the source (Fig. 3B). It therefore appears likely that the plume extends considerably

beyond the survey bound. Furthermore, the overall decrease in methane maxima and baseline minima as a function of distance from the well site, the similar concentration profiles across all track line crossings, and the absence of hydrocarbon anomalies at depths below the plume suggest that this horizontal plume is not due to naturally occurring seafloor petroleum hydrocarbon seeps.

The presence of a SW trending plume is consistent with findings from an earlier AUV survey conducted by the Monterey Bay Aquarium Research Institute (MBARI) on 2 and 3 June 2010 approximately 10 km southwest of the well site (15). The body of evidence, including the ROV video we observed, and the MBARI AUV surveys, along with these *Sentry* and ship rosette surveys, indicates that this plume persisted at this depth interval for months.

Gas chromatographic analyses for only monoaromatic hydrocarbons of several water samples gathered using survey guidance confirm benzene, toluene, ethylbenzene, and total xylenes (BTEX) concentrations in excess of $50 \mu\text{g L}^{-1}$ within the plume at 16 km downrange from the well site (table S2). A cross-sectional distribution of BTEX within the plume can be calculated from BTEX sample concentrations measured during vertical rosette profiling and the plume's horizontal profile measured by the AUV's mass spectrometer (figs. S11 and S12). A volumetric BTEX flux rate can then be estimated by integrating this cross section concentration distribution across the observed water column velocity of 7.8 cm s^{-1} .

This calculation indicates that more than 5500 kg day^{-1} of BTEX was introduced into this deepwater column plume, or approximately 40 barrels (6400 liters) day^{-1} of BTEX using a specific density of 0.85. BTEX is approximately 1% of the total amount of the oil released (16). Given an oil flow from the well of 53,000 to 62,000 barrels day^{-1} (8.4 to 9.9 million liters day^{-1}) (1), the leak released 530 to 620 barrels (84,000 to 99,000 liters) of BTEX day^{-1} . Thus, 6 to 7% of all of the BTEX leaked from the well was required to support this plume. These calculations reveal that natural oil seeps cannot be the source of this plume as the combined inputs for all of the northern Gulf of Mexico are approximately 1400 barrels (220,000 liters) of total oil day^{-1} or 14 barrels (2200 liters) of BTEX day^{-1} (17). Therefore, even if all of the natural seeps in the Gulf of Mexico were flowing into the plume, it would support less than half of the BTEX found in the plume. These findings confirm that a mechanism exists for direct hydrocarbon transfer into deep marine ecosystems. Because our analysis focuses on a limited range of hydrocarbons, the total amount of petroleum hydrocarbons in the plume and the full extent of possible risks to marine biota remain uncertain.

Dissolved oxygen concentrations provide estimates for the relative rate of hydrocarbon biodegradation and oxygen drawdown within the plume. Prior surveys of the area reported preliminary oxygen deficits of as much as 30% (18,

19) although dissolved oxygen estimates at the spill site using microelectrode sensors have been called into question (20). In certain instances during our rosette survey operations the oxygen microelectrode reported localized oxygen minimum layers in regions which were coincident with the plume depth (fig. S4). Winkler oxygen titrations (21, 22) generally did not confirm these large excursions (fig. S6) although in some instances such as a hydrocarbon layer encountered at a depth of 930 m at a station 20 km to the SW of the well site, we observed an oxygen drawdown of a few percent (Fig. 4). Nevertheless, the mean Winkler oxygen concentrations at the 1000 to 1200 m depth interval ($187 \pm 7 \mu\text{M}$) were indistinguishable from mean climatological values ($191 \pm 9 \mu\text{M}$) (23). Furthermore, oxygen:argon ratios recorded by the mass spectrometers during AUV and rosette operations are in close agreement with Winkler data (Fig. 4A), exhibiting no statistically significant correlation between oxygen and hydrocarbon levels (Fig. 4B). Given that the manufacturer of the oxygen microelectrode sensor advises that hydrocarbon contamination can affect its performance (24), we propose that hydrocarbon contamination could explain some of the low oxygen excursions we observed using this sensor.

The lack of systematic oxygen drawdown within the plume suggests that the petroleum hydrocarbons did not fuel appreciable microbial respiration on the temporal scales of our study. Assuming that the aforementioned WSW current carried the hydrocarbon-rich layer away from the well site at the measured velocity of approximately 7.8 cm s^{-1} (approximately 6.7 km d^{-1}), the plume at the end of our survey 35 km from the well site was at least 5 days old. Based on the 95% confidence interval of our Winkler oxygen data from the plume layer ($\pm 2 \mu\text{M}$), we estimate that microbial respiration in the plume was not appreciably more than approximately $0.8 \mu\text{M O}_2 \text{ day}^{-1}$ or, based on elemental formula for straight-chain hydrocarbons, approximately $0.5 \mu\text{M C day}^{-1}$. This suggests that if the hydrocarbons are indeed susceptible to biodegradation, then it may require many months before microbes significantly attenuate the hydrocarbon plume to the point that oxygen minimum zones develop that are intense enough ($[\text{O}_2] < 63 \mu\text{M}$ (25, 26)) to threaten Gulf fisheries.

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Figs. S1 to S12
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References

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Fig. 1. Vertical profile of water column chemistry approximately 4 km from the well site at 28.7352°N 88.3892°W. Aromatic hydrocarbon values are expressed on a relative (log) scale using in situ UV fluorimetry, whereas hydrocarbon measurements determined via mass spectrometry are ratioed to water (m/z 17) to correct for variability in instrumental response. Mass spectrometer concentration values are unitless (expressed on a relative scale).

Fig. 2. Mass spectra recorded at 10 m and 1160 m during the vertical profile described in Fig. 1.

Fig. 3. (A) A 3D reconstruction of natural gas distributions detected within the water column by mass spectrometry. Relative methane signal intensity (m/z 15:17) is displayed in the color bar on a \log_{10} scale (blue indicating lower methane, red indicating higher methane). The SW trending plume, designated by the black field, extends throughout the entire length of *Sentry* dive 2 and 3 surveys. Contour lines indicate bathymetric increments of 100 m. **(B)** Plot of methane signal intensity as a function of straight-line (linear) distance from the *Deepwater Horizon* well site. The gray colored lower band indicates signal range at or below two standard deviations from mean baseline variability.

Fig. 4. Vertical profile of water column chemistry approximately 20 km SW of the well site. **(A)** Dissolved oxygen estimates based on polarographic electrode (blue dots), Winkler titration (black diamonds), and oxygen:argon (red squares). Oxygen and argon have similar solubilities in water. Conservation of argon provides a comparative indicator for relative oxygen saturation. **(B)** Oxygen:argon relative to methane.







