ticles of hydrated NiO and NiFe₂O₄ form Ni metal when examined by means of transmission electron microscopy (21, 22). There are reports of unusual magnetism in semiconductors (ZnO and TiO₂) doped with cobalt (23, 24). The crystallographic position, clustering, phase separation, and oxidation state of the dopant are critical to understanding the origin of the reported ferromagnetism. Changes in the Co-O phase diagram under vacuum conditions that may produce Co metal more readily in nanoscale systems.

References and Notes
5. Materials and methods are available as supporting material on Science Online.

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 of oil, more than 35 kilometers in length, at approximately 1100 meters depth that persisted for months without substantial biodegradation. Samples collected from within the plume reveal monoaromatic petroleum hydrocarbon concentrations in excess of 50 micrograms per liter. These data indicate that monoaromatic input to this plume was at least 5500 kilograms per day, 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 micromolar oxygen per day.

The Deepwater Horizon blowout at the MC252 Macondo well site released more than 4 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 many 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 deep-water 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 U.S. 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 10-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 because this vehicle class’s demonstrated utility in characterizing deep-ocean hydrothermal vents (9) and cold seeps (10). Sampling made use of 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 more than 3500 discrete sample measurements, simultaneously tracking 10 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 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 ~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 66, 233 (2002).
associated with aromatic hydrocarbons such as benzene and toluene [i.e., mass/charge ratio (m/z) of 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 ventilation to the atmosphere or preferential solubility during upward hydrocarbon migration through the water column. 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 ~5 km from the well site in a circular arc spanning more than 300° (except in the north-northeast direction, 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 ~1100-m depth, west-southwest of the well site, and a weaker signal was detected northeast of the well site (Fig. 3A).

The first long-range Sentry survey—conducted as an east-northeast 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 southwest 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. With the use of its dynamic retasking 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 high as 200 m and, in certain areas, more than 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 southwest trending current at 1100-m depth, averaging 7.8 cm s⁻¹ at 247° 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 the water-current direction at this depth, indicative of topographically controlled transport (14) along an isodepth at the continental slope. Mass spectrometers.
Gas chromatographic analyses for only monomeric hydrocarbons of several water samples gathered using survey guidance confirm benzene, toluene, ethylbenzene, and total xylene (BTEX) concentrations in excess of $50 \mu g \text{l}^{-1}$ 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 can be 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$^{-1}$.

Our calculations indicate that more than 5500 kg day$^{-1}$ of BTEX (or $\sim 40$ barrels (6400 liters) per day of BTEX using a specific density of 0.85) was introduced into this deep-water-column plume. BTEX is $\sim 1\%$ of the total amount of the oil released (16). Given an oil flow from the well of 53,000 to 62,000 barrels per day (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 per day. 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 $\sim 1400$ barrels (220,000 liters) of total oil per day or 14 barrels (2200 liters) of BTEX per day (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. Earlier 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 that 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 south-west 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 ($187 \pm 7 \mu M$) were indistinguishable from mean climatological values ($191 \pm 9 \mu M$) (23). Furthermore, oxygen:argon
Deep-Sea Oil Plume Enriches Indigenous Oil-Degrading Bacteria

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The biological effects and expected fate of the vast amount of oil in the Gulf of Mexico from the Deepwater Horizon blowout are unknown owing to the depth and magnitude of this event. Here, we report that the dispersed hydrocarbon plume stimulated deep-sea indigenous γ-Proteobacteria that are closely related to known petroleum degraders. Hydrocarbon-degrading genes coincided with the concentration of various oil contaminants. Changes in hydrocarbon composition with distance from the source and incubation experiments with environmental isolates demonstrated faster-than-expected hydrocarbon biodegradation rates at 5°C. Based on these results, the potential exists for intrinsic bioremediation of the oil plume in the deep-water column without substantial oxygen drawdown.

Assessing the environmental and public health impacts of the Deepwater Horizon blowout is difficult owing to the extreme depth of the blowout and the large volumes of oil released. Moreover, the effectiveness of the primary initial mitigation strategy (e.g., injecting the oil dispersant Corexit 9500 directly at the wellhead in a water depth of 1544 m) is difficult to assess despite initial analysis of its potential toxicity (1). An optional strategy for remediation of the deep underwater plume is to use the intrinsic bioremediation potential of deep-sea microorganisms to degrade the oil. This strategy depends on a number of environmental factors, including a favorable response of indigenous microorganisms to an increased concentration of hydrocarbons and/or dispersant.

To determine the impact of the deep hydrocarbon plume on the marine microbes residing in the plume and the rates of hydrocarbon biodegradation, we collected deep-water samples from two ships between 25 May 2010 and 2 June 2010. In total, we analyzed the physical, chemical, and microbiological properties. Key references can be found in Tables S1 and S2 Supporting Online Material.