

# Composition and fate of gas and oil released to the water column during the *Deepwater Horizon* oil spill

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**Quantitative information regarding the endmember composition of the gas and oil that flowed from the Macondo well during the *Deepwater Horizon* oil spill is essential for determining the oil flow rate, total oil volume released, and trajectories and fates of hydrocarbon components in the marine environment. Using isobaric gas-tight samplers, we collected discrete samples directly above the Macondo well on June 21, 2010, and analyzed the gas and oil. We found that the fluids flowing from the Macondo well had a gas-to-oil ratio of 1,600 standard cubic feet per petroleum barrel. Based on the measured endmember gas-to-oil ratio and the Federally estimated net liquid oil release of 4.1 million barrels, the total amount of C<sub>1</sub>-C<sub>5</sub> hydrocarbons released to the water column was  $1.7 \times 10^{11}$  g. The endmember gas and oil compositions then enabled us to study the fractionation of petroleum hydrocarbons in discrete water samples collected in June 2010 within a southwest trending hydrocarbon-enriched plume of neutrally buoyant water at a water depth of 1,100 m. The most abundant petroleum hydrocarbons larger than C<sub>1</sub>-C<sub>5</sub> were benzene, toluene, ethylbenzene, and total xylenes at concentrations up to 78  $\mu\text{g L}^{-1}$ . Comparison of the endmember gas and oil composition with the composition of water column samples showed that the plume was preferentially enriched with water-soluble components, indicating that aqueous dissolution played a major role in plume formation, whereas the fates of relatively insoluble petroleum components were initially controlled by other processes.**

Gulf of Mexico | subsurface plumes

**D**uring the 3 mo following April 20, 2010, the Macondo well emitted several million barrels of gas and oil at the seafloor of the Gulf of Mexico following the sinking of the *Deepwater Horizon* drilling platform. Relative to oil spills occurring at the sea surface, petroleum hydrocarbons experienced a unique set of processes following their release at 1.5-km depth (1–4). This spill demonstrates the importance of interwoven chemical, physical, and biological processes in regulating the transport and fate of hydrocarbons in the deep marine environment. Compositional information for petroleum (gas and oil) released by the well at the seafloor is essential for evaluating the fates of hydrocarbons in the sea. Moreover, such information provides direct constraints on estimates of the total mass of individual hydrocarbons released to the environment and the flow rates at the site of the spill (5). Gases are of particular interest because the gas fraction represents a large component of the carbon released, and it was biodegraded rapidly in the water column (3, 4). Compositional data for released oil is also necessary for forensic analyses when distinguishing Macondo well oil from hydrocarbons released from other sources in the Gulf of Mexico.

Numerous studies have examined factors that influence the compositional evolution of oil spilled at the sea surface (6–10), where evaporation and dissolution may simultaneously remove hydrocarbons from the floating oil. Because these competing

processes complicate efforts to differentiate aqueous dissolution from other loss processes, few studies have attempted to quantify aqueous dissolution of hydrocarbons to the water column (11). Petroleum released from the Macondo well at 1.5-km depth, however, allows the partitioning of hydrocarbons into the aqueous phase to be studied in the absence of atmospheric evaporation.

To acquire a representative endmember of gas and oil, two samples of fluids exiting the Macondo well were collected on June 21, 2010, using isobaric gas-tight (IGT) samplers deployed from a remotely operated vehicle (ROV) (Fig. 1 and Fig. S1) (12). The gas-tight samplers maintained the collected fluids at hydrostatic seafloor pressures, thereby precluding the loss of volatile species prior to analysis at our shore-based laboratories. One sample (MW-1) was acquired between the stub of the lower marine riser package (LMRP) and the lower annulus of the Top Hat #4 collection device. A second sample (MW-2) was collected above one of the Top Hat #4 vents. These fluids, collected in situ during the spill using an approach that preserves the integrity of gas and oil composition, provide a unique opportunity for chemical analysis of petroleum hydrocarbons in the endmember fluid emitted from the well.

During the period from June 19 to June 28, 2010, we also collected water column samples within the region of a southwest trending deep water plume defined by Camilli et al. (1). This plume was initially identified by elevated levels of methane and light aromatic hydrocarbons (benzene, toluene, ethylbenzene, and total xylenes, referred to collectively as BTEX). In this study, we present a comprehensive dataset for a wider range of compounds including *n*-alkanes, branched alkanes, monoaromatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) (Fig. S2) (13). The compositional evolution of hydrocarbons during their trajectory through the water column can be used to diagnose the physical, chemical, and biological processes acting on petroleum released to the deep sea.

## Results and Discussion

Owing to its collection from within the LMRP, sample MW-1 contained predominantly petroleum hydrocarbons (gas and oil) and a minor amount (approximately 5% vol/vol) of an aqueous fluid of seawater composition. In contrast, MW-2 contained approximately 23% seawater, presumably due to turbulent mixing of ascending oil, gas, and water at the collection site a few meters

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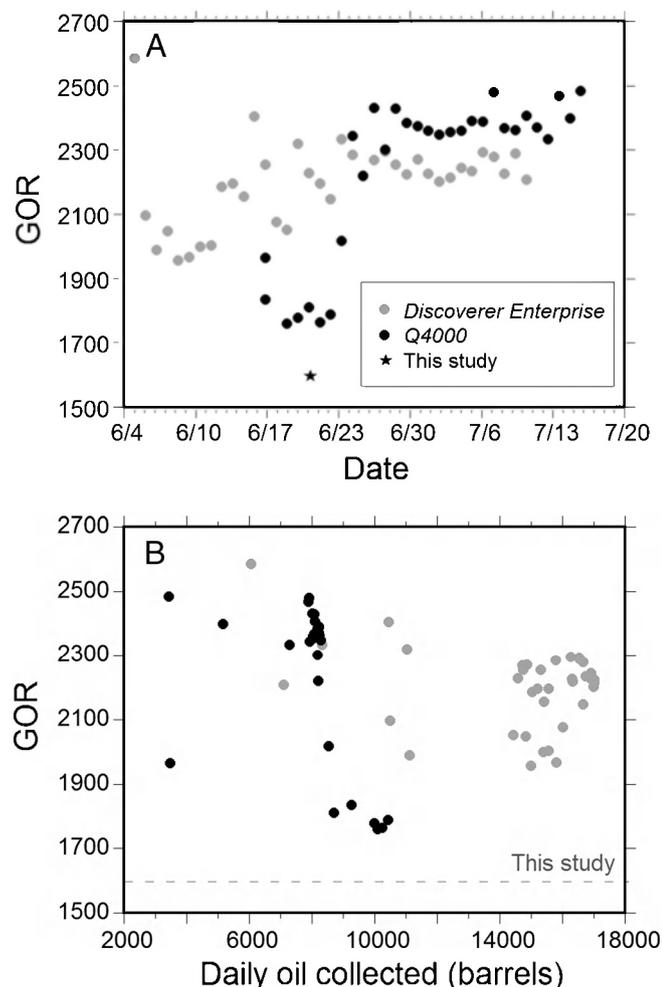


Fig. 2. Plots of GOR as a function of (A) date and (B) daily oil collected by the recovery vessels *Discoverer Enterprise* and *Q4000* (19).

in this study on June 21. On June 24, 2010, however, the GOR for fluids recovered on the *Q4000* underwent an abrupt increase to values near 2,400 and remained at this level until July 16, 2010 (Fig. 2) (18).

Analysis of *Q4000*'s daily GOR values from the two periods indicates that their means and distributions are statistically different with a greater than 99% confidence level. In contrast, hydrocarbons simultaneously captured on *Discoverer Enterprise* recovery vessel using the Top Hat #4 across both periods do not exhibit this abrupt GOR change, indicating that the apparent GOR variability recorded by these surface vessels is attributable

to the collection process itself, not variability in the endmember GOR. Indeed, daily GOR values for fluids recovered from the Top Hat #4 reveal an inverse correlation with increasing oil collection rate (Fig. 2). Extrapolation of these trends to higher oil collection rates would yield decreased GOR values that are consistent with the MW-1 endmember GOR that was also collected from within Top Hat #4. Similar trends exist for fluids collected before and after the step change on the *Q4000*.

Using the federally estimated net liquid oil release of 4.1 million barrels to the Gulf of Mexico (19), the net total  $C_1$ - $C_5$  hydrocarbons released to the water column was  $1.7 \times 10^{11}$  g. Comparison of our calculations to other studies (Table S1) reveals differences that are primarily due to GOR values employed. For example, Valentine et al. (3) used a GOR of 3,000 that yields total methane, ethane, and propane releases that are higher than our values by a factor of two. By comparison, Joye et al. (20) found fluxes nearly four times greater than ours for their high-end estimate.

The composition of the MW-1 oil fraction contained 74% saturated hydrocarbons, 16% aromatic hydrocarbons, and 10% polar hydrocarbons (Table 1). Along with other results, these data are consistent with a moderately mature, light sweet crude oil, with no evidence of subseafloor biodegradation (Figs. S2 and S3, Table 1, and Table S2). The polar fraction (10%) is comprised of molecules containing oxygen, nitrogen, and sulfur spanning a wide molecular weight range. Many of these compounds are resistant to evaporation, biodegradation, and photolysis. Hence, they have the potential to remain in the environment long after other oil components have been removed or degraded (21, 22). Because many of these polar compounds are not typically analyzed in field samples, the resulting 0.41 million barrels of polar hydrocarbons released into the Gulf of Mexico may be overlooked in studies examining the fate of oil released during this spill.

In addition to bulk analyses, the gas and oil fractions were analyzed for select compounds (Table S2). We have used our results from the analysis and relative amounts of gas and oil fractions to calculate the total amount released and the composition of the "reconstituted" reservoir fluid on a mass/mass basis. This exercise indicates that the most abundant compound released from the Macondo well on a mass basis was methane at  $0.15 \text{ g g}^{-1}$  of reconstituted fluid. The total  $C_1$  to  $C_5$  hydrocarbons were  $0.24 \text{ g g}^{-1}$ , and the other 140 hydrocarbon compounds were  $0.24 \text{ g g}^{-1}$  of the total mass of reconstituted fluid. This indicates that traditional molecular-level methods to characterize oil can account for only half of the material that flowed from the Macondo well.

To constrain the fate of hydrocarbon components released to the deep sea, several convolved processes need to be considered. Petroleum emitted from the LMRP rapidly partitions into four phases in the deep water column: a gas phase, a liquid oil phase, an aqueous phase, and a hydrate phase. Once in the water column, these phases may physically segregate during buoyancy-

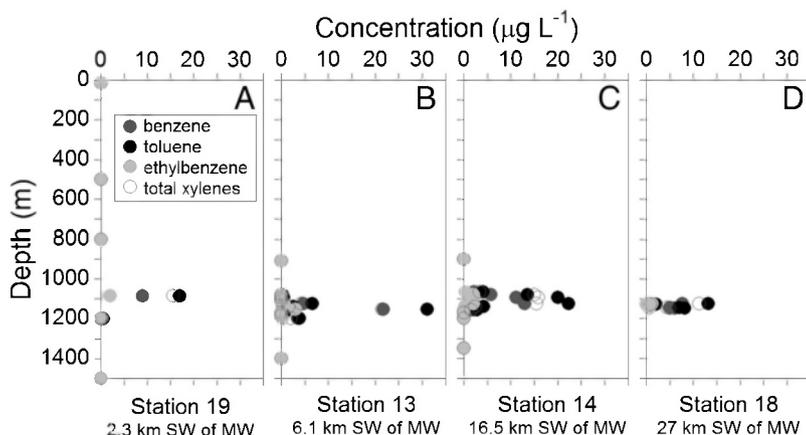


Fig. 3. Water column profiles of BTEX collected at (A) 2.3, (B) 6.1, (C) 16.5, and (D) 27 km from the Macondo well. These stations were within the region of the deep water plume identified by Camilli et al. (1) in June 2010 (See Table S4 for actual BTEX values in these water samples). BTEX composed 2.2% of the total oil in MW-1 (Table S2).

driven ascent of light liquid oil droplets and gas bubbles toward the sea surface and descent of heavier liquid oil droplets, enriched in dense components such as long-chain *n*-alkanes (23), toward the seafloor. Moreover, in near-field environments where separate oil, gas, and aqueous phases may coexist, partitioning of components between phases will evolve continuously due to depth-dependent changes in pressure and temperature. These processes were likely influenced by the seafloor injection of dispersants that may enhance aqueous dissolution and the stabilization of oil droplets. Current-driven advective transport of hydrocarbon-rich plumes provided an opportunity for continued aqueous dissolution and microbial degradation of bioavailable components.

Quantitative compositional data for gas and oil exiting the Macondo well provides an opportunity to examine chemical, physical, and biological processes affecting their abundance during transport through the water column. Here, we assess the role of aqueous dissolution as a possible driver for the previously reported formation of deep water hydrocarbon-enriched plumes of neutrally buoyant water at 1,100-m depth. The abundance of low molecular weight *n*-alkanes and aromatic compounds observed in the hydrocarbon-rich plume at 1,100 m are far below their aqueous saturation values at ambient conditions, suggesting that gas and oil droplets did not reach complete equilibrium with the aqueous phase, and partitioning into the deep water column is a kinetically controlled process. However, the rates at which hydrocarbon compounds dissolve from gas bubbles and oil droplets are likely influenced by their aqueous solubilities (11). To investigate the relationship between aqueous solubility and abundance in the 1,100-m plume, we evaluated the fractionation of hydrocarbon components into the deep water column relative to two highly water-soluble oil components: methane and benzene.

Abundant evidence suggests that methane released at the seafloor was quantitatively trapped at 1,100-m depth. Aqueous methane was the most abundant hydrocarbon component in deep water plumes, reaching values as high as 183  $\mu\text{mol kg}^{-1}$  in a mid-June 2010 survey within an approximately 10-km radius of the well (3). Methane was nearly absent at more shallow depths, suggesting that methane bubbles have dissolved completely upon reaching 1,100-m depth (1, 3). This is further confirmed by observed methane concentrations at natural background levels in the atmosphere overlying the sea-surface oil slick (24) and measured sea-to-air fluxes indicating that approximately 0.01% of the methane released from the reservoir was released into the atmosphere (25). The observed near-complete dissolution of methane in deep waters is consistent with previous field and modeling studies in systems of similar water column depth (26, 27).

Assuming that all of the released methane resides in deep water plumes, quantities of ethane and propane retained can be estimated by examining their abundance relative to that of methane. For this purpose, we define the fractionation index for a given compound as

$$F_{i, \text{methane}} = \frac{\left( \frac{C_{i, \text{water column}}}{C_{\text{methane, water column}}} \right)}{\left( \frac{C_{i, \text{MW-1}}}{C_{\text{methane, MW-1}}} \right)} \quad [1]$$

where  $F_{i, \text{methane}}$  is the fractionation index for species *i*,  $C_{i, \text{water column}}$  is the observed molal concentration of component *i* in the water column,  $C_{\text{methane, water column}}$  is the molal concentration of methane in the water column,  $C_{i, \text{MW-1}}$  is the molal concentration of component *i* in the original oil (MW-1 sample), and  $C_{\text{methane, MW-1}}$  is the molal concentration of methane in the MW-1 sample. The resulting index is an indicator of the chemical fractionation of component *i* in the deep water column relative to methane. A value of  $F_{i, \text{methane}}$  equal to unity corresponds to material that is channeled completely into deep water plumes to the same extent as methane. An  $F_{i, \text{methane}}$  value of zero corre-

sponds to material that is completely retained within the ascending oil and likely reaches the sea surface.

The compositional evolution of methane, ethane, and propane at 1,100 m suggests that phase partitioning processes influenced these low molecular weight hydrocarbons differently. Valentine et al. (3) used the spatial variations in the isotopic and chemical compositions of  $C_1$ - $C_3$  hydrocarbons in plume water samples to demonstrate the preferential microbial degradation of propane in the plume. The isotopic compositions for  $C_1$ - $C_3$  hydrocarbons in our sample MW-1 collected at the LMRP is nearly identical to the near-field plume values of Valentine et al. (3) (Table 1), consistent with an absence of biodegradation in the region of the plume nearest the Macondo well. However, the relative distributions of methane, ethane, and propane for these nonbiodegraded plume samples show small but noteworthy differences relative to the MW-1 sample. For example, the molal methane/ethane ratio of 10.85 consistently observed in nonbiodegraded plume samples (3) is slightly higher than the value of 9.9 observed in the pristine petroleum. These concentration ratios produce an  $F_{\text{ethane, methane}}$  value of 0.91, indicating that most of the ethane emitted from the Macondo well was retained in the deep sea, but to a slightly lesser extent than methane. Similarly, the  $F_{\text{propane, methane}}$  value of 0.78 for nonbiodegraded samples indicates that most of the propane released from the Macondo well resided in the subsurface, but to a lesser extent than ethane and methane. These results imply that a sizeable portion of ethane (9%) and propane (22%) was retained in the buoyant liquid oil phase that continued ascent to the sea surface. The rapid dissolution of methane, ethane, and propane is consistent with their high aqueous solubilities (Table S3) at ambient conditions in the deep water column (100–150 bar and 4–6 °C). Because the aqueous solubility of short-chain *n*-alkanes decreases with increasing chain length, the observed trend suggests that aqueous dissolution governed the fractionation of these gases into the deep water column.

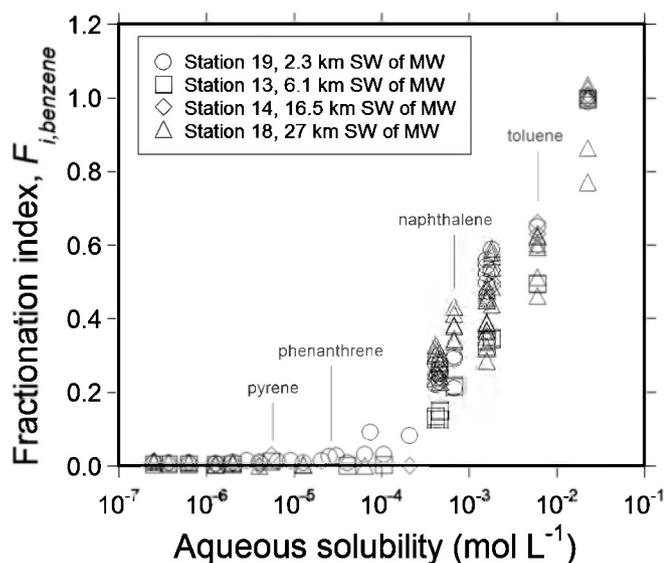
Joye et al. (20) measured  $C_1$  to  $C_5$  gases at 1,100 m depth from 2 to 11 km southwest and west of the Macondo well from May 25 to June 6, 2010, and did not observe the inverse correlation of methane/ethane and methane/propane ratios with total hydrocarbon abundance documented by Valentine et al. (3). They observed methane/ethane and methane/propane ratios of 9.9 and 14.7, respectively, values that are remarkably similar to the MW-1 sample (Table 1). An explanation for the differences in the data of Valentine et al. (3) and Joye et al. (20) remains elusive but may be related to numerous activities at the well in late May and early June that likely affected the flow and partitioning of released gases. For example, the riser insertion tube was removed on May 25, the “top kill” began on May 26 and ended on May 29, the initial shearing of the riser pipe occurred on June 1 and was followed by a second shearing on June 2, and installation of the Top Hat #4 collection device occurred on June 3 (28). It should be noted that all of the Valentine et al. (3) samples were collected after these events.

Looking beyond hydrocarbon gases, we investigated the fractionation of higher molecular weight petroleum components into the deep water column by comparing their abundances to benzene. Benzene is highly water-soluble, suggesting that it too may have dissolved rapidly in the deep sea. Indeed, benzene concentrations were systematically elevated (0.4–21.7  $\mu\text{g L}^{-1}$ ) in the 1,100-m-depth plume and nearly absent at depths shallower than 1,000 m (1) (Fig. 3, and Table S4). A comprehensive survey of hydrocarbons in air above the Macondo well site revealed that very little benzene reached the sea surface (24). Taken together, water column and surface measurements suggest that benzene was predominantly retained in the deep water column. Replacing  $C_{\text{methane, water column}}$  and  $C_{\text{methane, MW-1}}$  in Eq. 1 with the concentrations of benzene in the water ( $C_{\text{benzene, water column}}$ ) and original oil ( $C_{\text{benzene, MW-1}}$ ), respectively, we calculated

benzene-normalized fractionation indices ( $F_{i,\text{benzene}}$ ) for less water-soluble hydrocarbons.

Using the benzene-normalized fractionation index,  $F_{i,\text{benzene}}$ , we tested the hypothesis that aqueous partitioning controlled the preferential retention of non-gas petroleum components. We examined the relationship between observed  $F_{i,\text{benzene}}$  values and compound aqueous solubilities ( $S_i^{\text{ad}}$ ) for a set of 33 detected oil components, including monoaromatic alkylated hydrocarbons, naphthalenes, dibenzothiophenes, and several other alkylated and unsubstituted PAHs (Table S3). (Assuming ideal Raoultian behavior, the aqueous solubility of a given compound in the MW-1 oil is equal to the aqueous solubility of the pure liquid multiplied by the mole fraction in the oil. For compounds that are solids at ambient conditions, aqueous solubility refers to the subcooled liquid aqueous solubility; see *SI Text*.) Across this compound set, we found that the fractionation index decreased systematically with decreasing aqueous solubility (Table S3). This trend is readily apparent in the representative stations shown in Fig. 4. Similar trends were observed at 20 sampling locations (positions of unique latitude, longitude, and depth) where hydrocarbons were detectable, at distances ranging from 1.7 to 34.6 km from the Macondo well and at water depths ranging from 1,065 to 1,221 m (Fig. S4). With a single exception, *n*-alkanes were not found at detectable concentrations at sampling locations where benzene was present. Uniquely, the 1,201-m depth sample at station 19 contained significant levels of *n*-alkanes and other sparingly soluble compounds but was depleted in water-soluble compounds such as BTEX (Fig. S5). This exceptional sample is consistent with the capture of liquid oil droplets that had been partially dissolved into the ambient water, thereby exhibiting enrichment in sparingly soluble components relative to water-soluble components.

Collectively, the observed relative abundances of  $C_1$ - $C_3$  hydrocarbons and longer-chain petroleum constituents provide compelling evidence that the 1,100-m plume identified by Camilli et al. (1) is comprised of dissolved hydrocarbons. In turn, the results provide strong evidence that advective transport in



**Fig. 4.** Fractionation index ( $F_{i,\text{benzene}}$ ) as a function of aqueous solubility for 33 different hydrocarbon compounds observed in the southwesterly hydrocarbon plume observed by Camilli et al. (1) at four different stations ranging from 2.3 to 27 km distance from the Macondo well (same stations as shown in Fig. 3). A fractionation index value of 1 corresponds to material that has completely departed the ascending oil, relative to benzene, and contributes to the plume. A low fractionation index corresponds to material that is predominantly retained within the ascending oil. For compounds that are solids at ambient conditions, aqueous solubility refers to the subcooled liquid aqueous solubility; see *SI Text* for a more complete discussion of this term.

solution is the principal means by which hydrocarbons are transferred from the well to the deep sea. Evidence for the presence of oil droplets was only observed in one sample. Selective partitioning of water-soluble petroleum components into the deep sea is also consistent with the results of Ryerson et al. (24), who documented a positive correlation between the aqueous solubilities of several hydrocarbon components and their extents of depletion in atmospheric samples collected above the oil spill. These authors suggested that the depleted compounds were likely retained within the water column. The rapid dissolution of highly soluble oil components in the deep water is also consistent with the reported near-quantitative sequestration of the highly water-soluble dispersant component dioctyl sodium sulfosuccinate at 1,100-m depth (29).

The ultimate fate of these water-soluble petroleum hydrocarbons in the deep water plume is unknown, although biodegradation may have been an important process. However, the absolute and relative abundances of BTEX compounds show no systematic spatial trends (Figs. 3 and 4), suggesting that negligible dilution or biodegradation occurred during the 4 d required for their transport in the plume over a distance of 27 km (1). This is consistent with previously reported estimates of respiration rates that indicate hydrocarbon degradation in the plume was unlikely to be in excess of  $7 \mu\text{g L}^{-1} \text{d}^{-1}$ , including degradation of hydrocarbon gases and petroleum (1). Because Valentine et al. (3) suggested that the microbial respiration of hydrocarbon gases outpaced petroleum respiration by at least a factor of two, the degradation rate for petroleum hydrocarbons may have been on the order of  $2 \mu\text{g L}^{-1} \text{d}^{-1}$ . This degradation rate, in conjunction with the hydrocarbon concentrations reported here, yields a half-life on the order of 1 mo for petroleum hydrocarbons. By contrast, Hazen et al. (2) reported half-lives for *n*-alkanes on the order of a few days. The absence of observable gradients in the concentrations of BTEX compounds within this plume along with the preceding half-life calculation indicates that water-soluble petroleum hydrocarbons persisted longer than the gas and *n*-alkane fractions.

## Conclusion

The endmember sample of gas and oil that flowed from the Macondo well was collected with an IGT sampler and analyzed. The material had a GOR of 1,600 standard cubic feet per petroleum barrel. Using the federally estimated net liquid oil release of 4.1 million barrels (19), the total  $C_1$ - $C_5$  hydrocarbons released to the water column was  $1.7 \times 10^{11}$  g.

The deep sea entrainment of water-soluble hydrocarbons has far-reaching implications for deep water oil spills. Our results demonstrate that most of the  $C_1$ - $C_3$  hydrocarbons and a significant fraction of water-soluble aromatic compounds were retained in the deep water column, whereas relatively insoluble petroleum components were predominantly transported to the sea surface or deposited on the seafloor, although the relative proportions are not known.

The resulting apportionments of hydrocarbon transfers to the water column and atmosphere are therefore very different for a deep water oil spill versus a sea-surface oil spill. During sea-surface oil spills, highly water-soluble components such as BTEX,  $C_3$ -benzenes, and naphthalene quickly volatilize and are rapidly lost to the atmosphere within hours to days, thereby limiting the extent of aqueous dissolution into the water column. In the case of the *Deepwater Horizon* oil spill, however, gas and oil experienced a significant residence time in the water column with no opportunity for the release of volatile species to the atmosphere. Hence, water-soluble petroleum compounds dissolved into the water column to a much greater extent than is typically observed for surface spills.

## Materials and Methods

**Collection of Samples with IGTs.** Samples MW-1 and MW-2 were collected from the Macondo well on June 21, 2010, using IGT samplers (12) deployed

from the *Millennium 42* ROV operating from the vessel *Ocean Intervention III*. Following retrieval of the samplers on board the ship, the IGTs were delivered to Woods Hole Oceanographic Institution (WHOI) for sample processing. Each sampler was vented into a closed system that allowed for separation and quantitative measurement of the total amount of gas, oil, and seawater (Fig. S1). The gas and oil contents were used to calculate a GOR.

**Gas and Aqueous Phase Analysis.** The composition of gases and stable carbon isotope values ( $\delta^{13}\text{C}$ ) in MW-1 and MW-2 were performed by Isotech Laboratories. Composition analysis was performed chromatographically and also used to isolate gases for isotope analysis employing combustion to  $\text{CO}_2$  and dual-inlet analysis isotope ratio mass spectrometry. The stable hydrogen isotope values ( $\delta\text{D}$ ) of gases were measured at WHOI by cryofocusing (30) prior to analysis by pyrolysis gas chromatography isotope ratio mass spectrometry. Uncertainties for the compositional analyses are  $\pm 2\%$  and  $\pm 0.1\%$  and  $\pm 2\%$ , for the carbon and hydrogen isotopic analyses, respectively. The anion content of the aqueous phases of MW-1 and MW-2 were measured by ion chromatography.

**Oil Analysis.** The oil samples were analyzed by numerous techniques both at WHOI and outside laboratories. Characterization was considered for three categories: bulk, compound class, and molecular-level. Bulk analyses included density; American Petroleum Institute (API) gravity; and percentage of saturated hydrocarbons, aromatic hydrocarbons and polar hydrocarbons. Compound class analysis was performed by gas chromatography (GC) and comprehensive two-dimensional gas chromatography (GCxGC) with flame ionization detection (FID) and mass spectrometry (MS). Molecular-level quantitation of individual compounds as well as carbon and hydrogen isotope measurements and biomarker analysis (by GCxGC-FID) were also performed. See *SI Text* for a complete discussion of these analyses.

**Gulf of Mexico Water Sampling and Analysis.** Approximately 100 water samples were collected in collaboration with the ongoing Natural Resource Damage Assessment program aboard the research vessel (R/V) *Endeavor* (cruise 478) (13). Water samples from 15- to 1,500-m water depths were analyzed for approximately 100 volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). Samples were collected using a rosette of 12 10-L Go-Flo bottles (1) and transferred to 40- and 900-mL amber glass bottles with Teflon-lined caps, for VOC and SVOC analysis, respectively.

Selection of sampling locations and water depths was guided by in situ sensors, including the *TETHYS* mass spectrometer and AquaTracka fluorometers mounted on the rosette, and surveys from the autonomous operated underwater vehicle *Sentry* (1).

VOCs were analyzed using US Environmental Protection Agency (EPA) SW-846 Method 8260B, modified. SVOCs were measured following the guidance procedures in EPA SW-846 Method 8270C, modified, and 8015. The complete analysis for water samples, in duplicate, for VOC and SVOC provided approximately 17,000 results. We only used data that was above the laboratory blank and detection limit as well as chromatographically resolved and identified for each specific compound or compound class. The end result was approximately 1,000 usable datapoints.

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