Chemical data quantify *Deepwater Horizon* hydrocarbon flow rate and environmental distribution

Thomas B. Ryerson[a,1], Richard Camilli[b], John D. Kessler[c], Elizabeth B. Kujawinski[d], Christopher M. Reddy[d], David L. Valentine[e], Elliot Atlas[f], Donald R. Blake[g], Joost de Gouw[a,h], Simone Meinardi[g], David D. Parrish[a], Jeff Peischl[a,h], Jeffrey S. Seewald[d], and Carsten Warneke[a,h]

[a]Chemical Sciences Division, National Oceanic and Atmospheric Administration Earth System Research Laboratory, Boulder, CO 80305; [b]Applied Ocean Physics and Engineering Department and [d]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543; [c]Department of Oceanography, Texas A&M University, College Station, TX 77843; [e]Department of Earth Science and Marine Science Institute, University of California, Santa Barbara, CA 93106; [f]Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149; [g]Department of Chemistry, University of California, Irvine, CA 92697; and [h]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

Edited by Philip Gschwend, Massachusetts Institute of Technology, Cambridge, MA, and accepted by the Editorial Board November 29, 2011 (received for review June 30, 2011)

Detailed airborne, surface, and subsurface chemical measurements, primarily obtained in May and June 2010, are used to quantify initial hydrocarbon compositions along different transport pathways (i.e., in deep subsurface plumes, in the initial surface slick, and in the atmosphere) during the *Deepwater Horizon* oil spill. Atmospheric measurements are consistent with a limited area of surfacing oil, with implications for leaked hydrocarbon mass transport and oil drop size distributions. The chemical data further suggest relatively little variation in leaking hydrocarbon composition over time. Although readily soluble hydrocarbons made up ~25% of the leaking mixture by mass, subsurface chemical data show these compounds made up ~69% of the deep plume mass; only ~31% of the deep plume mass was initially transported in the form of trapped oil droplets. Mass flows along individual transport pathways are also derived from atmospheric and subsurface chemical data. Subsurface hydrocarbon composition, dissolved oxygen, and dispersant data are used to assess release of hydrocarbons from the leaking well. We use the chemical measurements to estimate that $(7.8 \pm 1.9) \times 10^6$ kg of hydrocarbons leaked on June 10, 2010, directly accounting for roughly three-quarters of the total leaked mass on that day. The average environmental release rate of $(10.1 \pm 2.0) \times 10^6$ kg/d derived using atmospheric and subsurface chemical data agrees within uncertainties with the official average leak rate of $(10.2 \pm 1.0) \times 10^6$ kg/d derived using physical and optical methods.

Gulf of Mexico | deepwater blowout | marine hydrocarbon partitioning | oil spill flow rate

Knowledge of the composition, distribution, and total mass of the hydrocarbon mixture (gas plus oil) emitted following loss of the *Deepwater Horizon* (*DWH*) drilling unit is essential to plan mitigation approaches and to assess environmental impacts of the resulting spill. Estimates of *DWH* hydrocarbon flow rate were originally derived using physical and optical methods applied during the spill; values were subsequently refined, and an official government estimate of oil flow rate was published (1). Analysis of airborne atmospheric chemical data provided information on hydrocarbon evaporation into the air and a lower limit to the flow rate (2); however, a more detailed description of environmental distribution has not been available. Here, we present combined atmospheric, surface, and subsurface chemical data to constrain physical transport pathways, and the resulting composition and mass flow rate of *DWH* hydrocarbon mixtures along each pathway, following subsurface release from the leaking well in early to mid-June 2010.

Our analysis primarily focuses on the period following installation of Top Hat no. 4 on June 3 (3), which includes flights by a chemically instrumented P-3 aircraft (2, 4) and remotely operated vehicle (ROV) sampling of leaking fluid at the well (5), and ends roughly in late June at the conclusion of the R/V *Endeavor* cruise (Fig. S1). The suite of deployed subsurface, surface, and airborne measurements offers spatial, temporal, and chemical detail that is unique to this period and to this spill. We use atmospheric, surface, and subsurface measurements of hydrocarbons, dissolved oxygen, and dispersant from throughout this period, as well as considering additional chemical data following closure of the well, to define the initial compositions, distributions, and mass flow rates of the hydrocarbon mixtures evolving along different pathways following release into the marine environment.

Results

1. Composition Data Constrain Physical Transport Pathways. *DWH* hydrocarbons were released at a depth of ~1,500 m in a high-pressure jet, resulting in gas bubbles and liquid oil droplets with an initial number and volume distribution that is not yet well quantified (1). Size and chemical composition of the hydrocarbon bubbles and droplets evolved extremely rapidly following release from the well (6). A complex interplay of physical processes determined hydrocarbon-water plume mixing dynamics (7, 8) and affected the composition and 3D distribution of the hydrocarbon mixtures within the water column, at the surface in the resulting oil slick, and in the overlying atmosphere (2).

Prediction of mass fluxes along environmental transport pathways following a deepwater blowout requires accurate understanding of time-dependent dynamical behavior and evolving chemical composition along various transport pathways, on time scales of seconds to weeks following release. Three observed features of the *DWH* spill offer key insights into marine transport pathways:

a) Short surfacing time constrains oil droplet size. Visual observations from response vessels suggested a ~3-h lag

Author contributions: T.B.R., R.C., J.D.K., E.B.K., C.M.R., and D.L.V. designed research; T.B.R., R.C., J.D.K., E.B.K., C.M.R., D.L.V., E.A., D.R.B., J.d.G., S.M., D.D.P., J.P., J.S.S., and C.W. performed research; T.B.R., R.C., J.D.K., E.B.K., C.M.R., D.L.V., E.A., D.R.B., J.d.G., S.M., D.D.P., J.P., J.S.S., and C.W. analyzed data; and T.B.R., R.C., J.D.K., E.B.K., C.M.R., and D.L.V. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission. P.G. is a guest editor invited by the Editorial Board.

[1]To whom correspondence should be addressed. E-mail: thomas.b.ryerson@noaa.gov.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1110564109/-/DCSupplemental.