

Air quality implications of the *Deepwater Horizon* oil spill

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During the *Deepwater Horizon* (*DWH*) oil spill, a wide range of gas and aerosol species were measured from an aircraft around, downwind, and away from the *DWH* site. Additional hydrocarbon measurements were made from ships in the vicinity. Aerosol particles of respirable sizes were a significant air quality issue for populated areas along the Gulf Coast. Yields of organic aerosol particles and emission factors for other atmospheric pollutants were derived for the sources from the spill, recovery, and cleanup efforts. Evaporation and subsequent secondary chemistry produced organic particulate matter with a mass yield of $8 \pm 4\%$ of the oil mixture reaching the water surface. Approximately 4% by mass of oil burned on the surface was emitted as soot particles. These yields can be used to estimate the effects on air quality for similar events as well as for this spill at other times without these data. Whereas emission of soot from burning surface oil was large during the episodic burns, the mass flux of secondary organic aerosol to the atmosphere was substantially larger overall. We use a regional air quality model to show that some observed enhancements in organic aerosol concentration along the Gulf Coast were likely due to the *DWH* spill. In the presence of evaporating hydrocarbons from the oil, NO_x emissions from the recovery and cleanup operations produced ozone.

On April 20, 2010, an explosion and subsequent leak beneath the *Deepwater Horizon* (*DWH*) drilling platform led to the largest marine oil spill in United States history. The air quality issues arising from the oil spill are different for workers at the site than for the population along the coast. Primary emissions are of more concern near the site and secondary pollutants are more important downwind. The key atmospheric pollutants considered in this paper are hydrocarbons (HCs), particulate matter (PM) or aerosol particles, ozone, carbon monoxide, and nitrogen dioxide. Four sources of primary air pollutants attributable to the *DWH* oil spill are detected in our observations: (a) HCs evaporating from the oil; (b) smoke from deliberate burning of the oil slick; (c) combustion products from the flaring of recovered natural gas; and (d) ship emissions from the recovery and cleanup operations. Here, we examine these primary emissions and the subsequent production of ozone and secondary organic aerosol (SOA). Furthermore, we use aircraft data to derive the amount of atmospheric particulate matter formed per mass of oil that reached the surface. These results can be used to estimate implications for air quality during the *DWH* spill at other times and locations and can also provide information about effects on air quality by past or future spills.

Measurements

On June 8 and 10, 2010, the National Oceanic and Atmospheric Administration (NOAA) WP-3D aircraft carried an extensive suite of instruments that measured trace gases and aerosol spe-

cies (Table S1) near the *DWH* site. HCs were also measured from ships in the vicinity of *DWH*, including the NOAA *R/V Thomas Jefferson* that sailed close to the *DWH* site on June 22–27, 2010. Samples from the ship were taken from about 6–10 m above the water surface.

By June 8, a containment cap had been loosely installed on the wellhead and surface recovery vessels were able to capture a fraction of the leaking oil and natural gas. Oil on the sea surface was burned periodically (1, 2) on June 8. On both flights, the aircraft flew a rectangular pattern about 8 km from the *DWH* site and then flew transects perpendicular to the wind direction at progressively farther distances downwind (Fig. S1). The flights also surveyed the air about 40 km off the Gulf Coast and upwind of *DWH*. On both days there was a well-mixed marine boundary layer about 600 m deep (3). Most aircraft data were obtained at 200 m altitude with some at lower or higher altitudes to verify the characteristics of the boundary layer and air just above it.

Measured concentrations of atmospheric pollutants varied depending on the location of the aircraft or ship relative to the *DWH* site and the resulting surface oil, the residence time of oil on the surface, chemical reactions of pollutant species in the atmosphere, and meteorological conditions. The mixing ratios of several gaseous and aerosol species at various locations are summarized in Tables S2 and S3. Assuming a constant source of precursors and similar production rates, the factor of 2–3 difference in concentrations between the June 8 and 10 flights is roughly consistent with the variation in the dilution rate due to different wind speeds for the 2 d.

The aircraft transects that were farthest (approximately 47 km) downwind of *DWH* indicated a plume about 4 km wide (full width half maximum, FWHM) of volatile species such as light alkanes and aromatics that evaporated from the oil (Fig. 1 and Fig. S2). Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), emitted by flaring of recovered natural gas and ship operations close to the spill site, reacted to form nitric acid, peroxyacetyl nitrate (PAN), and other oxidation products that are included with NO_x in the total of reactive nitrogen, NO_y . The small signal of NO_x relative to NO_y in this transect indicates that most of the NO_x was converted to other

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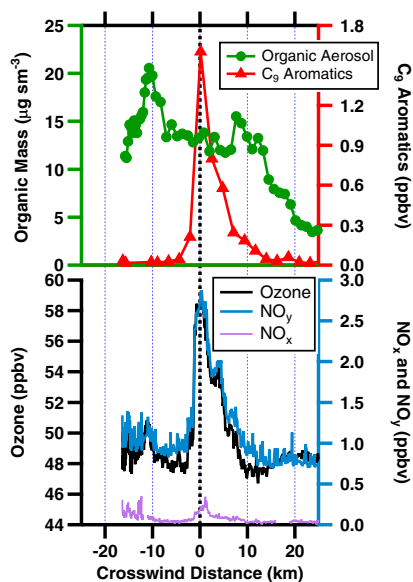


Fig. 1. Measured mixing ratios during the farthest downwind transect across the *DWH* pollution plume. Downwind distances from *DWH* were 47 ± 5 km except the most negative crosswind portion was 26 to 42 km downwind because of the path of the aircraft relative to the plume.

forms within the roughly 3 h since emission. These narrow plumes were embedded within a plume more than 30 km wide (FWHM) of organic aerosol particles.

Results and Discussion

HCs Evaporating from Oil That Surfaced. By mass, the largest air emissions from the spill consisted of HCs evaporating from oil. These HCs can affect air quality in three ways. First, some of the measured compounds, including benzene, toluene, and naphthalene, are classified as hazardous air pollutants (<http://www.epa.gov/ttn/atw/orig189.html>, <http://www.epa.gov/ttn/atw/pollutants/atwsmod.html>). Second, evaporating HCs, especially intermediate volatility organic compounds (IVOCs) with vapor pressures comparable to C_{14} - C_{16} alkanes, reacted in the atmosphere to produce lower volatility products that then form SOA (4). Third, the HCs reacted with NO_x and sunlight to form secondary pollutants such as ozone and PAN.

The chemical composition of the measured HCs downwind of the *DWH* site was dominated by alkanes with smaller contributions from aromatic species (about 9% by mass) (3). Gas phase polycyclic aromatic hydrocarbons (PAHs) other than naphthalene were not measured. Average mixing ratios for selected alkanes and aromatic HCs are shown in Fig. 2 for several locations: ship measurements close to the *DWH* site, aircraft transects about 10 km downwind, and polluted air in the Houston Ship Channel and relatively unpolluted air in the central Gulf of Mexico from a 2006 study (5).

The largest HC mixing ratios were obtained within 1 km of the *DWH* site from the ship (Fig. 2 and Table S3). The average total measured HC concentration in the air near the surface was 3.0 ppm of carbon after recovery began. These mixing ratios from the ship were especially large because the ship approached closer to the *DWH* site than the aircraft and because the samples were obtained close enough to the sea surface that the HCs were not fully diluted throughout the depth of the boundary layer. Near the *DWH* site, the mixing ratios of C_4 - C_{10} n-alkanes and the C_8 - C_9 aromatics were much higher than those typically found in heavily polluted areas such as the Houston Ship Channel

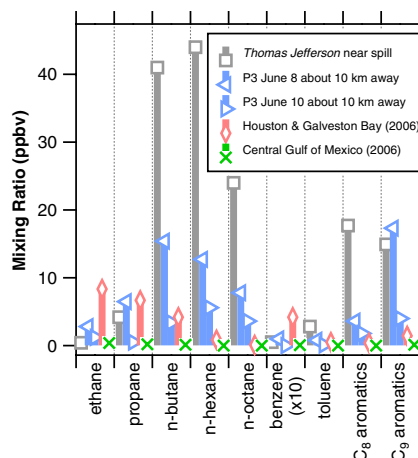


Fig. 2. Average selected hydrocarbon mixing ratios obtained from the NOAA ship *Thomas Jefferson* on June 22–27, 2010 within a 10 km radius of the *DWH* site and from the NOAA aircraft on June 8 and 10, 2010 at a distance 10 km downwind. Houston/Galveston Bay and unpolluted, central Gulf of Mexico data were obtained from another NOAA ship in 2006 (5).

(5). During the period of the spill, the flux of evaporating HCs from the spill (3) exceeded the average volatile organic carbon (VOC) emission inventory from the Houston-Galveston-Brazoria CMSA (<http://www.epa.gov/air/data/geosel.html>), although the mix of HCs was very different. The lighter alkanes and aromatics (notably benzene) were enhanced in the air to a lesser degree than would be expected from the leaking oil and gas composition because a large fraction of those species dissolved in the water column during transport of the oil to the surface (3). Although some concentrations of aromatics measured from the ship within 1 km of the *DWH* site were large, they were below the Occupational Safety and Health Administration (OSHA) standards for occupational exposure assuming they were constant with time. However, concentrations in other locations and wind conditions would be different and could have been higher in the vicinity of freshly surfaced oil. The health impacts due to HCs for the *DWH* spill workers have been studied by others (see <http://www.epa.gov/bpspill/vocs.html>).

The June 10 aircraft data show that the plume of C_9 aromatics was roughly 2 km wide (FWHM) at a distance of 9 km downwind from *DWH*. Such a narrow plume indicates that the C_9 aromatics and other volatile HCs evaporated from a relatively small area in the vicinity of the *DWH* site (3). The sum of the measured aromatics (toluene, C_8 - C_{11} aromatics, and naphthalene) was more than 20 parts per billion by volume (ppbv) in the air downwind of the spill region and was dominated by the C_8 and C_9 aromatics. Benzene was never measured at concentrations higher than 0.1 ppbv in the evaporating plume (up to 0.75 ppbv of benzene was found in the smoke from in situ burning). Concentrations of naphthalene were less than 0.5 ppbv. Peak mixing ratios of HCs decreased as the air moved farther downwind, primarily due to dilution in the mixed boundary layer. The plumes sampled by the farthest downwind transects were up to 3 h old, which is long enough for some of the more reactive species to have been partially removed by photochemical reactions.

Particulate Matter (PM) or Aerosol Particles. Two types of particles were formed either at the spill site or downwind: SOA from the evaporating HCs and soot from in situ burning of surface oil or from recovery operations.

The maximum measured increase in submicron particulate (almost exclusively organic) mass downwind of the spill was $20 \mu\text{g m}^{-3}$ on June 8 and $7 \mu\text{g m}^{-3}$ on June 10 (Fig. 3 and Table S2). For comparison, the June 8 increase is larger than the maximum submicron SOA mass concentration of $15 \mu\text{g m}^{-3}$

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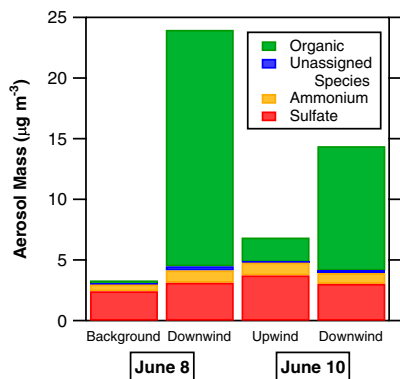


Fig. 3. Background or upwind and downwind (>40 km) aerosol mass concentrations for the two flight days. There was clear production of organic aerosol mass from the spill. Changes in the measured sulfate and ammonium were within the range of background variability.

observed in 2006 in the Houston area (7, 8), albeit these urban aerosols certainly had a different composition. The National Ambient Air Quality Standard (NAAQS) for particulate matter less than $2.5 \mu\text{m}$ in diameter is $15 \mu\text{g m}^{-3}$ for the annual average and $35 \mu\text{g m}^{-3}$ for the 24-h average (<http://www.epa.gov/air/criteria.html>).

Particles smaller than $1 \mu\text{m}$ in diameter accounted for most of the increased SOA mass downwind of the spill site. In addition, the measured mass distribution of particles indicated that small, fresh organic particles formed and existing particles grew by acquiring organic material (9). This demonstrates that the increase in organic mass was the result of condensation of less volatile products rather than wind-driven oily spray, which would produce mainly larger particles. Despite significant concentrations in the oil (potentially as much as 1.4% by mass) (10–12), mass spectra of the aerosol particles downwind of *DWH* indicate that PAHs (13) contributed less than 0.1% to the particulate mass (Fig. 4).

The aerosol plume was wider than the plume of directly emitted species (Fig. 1 and Fig. S2). The aerosol mass flux, calculated using standard methods (3) (also see *SI Text*), increased with distance downwind (Fig. 5). In contrast, the flux of volatile species evaporating from the spill was fairly constant downwind. Combining oil composition information with the measured HC and aerosol fluxes allows an estimate to be made of the overall yield of SOA formed. On June 10, $8 \pm 4\%$ of the surfacing oil was

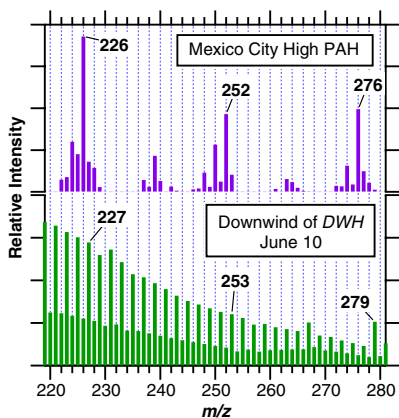


Fig. 4. High mass portions of aerosol mass spectra from Mexico City known to have large PAH contributions (13) (upper panel) and downwind of the *DWH* site on June 10 (lower panel). The *DWH* aerosols have distinct peaks at odd m/z and the peaks from individual PAHs (which would appear at m/z 226, 252, and 276, among others) are much smaller in intensity, indicating that PAHs did not contribute significantly to the aerosol mass.

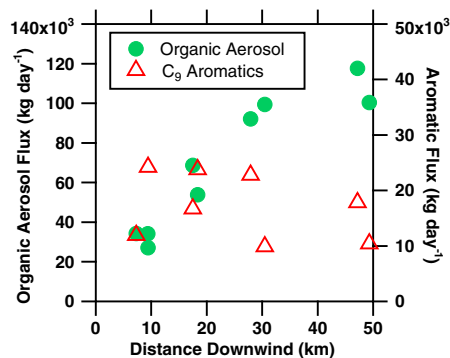


Fig. 5. Horizontal fluxes of organic aerosol mass and selected aromatic hydrocarbons (C_9 aromatics) as a function of distance downwind from the *DWH* spill site on June 10, 2010. The organic aerosol mass flux increases with distance, whereas the flux of C_9 aromatics is nearly constant, with scatter mostly due to integrating over a limited number of data points in each transect through the narrow plume.

converted to SOA within the first 3 h of downwind transport (see *SI Text* for calculation details).

A plume of smoke from in situ burning was sampled on June 8 from the aircraft. Aerosol composition measurements show that black carbon (BC) was the dominant aerosol constituent in this smoke (14). Using aerosol extinction data, approximately 4% of the carbon emitted into the air from the burn was soot. This corresponds to about 3.5% of the carbon in the surface oil that was ignited if 90% burned (Table S4, see *SI Text* for calculation details). A direct measurement of BC resulted in a $3.6 \pm 1.4\%$ yield relative to the amount of carbon burned (14). For the plume from flaring recovered gases, the emission factor of BC was about 0.04% g/kg fuel burned (Table S4).

Assuming the smoke plume we measured was representative of other surface oil burns and the SOA formation rate on June 10 was representative of other days during the spill, the soot emission factor and SOA yield were used to estimate the daily rates of aerosol mass either being emitted or produced in the air for the entire *DWH* spill event (Fig. 6). Overall, the cumulative amount of SOA formed from surface oil over the course of the spill was roughly a factor of 10 larger than the amount of soot emitted from the burns. Such mass comparisons should be interpreted with care because the particles had different sizes and composition and the soot particles from the in situ burns and flaring were lofted higher than the observed SOA plume (14).

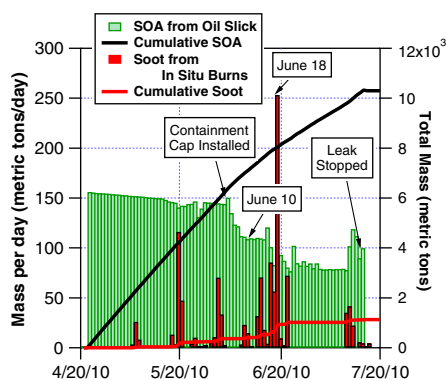


Fig. 6. Estimated SOA mass produced per day due to evaporation of the surface oil and daily emission rates of soot particles from *in situ* burns. The cumulative amounts of each aerosol source provide an estimate of the total aerosol mass into the atmosphere when the wellhead was leaking. A calculated decrease due to partial containment is seen around June 7. Note that there will be less SOA formed if fresh oil is skimmed or burned (see *SI* for details).

Ozone, Carbon Monoxide, and Nitrogen Oxides. Other criteria pollutants can be formed by combustion processes at the spill site. In addition, the airborne HCs and NO_x released near the spill contributed to photochemical formation of secondary pollutants—ozone and PAN (a lung and eye irritant often measured in urban photochemical smog). Thus, mitigation and cleanup efforts that produced NO_x likely increased ozone levels around the site.

Emission factors of various pollutants were determined from correlations observed by the fast time response instruments during passes through the plumes (Fig. S3 and *SI Text*). For the surface oil burning plume sampled on June 8, the emission ratio for carbon monoxide (CO) was 54 g CO per kg of surface oil ignited (Table S4), or 2.7% on a carbon mass basis relative to the amount of carbon in the oil ignited. Combined with the 3.5% emission ratio for soot, these emissions are characteristic of incomplete fuel combustion and are within the range of previous measurements on test and other in situ burns of crude oil on water (2, 12, 14, 15). The NO_x emission factor for this source was about 2.3 g (as NO₂) per kg of fuel ignited (Fig. S3 and Table S4), which is also consistent with other in situ burns (15).

Separate plumes from the flaring of captured gases and ships performing recovery and cleanup operations were measured in the aircraft transects immediately downwind of the *DWH* site on June 10. Farther downwind, the individual flaring and ship plumes mixed into one plume, as in Fig. 1. Median emission factors in these separate or overlapping plumes were about 11 g CO per kg fuel burned and 27 g NO_x (as NO₂) per kg of fuel burned. These values are within the expected range for flaring and ship emissions (16) (see also <http://www.epa.gov/ttnchie1/ap42/>). Enhancements of CO and BC particles in these plumes were characteristic of nearly complete combustion (3). Because the flare plume was lofted higher than the ship plumes, the emission factor for NO_x from this flare was determined separately from the ship plumes and was about 2 g (as NO₂) per kg of fuel burned, which is typical for flares (see <http://www.epa.gov/ttnchie1/ap42/>). The downwind enhancement of CO was less than 16 ppbv, which is small compared to concentrations observed in urban areas, and the enhancement of NO_y was less than 8 ppbv, which is comparable to urban areas (17).

Because the flaring, recovery, and cleanup operations producing NO_x were focused around the *DWH* site where the oil was surfacing, the largest ozone mixing ratios were found directly downwind of the site (Fig. 1 and Fig. S2). On June 10, the maximum ozone enhancement was about 10 ppbv (as in Fig. 1) and the maximum PAN enhancement was about 350 part per trillion by volume (pptv) (Table S2). On June 8, the maximum enhancements were about 30 ppbv for ozone and 750 pptv for PAN (Table S2). The maximum ozone mixing ratio, 83 ppbv on June 8, was comparable to maximum 8-h mixing ratios observed in US urban areas (17).

Downwind of the spill site, the total measured HC to NO_x ratio was greater than 100 atoms C per atom N, which is at least a factor of 5 larger than typical ratios in an urban environment (see <http://www.epa.gov/ttn/chief/emch/index.html>). Despite the proportion of relatively unreactive alkanes in the evaporating HCs (3), ozone production was NO_x limited (i.e., additional NO_x is needed to promote faster ozone formation). A linear correlation of ozone with NO_x oxidation products (calculated from NO_y-NO_x) showed that about six molecules of ozone were produced per molecule of NO_x oxidized, which indicates an ozone production efficiency similar to that found in urban areas in the southern United States (18). Additional ozone may have been produced when the evaporating HCs were transported near the coast where there were more NO_x sources.

Effect on Air Quality for the Gulf Coast. One of the concerns of the oil spill was its impact on air quality for the Gulf Coast, which was at times downwind of *DWH*. Because the SOA particles that

formed over the *DWH* oil spill were present in relatively large concentrations, were dispersed in a wide plume, and continued to increase in mass downwind, these particles potentially had a measurable effect on ambient levels of aerosol particles in coastal communities directly downwind of the spill. Volatile HC and ozone mixing ratios were also enhanced downwind of the oil spill, but they were confined to narrower plumes.

To simulate the fate of SOA from the *DWH* oil spill, the WRF-CHEM regional air quality model (19) was modified with a volatility basis set approach (20). Details of the model are described in the *SI Text*. The salient features of the model for the purposes of assessing the effect on air quality are that it creates a plume of SOA with a flux similar to the aircraft observations (Fig. S4) and then calculates transport and deposition.

The model is used with 4-km resolution to demonstrate the transport of SOA from the *DWH* spill toward the coast for June 10 when the wind direction was from the south (Fig. 7). A plume is formed downwind of *DWH* passing over the Mississippi coast. The model does not predict SOA formation in the areas that are not directly downwind of the spill site, in agreement with the aircraft measurements.

To determine the influence of large-scale meteorology on SOA from *DWH* over the United States, a 20-km resolution model was run for the month of June 2010. The results from this model were compared with hourly organic carbon (OC) measurements available along the Gulf coast from the Southeastern Aerosol Research and Characterization (SEARCH) network (21). The model-predicted OC at the Gulfport, MS site (Fig. 7, just north of the coastline) shows fairly good agreement with the observations (Fig. 8). Peaks in the observations generally correspond to times when the model predicts large *DWH* spill contributions, giving some confidence in the timing and levels of predicted OC. OC comparisons at the Oak Grove, MS site (80 km north of Gulfport, MS) exhibit similar agreement (Fig. S5 *Top*), with peak values in both measured and modeled OC from the *DWH* spill reduced by a factor of 2 compared to the Gulfport, MS site as expected from dilution and deposition when marine air moves inland.

The maximum continental area impacted by SOA from the *DWH* spill was also determined from the 20-km model. Fig. S5 *Lower* shows the simulated surface distribution of SOA during the early morning of June 12 in the southeast US region. This was the time with maximum SOA impact from *DWH* north of

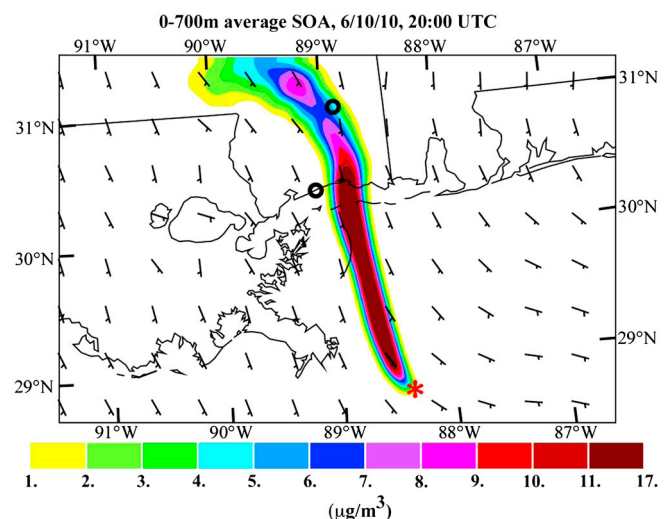


Fig. 7. Prediction at the surface of the average SOA contribution from the *DWH* oil spill for 20:00 UTC (3 pm local time), June 10, 2010. The red asterisk shows the *DWH* spill site location. The small black circles are the locations of the Gulfport (coastal MS) and Oak Grove (inland MS) SEARCH monitoring sites.

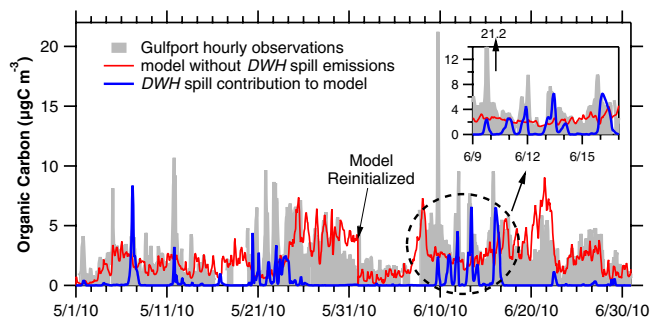


Fig. 8. Time series of observed particulate organic carbon at Gulfport, MS. Also shown are modeled concentrations without the *DWH* spill and from the spill. The effect of emissions from the spill on the measured organic carbon is apparent during periods with onshore winds from over the spill, as depicted in the inset and a few events in May.

30° latitude for the June simulation. Very little impact was seen north of 34° latitude. Vertical mixing within the planetary boundary layer diluted the plume during the daytime so there was no significant multiday accumulation over land.

Overall, the model-predicted short episodes at coastal sites with more than $10 \mu\text{gC m}^{-3}$ of OC in particles from the *DWH* spill. These aerosol enhancements were typically less than 24 h in duration and are generally consistent with the hourly coastal observations from the SEARCH network. The plume of SOA moved to various places along the coast depending upon the direction of onshore winds.

Implications for Other Oil Spills. Several factors affected the ultimate impact of the spilled oil on air quality in the surrounding region. In the case of the *DWH* spill, most of the lighter HCs (smaller than C_4 alkanes and C_6 - C_7 aromatics) released from the leak at about 1,500 m below the sea surface were dissolved in the water column before reaching the surface (3). As a result, the mixing ratios of the hazardous air pollutants (benzene, toluene, and to a lesser extent other aromatics in the air above the spill) were not as enhanced as would have been expected for a shallow-water or surface spill (22). The spill was also far enough offshore that there was some dispersion of the pollutants before they reached populated areas.

A reasonable first approximation for the formation of SOA from another spill would be to scale the observations from *DWH* by the size of the spill. There are at least five factors to consider in this simple approximation. First, the SOA formed mostly from IVOCs in the oil (4), and these will have different concentrations depending on oil composition. Second, the Gulf of Mexico in summer is a warm and sunny environment, conditions that favor evaporation, oxidation, and subsequent production of SOA. Also, the vertical dispersion of the pollutants would be very different over land or colder water. Third, the model indicates that the large flux of HCs from the *DWH* spill reduced the amount of hydroxyl radical (OH) in the center of the plume. Photochemical reactions would probably proceed more rapidly in a more dilute plume. Fourth, the ozone and SOA formation chemistry could be quite different in a more NO_x -rich environment such as close to urban areas. Finally, semivolatile organic compounds partition more readily into the aerosol phase when aerosol mass concentrations are higher (23). This effect could make aerosol formation nonlinear with the size of the spill.

Summary

The leaking oil and natural gas at the *DWH* spill site and the associated recovery and cleanup operations led to emissions of pollutants to the atmosphere. HCs evaporating from the oil slick were the largest source of primary air emissions. Once in the air, these HCs produced SOA and gaseous pollutants such as ozone and PAN. Large concentrations of PAHs were not found in the SOA. Significant ozone production was confined to the area downwind of both evaporating HCs from the spill and NO_x emissions from the cleanup and recovery operations. The emission factors for NO_x , CO, and soot or black carbon from in situ burning of surface oil, flaring, and ship emissions were similar to those previously reported.

Whether the oil evaporates or is burned in situ on the water surface, a small but significant percentage is converted into aerosol particles smaller than $1 \mu\text{m}$ in diameter. These particles can penetrate into the lungs with potential health effects (24). There are, however, key differences in these two sources of particulate matter from the oil spill. During the course of the spill, the total mass of SOA formed in the atmosphere was approximately an order of magnitude larger than the soot mass emitted from the burns. The soot particles from in situ burns were confined to narrow plumes so the absolute concentrations of particles from the burns were much higher. Furthermore, the heat associated with the in situ burning lofted some of the soot particles above the marine boundary layer where they could be transported farther than the SOA. In situ burns were also generally scheduled during offshore winds whereas SOA will form whether or not the wind is blowing towards populated areas.

Our results indicate that air quality is affected not only by direct emissions from the spill and related operations but also by the reaction products in the atmosphere such as ozone and SOA. In warm, sunny conditions, most of the HCs observed from the *DWH* spill have photochemical lifetimes of less than a few days before they react in the atmosphere. Thus, the potential for long-range transport of the HCs is limited. In contrast, aerosol particles typically survive for days in the lower atmosphere and it is likely that SOA from the *DWH* site impacted aerosol levels in populated areas near the Gulf Coast. Results from a regional transport model support this conclusion. Fortunately, the impact on air quality from the *DWH* spill was limited in scope. A spill of similar size closer to populated areas, closer to the surface, or in a region with larger NO_x sources could have a larger impact.

Materials and Methods

The data used for this work are publicly available (<http://www.esrl.noaa.gov/csd/tropchem/2010gulf/>). The methods and instruments used to measure the trace gases and aerosol air pollutants described in this paper are listed in Table S1. Additional calculations are given in the *SI Text*. Downwind distances relative to location of the *DWH* spill site (28.74°N , 88.37°W) were defined using aircraft observations of wind speed and direction. Crosswind distances were defined perpendicular to the prevailing wind as negative to the southwest and positive to the northeast of the plume centerline (Fig. S1).

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