

Air Chemistry in the Gulf of Mexico Oil Spill Area NOAA WP-3D Airborne Chemical Laboratory Flights of 8 and 10 June 2010

NOAA Point of Contact:

1. Dr. A. R. Ravishankara, NOAA, ESRL/Chemical Sciences Division,
A.R.Ravishankara@noaa.gov; 303 497 5821
2. Jana Goldman, NOAA Office of Oceanic and Atmospheric Research,
Jana.Goldman@noaa.gov; 301 734 1123

As a part of a multi-agency response to the Deepwater Horizon (DWH) spill, NOAA conducted two aircraft flights to characterize the resulting air pollution in the Gulf of Mexico. During May, one of NOAA WP-3D aircraft, equipped with an extensive suite of in-situ chemical sensors (Appendix 1), was deployed in California as part of a long-planned, large, multi-agency field study of climate change and air quality issues. To conduct flights over the oil spill the aircraft was temporarily deployed to MacDill Air Force Base in Tampa, Florida from where it was flown within and above the marine boundary layer (MBL) over the Gulf of Mexico on 8 and 10 June 2010. The flights targeted the area in the vicinity of and downwind of the DWH spill site. This work supports NOAA's air quality modeling associated with the BP oil spill, and complements on-going air monitoring on ships in the vicinity of the oil spill as well as EPA's ASPECT air quality surveillance airplane mission. Evaluation of the data from the NOAA flights assists the multi-agency response by providing a detailed and independent set of air quality data, using highly sensitive and selective research-grade instruments, for informing consideration of air quality risks for workers at sea and the public ashore.

Context

Measured concentrations of atmospheric pollutants varied depending on the location of the aircraft relative to the oil spill, the rate at which crude oil was being transported to the surface from the well, the residence time of oil on surface, the "aging" of pollutant species in the atmosphere, and meteorological conditions. The reported data have been subjected to level 1 QA/QC (Appendix 2). All the chemical species whose concentrations were measured, and the ancillary data are available on the web at <http://www.esrl.noaa.gov/csd/tropchem/2010gulf/>. The emphasis of this report is on air pollutants believed to have the greatest potential to contribute to health impacts, including a wide suite of organic compounds, and precursors of ozone and particulate matter (PM).

To place the concentrations measured over the Gulf in context, they are qualitatively compared to maximum concentrations measured during a recent flight using the same aircraft and the same complement of instruments over the Los Angeles urban area, as well as compared to other reports of concentrations measured in U.S. urban areas.

Synthesis and Summary

The major findings from the 8 and 10 June WP-3D flights are:

1. Near the DWH site the MBL, the lower layer of the atmosphere (from the surface of the Gulf to ~ 2000 ft), which effectively traps most of the air pollution emitted from the surface, was polluted with organics from the spill and the products of their atmospheric chemical processing.

- (a) The sum of the measured aromatics (benzene, toluene and C₈-C₁₁ aromatics) in this region was below 20 ppbv but well above maximum concentrations measured recently over the Los Angeles urban area. The measured values are listed in Tables 1 and 2.
 - (b) The highest concentrations of particulate matter (PM) were about 25 µg m⁻³. The PM was composed primarily (~80%) of organics. These concentrations of organic PM are comparable to a day with very high concentrations in a major U.S. city (e.g., see Zhang et al., 2007). The limited composition information that is available suggests that the makeup of these aerosols differs from common urban aerosols, as might be expected considering the unique nature of the source of hydrocarbons.
 - (c) The highest concentrations of ozone were 70-80 ppbv, which are comparable to average maximum concentrations observed in U.S. urban areas (see <http://www.epa.gov/airtrends/ozone.html>)
 - (d) The MBL was fairly well mixed vertically and, except for smoke plumes, the air above the MBL was clean and unaffected by emissions from the DWH spill.
2. The greatest concentration of gaseous hydrocarbons (alkanes and aromatics) was observed in a relatively narrow plume (<20 km wide) that emanated from a relatively small area around the DWH site and was transported away from the site by the prevailing winds. Concentrations of gaseous hydrocarbons in this narrow plume diminished as the plume was transported downwind, presumably due to dilution. A plume comprised primarily of organic aerosol was also observed downwind of the DWH spill site. However, this organic aerosol plume was much broader than the gaseous hydrocarbon plume described above and the aerosol concentrations were observed to grow over the entire broad width of the plume as it was transported downwind.
 3. On both 8 and 10 June, measurements in coastal areas that were not directly downwind from the DWH site were relatively unaffected by the pollution seen closer to the site. However, on 10 June, the largest PM and oxygenated volatile organic carbon (VOC) products were observed close to the southern tip of Louisiana, which was directly downwind of the DWH site. On 8 June the pollution plume was transported toward the central Gulf. PM measurements along the Gulf coast will enable an assessment of possible coastal impacts of the transported plume when wind conditions transport pollution from the spill site toward the shore.

Discussion

To present a representative statistical summary of the measurements, for each flight we defined three boxes enclosing flight track segments (Figs. 1 and 3) labeled as “Near shore” (relevant for potential public exposure), “DWH Spill Region” (relevant for potential exposure to workers at and around the DWH site), and “Downwind DWH Plume” (relevant for exposure to workers in the clean-up operations and other environments). For the 8 June flight we defined a fourth box indicative of relatively clean “Background Gulf air” (which may represent the concentrations expected in the absence of the DWH oil spill influences.) Tables 1 and 2 give the statistics for all the measurements made below 900 m altitude in each box. These data are representative of the MBL. The following paragraphs summarize some notable features of the data.

Hydrocarbons and other organic species. Directly downwind from the DWH site, concentrations of all aromatic hydrocarbons were enhanced (Figs. 2a and 4a present one example class of compounds). For benzene and toluene, the enhancements were up to a factor of 2 higher than the maximum concentrations observed on the flight over Los Angeles. However, the heavier aromatic compounds (C-8 through C-11 aromatics) had much higher concentrations (up to a factor of 10 or more) than those observed on that flight. On 8 June concentrations were about a factor of 2 higher, as wind speeds were lower, than on 10 June; the lower wind speed allows for a larger build up given the same evaporation rate from the spill site. The analysis of the whole air samples collected in canisters during the 8 June flight confirms the high concentrations of aromatic hydrocarbons measured by the Proton Transfer Reaction Mass Spectrometer (PTRMS) and also shows large concentrations of other hydrocarbons (primarily alkanes) known to be present in crude oil from this site. Figure 5 compares the composition of the hydrocarbons measured in the atmosphere (canister samples collected during the June 8 flight) with that reported for the leaking oil. There are marked similarities between the composition of the oil and the atmospheric species, although the lightest species were relatively depleted in the atmosphere. Measured gas-phase hydrocarbons were not enhanced over all areas with oil on the surface; they apparently are emitted from a relatively small area confined near the DWH spill site.

Farther downwind from the DWH spill site, oxygenated VOCs including acetaldehyde were produced by photochemical reactions of the emitted hydrocarbons in the atmosphere. There were also indications of the atmospheric loss of aromatic hydrocarbons. Concentrations of oxygenated VOCs were moderate and generally lower than what has been observed in urban areas (e.g. Jobson et al., 2004).

Near the coast of Alabama, oxygenated VOCs were somewhat enhanced in comparison with background conditions (see acetaldehyde in Tables 1 and 2), but their concentrations were much less than what has been observed in flights over urban areas. Concentrations of aromatic VOCs were close to our detection limit of ~35 pptv for the PTRMS instrument, in particular for the heavier species. This is consistent with the higher reactivities of these compounds, the influence of dilution, and meteorological factors that influence air pollution transport in the region.

On 8 June the background Gulf air south of Louisiana was relatively clean with all species close to their seasonal background concentrations.

Particulate Matter. On June 8 the concentrations of PM (microscopic particles suspended in air, also called aerosols) directly over the oil slick were comparable to those observed in U.S. urban air (e.g., Zhang et al., 2007). The percentage due to organics was higher than is typical for the eastern U.S. On 10 June wind speeds were higher and concentrations were correspondingly lower.

On both days aerosol concentrations increased significantly downwind of the DWH site (see Fig. 2b). The additional particle mass was composed almost entirely (~80%) of organics. On 8 June, the maximum mass concentrations were comparable to a day with very high concentrations in a major U.S. city (Zhang et al., 2007). These aerosols are probably produced from gas-phase hydrocarbons that are evaporating from the oil on the surface and subsequently converted into aerosol particles. Particulate matter containing organics that are generated in the atmosphere is called “secondary organic aerosol.” Such secondary aerosol would be expected to be transported fairly long distances. The organic aerosol plumes were wider than those of light

aromatics such as toluene, probably because species evaporating slowly from the oil slick away from the DWH site also contribute to secondary aerosol formation. Another key point to note is that we have not determined the chemical nature of the organics. Because of the unique mix of organic precursors, this organic aerosol is likely to have a distinctly different composition than that seen in urban aerosols.

Outside the 4 boxes shown in Fig. 1 and summarized in Table 1, on 8 June the aircraft made a short pass through the smoke from a controlled burn of crude oil on water. There were large amounts of black carbon in this smoke. We are still analyzing the data to estimate emissions of black carbon and other species from the controlled burn. On 10 June no such burning was sampled by the aircraft.

Near the Gulf Coast, aerosol concentrations were similar to typical $PM_{2.5}$ (total mass of particles smaller than 2.5 micrometer diameter) concentrations in major urban areas (e.g., Zhang et al., 2007). Maximum concentrations were due mostly to organic species.

On 8 June, the air south of Louisiana as measured by the aircraft was very clean with respect to particles. The aerosol concentration was comparable to remote areas of the continental United States. On 10 June the flight track and spill were in slightly different locations and the airplane did not sample such pristine air.

Ozone, carbon monoxide, nitrogen dioxide and PAN. Throughout the sampled region on both flights the highest measured averages of ozone, carbon monoxide and nitrogen dioxide were no higher than 83 ppbv, 168 ppbv, and 4.4 ppbv, respectively (Tables 1 and 2). These levels are comparable to or less than those often found in urban areas through the U.S. Peroxyacetyl nitrate (PAN) is an irritating air pollutant often observed in urban photochemical smog; the observed concentrations of this species were below those often encountered in urban areas in summer.

Above the marine boundary layer. The concentrations of all pollutants above the marine boundary layer were typical of the unpolluted atmosphere, with the exception of the lofted plumes from the controlled burns of oil.

Summary of measured concentrations from flights on June 8 and 10

On 8 and 10 June 2010 the NOAA WP-3D aircraft flew the tracks shown in Figs. 1 and 3, respectively. Each flight lasted over 7 hours including over 5 hours in the vicinity of the oil slick. Most of the tracks shown in Figs. 1 and 3 were flown at roughly 150 m above the sea surface, well within the MBL, with occasional ascents to 1000 m and descents to as low as 60 m. During the 8 June flight the winds were light and generally northeasterly with some variability throughout the region. The 10 June flight gave a very useful contrast with stronger winds more consistently from the southeast.

Spatial averages and maximum concentrations were calculated for the measurements collected during the flight track segments enclosed in the green boxes in Figs. 1 and 3. The results are summarized in Tables 1 and 2. Some examples of the high resolution measurements are shown in Figs. 2 and 4.

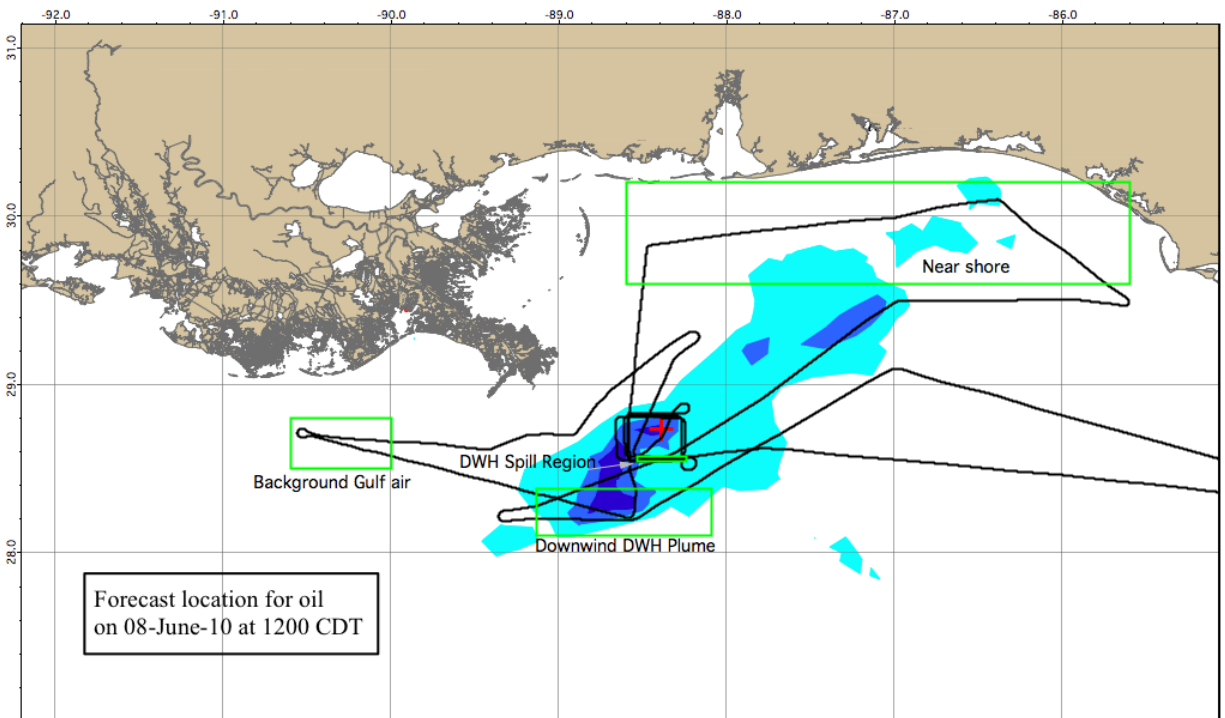


Figure 1. Track of NOAA WP-3D aircraft flight (black line) conducted on 8 June 2010 superimposed on the forecast location of the oil (shades of blue indicating increasing oil amounts) at the time of the flight. The red “plus” indicates the DWH site. The four boxes outlined in green indicate the portions of the flight data that are discussed below.

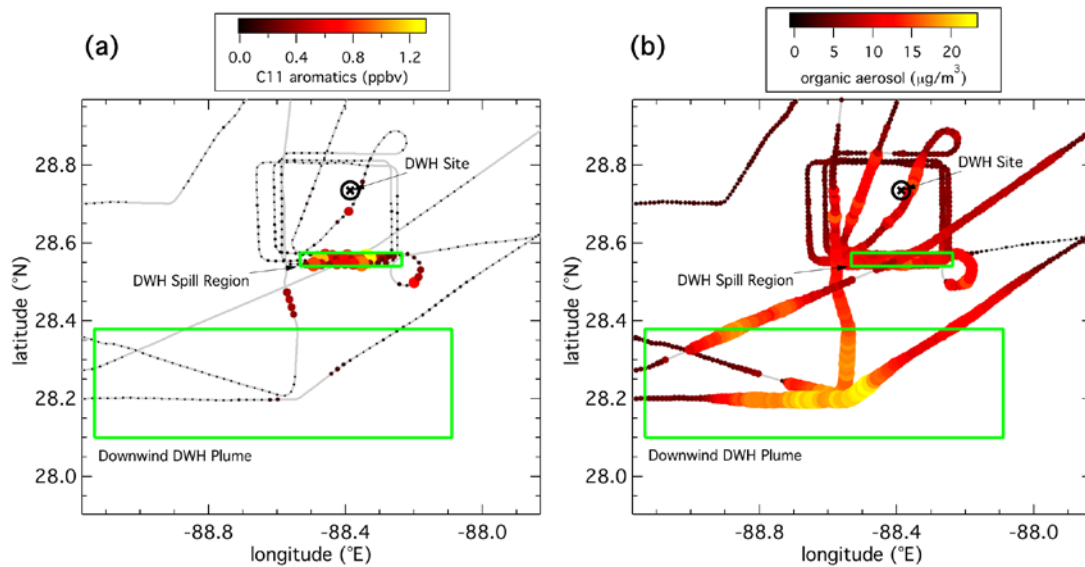


Figure 2. Portion of NOAA WP-3D aircraft flight track conducted on 8 June 2010 with symbols included for measurements of **a)** aromatic hydrocarbons with 11 carbon atoms, and **b)** the organic component of particulate matter. Symbols are colored and sized according to the concentrations, with small black dots denoting the lowest measured concentrations. Near-surface winds at the DWH site were light and generally out of the north and northeast.

Table 1. Statistical summary of preliminary results of measurements conducted during 8 June 2010 flight segments within the MBL in the four boxes illustrated in Fig. 1. For comparison purposes the last column shows maximum values observed during a recent research flight by the same aircraft with the same set of instruments over the Los Angeles urban area. These reported values are to be considered preliminary until all of the data reduction procedures are completed.

Variable	Units	DWH spill region		Downwind DWH plume		Near shore		Background Gulf air		Maximum Los Angeles
		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	
Ozone	ppbv	57	83	45	60	54	69	30	35	75
Carbon monoxide	ppbv	145	152	140	163	156	168	90	97	540
Nitrogen dioxide	ppbv	0.1	0.5	0.1	1.3	0.1	2.1	0.1	1.6	29
PANs	ppbv	0.4	1.0	0.3	0.6	0.3	0.7	0.1	0.1	
Acetaldehyde	ppbv	2.02	3.38	1.05	2.69	0.50	0.71	0.26	0.52	3.9
Benzene	ppbv	0.20	0.53	0.06	0.17	0.05	0.10	< 0.01	0.06	0.47
Toluene	ppbv	0.65	2.06	0.04	0.30	0.02	0.07	0.01	0.04	1.2
C8 aromatics	ppbv	1.58	5.96	0.05	0.65	0.01	0.02	< 0.01	0.02	0.87
C9 aromatics	ppbv	1.88	9.21	0.06	0.77	< 0.01	0.03	< 0.01	0.02	0.34
C10 aromatics	ppbv	1.06	3.78	0.03	0.41	< 0.01	0.02	< 0.01	0.01	***
C11 aromatics	ppbv	0.62	1.67	0.02	0.21	< 0.01	0.03	< 0.01	0.02	***
Naphthalene	ppbv	0.28	0.50	0.02	0.16	< 0.01	0.02	< 0.01	0.03	***
total AMS PM	$\mu\text{g m}^{-3}$	14.1	18.8	14.8	25.9	7.3	14.4	2.1	3.1	18
Organic AMS PM	$\mu\text{g m}^{-3}$	11.6	16.0	12.1	23.3	4.3	11.1	0.2	0.7	7.5
Sulfate AMS PM	$\mu\text{g m}^{-3}$	1.6	2.0	1.9	2.8	2.1	4.4	1.5	2.2	1.9
Sampling transect	kilometers	26		92		260		53		

AMS = Aerosol Mass Spectrometer. The concentrations do not include non-volatile material or particles larger than about 0.6 micrometer diameter.

PM = Particulate matter.

Maximum values are the maximum averages over 1 km of flight path.

*** Not measured; generally the concentrations of these species are so low that they are not normally monitored.

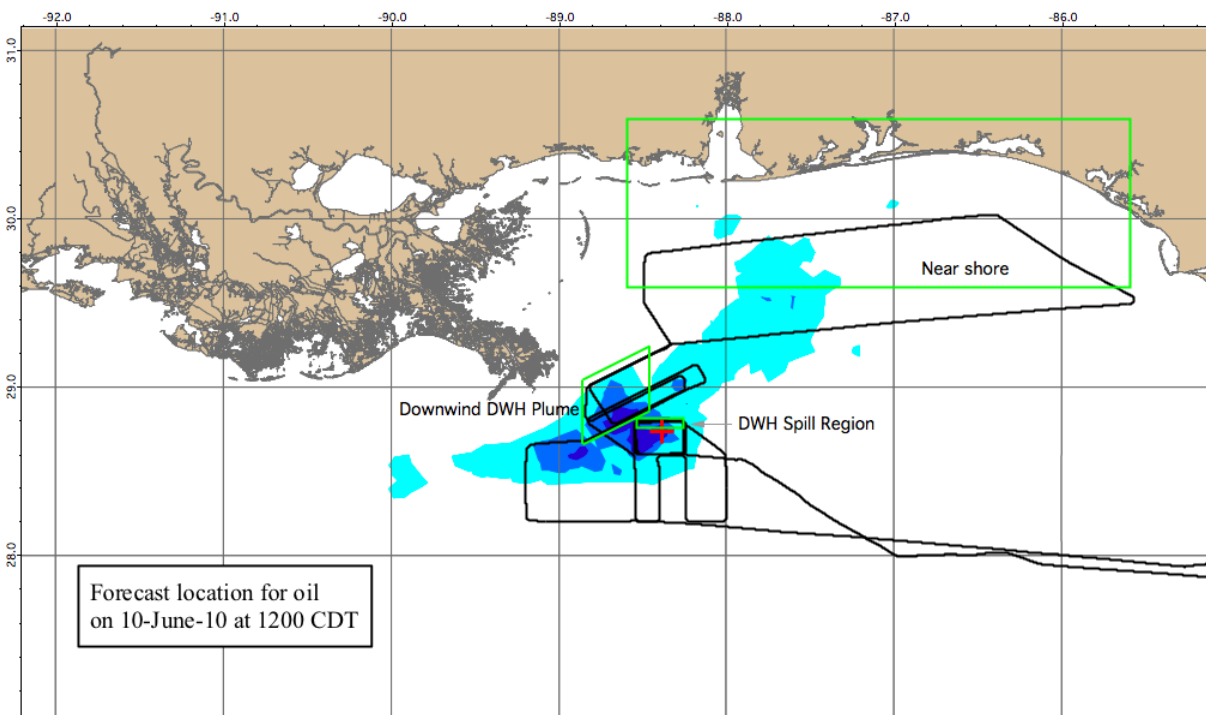


Figure 3. Track of NOAA WP-3D aircraft flight (black line) conducted on 10 June 2010 superimposed on the forecast location of the oil (shades of blue indicating increasing oil amounts) at the time of the flight. The red “plus” indicates the DWH site. The three boxes outlined in green indicate the portions of the flight data that are discussed below.

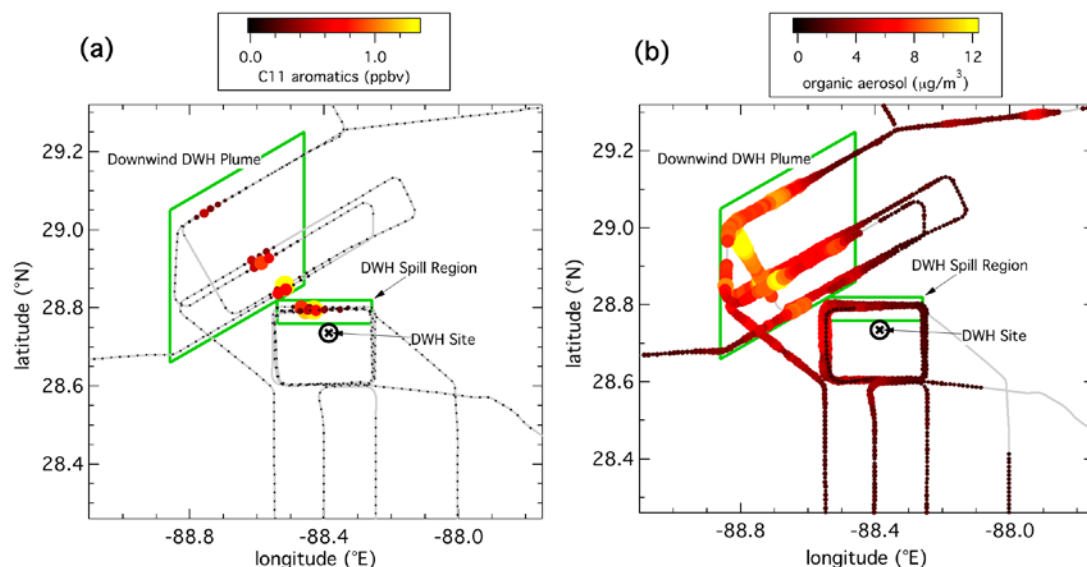


Figure 4. Portion of NOAA WP-3D aircraft flight track conducted on 10 June 2010 with symbols included for measurements of **a)** aromatic hydrocarbons with 11 carbon atoms, and **b)** the organic component of particulate matter. Symbols are colored and sized according to the concentrations, with small black dots denoting the lowest measured concentrations. Near-surface winds at the DWH site were out of the southeast.

Table 2. Statistical summary of preliminary results of measurements conducted during 10 June 2010 flight segments within the MBL in the three boxes illustrated in Fig. 3. For comparison purposes the last column shows maximum values observed during a recent research flight by the same aircraft with the same set of instruments over the Los Angeles urban area. These reported values are to be considered preliminary until all of the data reduction procedures are completed.

Variable	Units	DWH spill region		Downwind DWH plume		Near shore		Maximum Los Angeles
		Average	Maximum	Average	Maximum	Average	Maximum	
Ozone	ppbv	47	50	46	56	52	63	75
Carbon monoxide	ppbv	139	143	139	152	135	151	540
Nitrogen dioxide	ppbv	0.5	4.4	0.1	1.4	0.0	1.0	29
PANs	ppbv	0.1	0.2	0.2	0.5	0.2	0.3	
Acetaldehyde	ppbv	0.52	0.86	0.55	1.48	0.38	0.74	3.9
Benzene	ppbv	0.08	1.02	0.05	0.29	0.03	0.09	0.47
Toluene	ppbv	0.19	2.51	0.08	1.00	0.01	0.04	1.2
C8 aromatics	ppbv	0.40	7.32	0.21	3.12	< 0.01	0.02	0.87
C9 aromatics	ppbv	0.60	8.41	0.34	5.51	0.01	0.03	0.34
C10 aromatics	ppbv	0.35	2.64	0.21	3.29	< 0.01	0.01	***
C11 aromatics	ppbv	0.27	1.61	0.12	1.73	< 0.01	0.01	***
Naphthalene	ppbv	0.09	0.36	0.06	0.29	< 0.01	0.03	***
total AMS PM	$\mu\text{g m}^{-3}$	5.6	8.1	8.9	15.5	4.7	9.4	18
Organic AMS PM	$\mu\text{g m}^{-3}$	3.0	5.2	6.4	12.4	2.1	6.8	7.5
Sulfate AMS PM	$\mu\text{g m}^{-3}$	2.0	2.4	1.9	2.4	1.9	3.4	1.9
Sampling transect	kilometers	25		40		260		

AMS = Aerosol Mass Spectrometer. The concentrations do not include non-volatile material or particles larger than about 0.6 micrometer diameter.

PM = Particulate matter.

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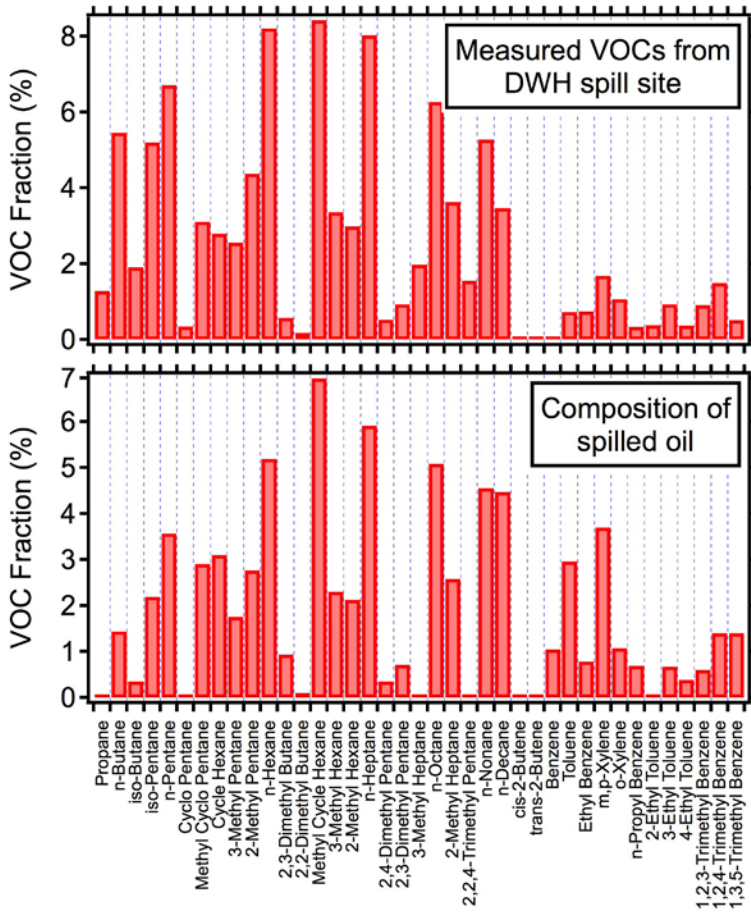


Figure 5: Composition of the VOCs emitted from the DWH incident site and measured by the WP-3D aircraft (top panel) compared to the composition of the leaking oil (bottom panel).

Appendix 1. NOAA WP-3D Aircraft Measurements of VOCs and Other Species

Hydrocarbons and products of atmospheric degradation of hydrocarbons measured sequentially every 20 seconds by the Proton Transfer Reaction Mass Spectrometer (PTRMS); each compound was measured at 1-second temporal resolution, which at the speed of the aircraft equals 100 m spatial resolution.

- | | |
|------------------------|--------------------|
| 1. acetaldehyde | 7. toluene |
| 2. methanol | 8. C8-aromatics |
| 3. acetonitrile | 9. C9-aromatics |
| 4. acetone | 10. C10-aromatics, |
| 5. methyl ethyl ketone | 11. C11-aromatics |
| 6. benzene | 12. naphthalene |

The Atmospheric Whole Air Sampler collected using 72 canisters (each canister took 3 to 5 seconds to fill) on board the aircraft, for analysis in the laboratory.

- | | | |
|------------------------|------------------------------|--------------------------|
| 1. ethane | 28. 2-ethyltoluene | 55. CFC-113 |
| 2. ethene | 29. 1,3,5-trimethylbenzene | 56. CFC-114 |
| 3. ethyne | 30. 1,2,4-trimethylbenzene | 57. H-1211 |
| 4. propane | 31. 1,2,3-trimethylbenzene | 58. H-2402 |
| 5. propene | 32. alpha-pinene | 59. H-1301 |
| 6. i-butane | 33. beta-pinene | 60. HFC-134a |
| 7. n-butane | 34. acetaldehyde | 61. HCFC-22 |
| 8. 1-butene | 35. methanol | 62. HCFC-142b |
| 9. trans-2-butene | 36. ethanol | 63. HCFC-141b |
| 10. cis-2-butene | 37. acetone | 64. HFC-152a |
| 11. i-pentane | 38. butanone | 65. HCFC-124 |
| 12. n-pentane | 39. MTBE | 66. HFC-123 |
| 13. isoprene | 40. MAC | 67. HFC-365mfc |
| 14. n-hexane | 41. MVK | 68. CHCl3 |
| 15. n-heptane | 42. methyl nitrate | 69. CH3CCl3 |
| 16. 2,3-dimethylbutane | 43. ethyl nitrate | 70. CCl4 |
| 17. 2-methylpentane | 44. i-propyl nitrate | 71. CH2Cl2 |
| 18. 3-methylpentane | 45. n-propyl nitrate | 72. C2HCl3 |
| 19. benzene | 46. 2-butyl nitrate | 73. C2Cl4 |
| 20. toluene | 47. 3-pentyl nitrate | 74. CH3Cl |
| 21. ethylbenzene | 48. 2-pentyl nitrate | 75. CH3Br |
| 22. m-xylene | 49. 3-methyl-2-butyl nitrate | 76. CH3I |
| 23. p-xylene | 50. OCS | 77. CH2Br2 |
| 24. o-xylene | 51. dimethyl sulfide | 78. CHBr3 |
| 25. n-propylbenzene | 52. carbon disulfide | 79. ethylchloride |
| 26. 3-ethyltoluene | 53. CFC-12 | 80. 1,2-dichloroethylene |
| 27. 4-ethyltoluene | 54. CFC-11 | |

For the whole air samples collected in canisters over the Gulf of Mexico, the analysis has been modified to include more heavy hydrocarbon species. The measurements from these canisters from the 10 June flight not yet available and hence not reported here.

N43RF layout – Gulf Oil Spill Mission

NOAA-CSD

version 3

06-05-2010

Guide for instrumentation

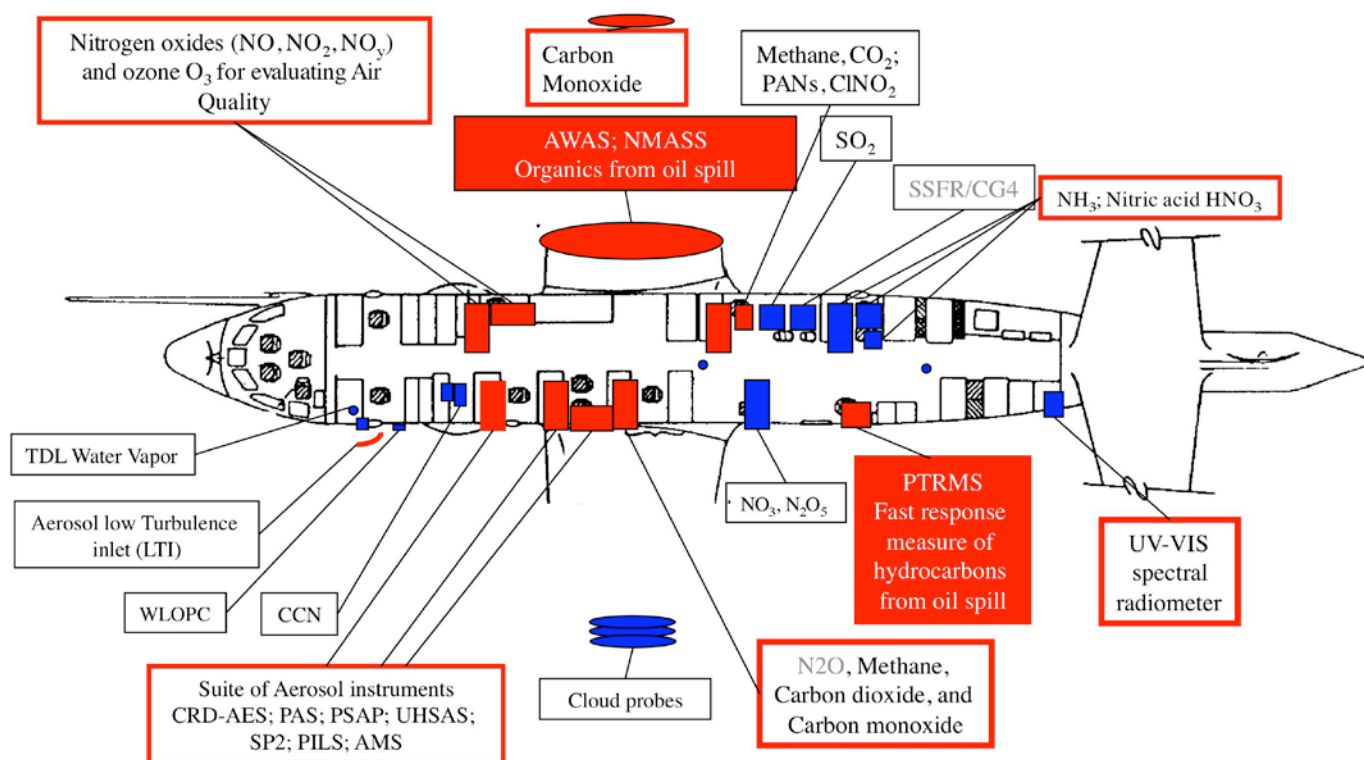
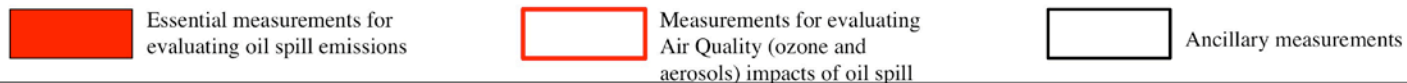


Fig. 3. Instruments on the WP-3D aircraft. Most instruments measure 1 second average concentrations, which correspond to 100 m spatial averages at the aircraft speed.

Definition of instrument acronyms:

AMS – Aerosol Mass Spectrometer
 AWAS - Atmospheric Whole Air Sampler
 CCN – Cloud Condensation Nuclei counter
 CRD-AES – Cavity Ring Down – Aerosol Extinction Spectrometer
 NMASS – Nucleation Mode Aerosol Size Spectrometer
 PANs – Peroxy Acyl Nitrates
 PAS- Photoacoustic Spectrometer
 PILS- Particles Into Liquid Sampler

PSAP- Particle Soot Absorption Photometer
 PTRMS - Proton Transfer Reaction Mass Spectrometer
 SP2- Single Particle Soot Photometer
 SSFR/CG4 – Solar Spectral Flux Radiometer
 TDL – Tunable Diode Laser
 UHSAS – UltraHigh Sensitivity Aerosol Spectrometer
 UV-VIS – Ultraviolet-visible
 WLOPC – White Light Optical Particle Counter

Appendix 2. Level 1 QA/QC Procedures

All measurements were made with either custom-built, one-of-a-kind research instruments or highly modified commercially available instruments. These instruments have been designed and/or modified to operate on the NOAA WP-3D research aircraft. For the most part the instrument performance has been documented in the peer-reviewed literature. Instrument operating procedures have been developed to ensure that quality data sets are collected from the measurements performed in the unique environment of an airborne platform. Following are some general principles that guide this development.

Detection interferences (if they occur) are documented when the instrument is evaluated prior to deployment on the aircraft. Known interferences are accounted for in Level 1 QA/QC.

Sample inlets on the aircraft are designed to minimize or eliminate sample losses by impaction or absorption. All inlets have been extensively and quantitatively characterized to ensure that no significant sample losses occur under flight conditions.

Calibrations are conducted using absolute reference methods, NIST traceable standard materials (where available), or by standards traceable to the WMO calibration scales for individual compounds. Most instruments are calibrated using standard addition of calibrated gas mixtures at the instrument inlet during flight on the aircraft.

Instrument baselines are obtained using chemical scrubbers that remove the species of interest from the ambient air being sampled. The calibration and baseline determinations are performed repeatedly as needed during all research flights; they have been accounted for in Level 1 QA/QC.

Canister samples collected on the aircraft are analyzed for volatile organic compounds (VOC) using standard gas chromatography and gas chromatography-mass spectrometric techniques. All canisters are carefully cleaned prior to use. A subset of the cleaned canisters are retained and analyzed as blanks to insure that no contamination remains from the previous samples.

References:

- Jobson, B. T., et al., Hydrocarbon source signatures in Houston, Texas: Influence of the petrochemical industry, *J. Geophys. Res.*, 109, D24305, doi:10.1029/2004JD004887 (2004).
Zhang, Q., et al., *Geophysical Research Letters*, 34, L13801, doi:10.1029/2007GL029979 (2007).