AQRP Monthly Technical Report

PROJECT TITLE	**ANALYSIS OF SURFACE PARTICULATE MATTER AND TRACE GAS DATA GENERATED DURING THE HOUSTON OPERATIONS OF DISCOVER-AQ**	**PROJECT #**	14-009
PROJECT PARTICIPANTS	R.J. Griffin, B.L. Lefer, and group members	**DATE SUBMITTED**	2/10/2015
REPORTING PERIOD	**From:** January 1, 2015 **To:** January 31, 2015	**REPORT #**	7

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. We understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

This project is broken down into eleven tasks. Naturally, some of the work for an individual task will be complementary to the needs of other tasks. Based on the original schedule, at this point, Tasks 1 through 5, 8, and 9 should be complete, and the work for Tasks 6 and 10 should have begun. Tasks 1 through 5 are considered complete; this work was described in previous monthly technical reports, and no further information will be given here. Progress on Tasks 6-11 is described here despite Tasks 7 and 11 being scheduled to being in March.

Task 6 – Relative Oxidation of Organic Aerosol (OA)

The variation in the degree of oxidation of the submicron OA across Houston during DISCOVER-AQ was examined based on different metrics. Atomic hydrogen to carbon (H:C), atomic oxygen to carbon (O:C), and organic mass to organic carbon (OM:OC) ratios and average carbon oxidation state ($\overline{OSc}$) were analyzed in terms of spatial distribution. The H:C ranged between 0.8 and 1.8 (average of 1.5 ± 0.1) with higher values observed in the eastern part of Houston, indicating a predominantly reduced (likely primary) character of the OA in this region. The O:C ratio and $\overline{OSc}$ varied between 0.2 and 1.4 and -1.5 and 1.5 across Houston, respectively. Average values of 0.43 ± 0.13 and -0.62 ± 0.37 were observed for these metrics, with higher levels identified in south and southwest Houston. The larger O:C ratio and $\overline{OSc}$ levels suggest that secondary OA including different degrees of processing is the major component of submicron OA in these areas. Although the O:C ratio and $\overline{OSc}$ values exhibit a similar trend, larger gradients in the degree of oxidation of the OA are observed based on $\overline{OSc}$, which agrees with previous reports indicating potential limitations of the O:C ratio in capturing changes in the oxidation degree of the aerosol, specifically regarding functionalization reactions occurring in the aging process.

The OM:OC ratio varied between 0.5 and 2.5 (average 1.70 ± 0.19), with larger values observed in the south and southwest parts of the Houston area. As the OM:OC ratio increases with an increase in the oxidation degree of the organics in the aerosol, it is expected that this metric resembles the O:C ratio and $\overline{OSc}$ distribution across Houston. The levels observed for H:C, O:C, and OM:OC ratios during DISCOVER-AQ show good agreement with previous studies that reported levels varying between 1.4 and 1.9, 0.2 and 0.8, and 1.41 and 2.0 for these metrics, respectively.

As indicated in a previous progress report, three contributing factors (HOA, OOA-I, and OOA-II) were identified during preliminary application of Positive Matrix Factorization (PMF) analysis to the OA data during the end of the field campaign (when elevated PM_1 concentrations were observed). The H:C and O:C ratios and $\overline{OSc}$ of these factors are presented in Table 1, along with values reported in the literature for these metrics. As shown in Table 1, the O:C ratio and $\overline{OSc}$ for OA during DISCOVER-AQ concur with values observed previously for PMF factors extracted from submicron OA data. Higher levels of O:C and $\overline{OSc}$ for OOA-II compared to OOA-I indicate that this factor corresponds to highly processed aerosol (low volatility OA), while OOA-I can be considered as "fresh" secondary OA typically classified as semi-volatile OA.

Table 1. Metrics of the degree of OA oxidation for preliminary PMF factors identified during DISCOVER-AQ and comparison with literature values.

Factor	H:C	O:C	$\overline{OSc}$	O:C [2]	$\overline{OSc}$ [1]
Hydrocarbon-like OA (HOA)	1.98	0.09	-1.80	0.06 to 0.1	-1.7 to -1.6
Oxygenated OA (OOA-I)	1.56	0.58	-0.40	0.52 to 0.64	-0.5 to 0
Oxygenated OA (OOA-II)	1.39	0.92	0.45	0.83 to 1.02	0.5 to 0.9

1. Kroll, J.H., et al., *Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol.* Nat Chem, 2011. **3**(2): p. 133-139. 2. Aiken, A.C., et al., *O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry.* Environmental Science & Technology, 2008. **42**(12): p. 4478-4485.

Although examination of the metrics described previously provides insight into the spatial/temporal variation of the oxidation degree of aerosol in the Houston area during DISCOVER-AQ, a more detailed analysis based on the variation of the PMF factors is necessary to better understand the dynamics of the organic fraction of submicron particles in Houston. Furthermore, preliminary factor analysis of the size-resolved organic aerosol composition is being performed currently, and it is expected that this three-dimensional factorization allows the identification of additional aerosol components and provides more robust information on the size distribution of these and their variation across the Houston area.

Task 7 – Importance of Secondary Processes

There is some overlap between Tasks 6 and 7 as the OOA components identified above often are used as a proxy for SOA. However, additional efforts are being made to identify secondary processes of relevance to the PM measured as part of DISCOVER-AQ. Preliminary efforts in this regard are focusing on the inorganic processes. To start, the DISCOVER-AQ inorgamic data have been formatted such that they easily can be input into a freely available inorganic aerosol thermodynamic model; this will allow estimation of the various forms of inorganic material present (for example, if the measured sulfate arises from ammonium sulfate or from ammonium bisulfate). This model output also will include liquid water content and hydrogen ion concentration.

With the results from the inorganic modeling, it will be possible to compare precursor mixing ratios (such as those for sulfur dioxide) to various particulate component concentrations (such as those for various forms of sulfate). In addition, the extent of neutralization of the particles can be considered in light of ammonia data obtained from Princeton University. It is expected that the particles will exhibit an acidic nature, despite available ammonia in the gas phase. The neutralization and ammonia data will be compared to the time series of HOA, OOA-I, and OOA-II to investigate a possible relationship between inhibited neutralization and OA.

Task 8 – Biogenic Influence

Efforts in this task have focused on the extraction of isoprene and terpene data from three-dimensional model runs for the DISCOVER-AQ period due to the lack of reliable measured hydrocarbon data for the mobile laboratory. The University of Houston Air Quality Forecasting group ran Community Multi-scale Air Quality (CMAQ) model simulations for every day during the campaign. The model ran at a 4-km spatial resolution with 1-hour time steps over southeast Texas. Isoprene and terpene data have been extracted for the mobile laboratory locations during the month of September 2013. For this process, the CMAQ grid box was identified for each location reported by the mobile laboratory global positioning system. The isoprene and terpene concentrations at the surface level were extracted for the closest model time step. The resulting time series shows an expected diurnal cycle with the largest peaks during the most polluted week of that month (September 25-26). Although there is no spatial overlap with the mobile laboratory, isoprene data measured by a gas chromatograph on top of the Moody Tower during this time period provides an opportunity for a reality check on the modeled data. When the model data are compared to this location, there is generally an underestimation from CMAQ, with the exception of the hottest days of the month. However, in general, the diurnal patterns correlate with each other. This provides confidence that any effort to link modeled biogenic hydrocarbon data to ozone or SOA formation will do well temporally but likely will provide a lower bound in terms of magnitude. Using output from Task 6, biogenic time series will be considered versus time series of proxies for SOA. In addition, biogenic time series will be provided for use in Tasks 10 and 11.

Task 9 - Analysis of NO_2

The comparison of Pandora measurements to P-3B column measurements during DISCOVER-AQ Texas were updated to the official P-3B derived columns provided by the DISCOVER-AQ team. These columns are very similar to the previous derived columns, as they are average concentrations of 100-meter bins through the profile of each spiral. The difference is that the lower tropospheric column height is consistent at a 0 to 3.5 km column (as opposed to the 0 to 5 km column previously derived). A quality flag also was provided to quantify the fraction of bins with valid data from 0 to 3.5 km. Only columns with a quality flag greater than 80% are included in this analysis. As with the previously derived column comparison, the root mean square error for the comparison of P3-B and in situ (Pandora) data increases as the scale of pollution increases. The mismatch of spatial coverage of each measurement causes more scatter in the comparison. The P-3B spiral encompasses a horizontal distance of approximately 5 km, and the spatial footprint of Pandora only covers a fraction of the spiral area. In areas of largest nitrogen dioxide (NO_2) spatial heterogeneity (e.g., the Deer Park location), the largest mismatches are apparent between the two measurements. Future analysis will examine the Pandora's location in relation to the aircraft spiral locations to see how much of this deviation is related to spatial heterogeneity.

Tasks 10 and 11 – Ozone and radical production rate calculations

Efforts on these tasks continue to focus on development of the necessary hydrocarbon inputs to allow photochemical zero-dimensional modeling to be performed at each location and time where the mobile laboratory was sampling. One method will be to construct biogenic hydrocarbon data from the modeling output discussed above. A second method is to use hydrocarbon data from the Moody Tower. Hydrocarbon data from Moody Tower were ratioed to either carbon monoxide (CO) or nitrogen oxides (NO_x) and sectored by wind direction (to characterize different air mass source regions). The average ratio for a source region can be used when the mobile laboratory was downwind of that region, and the measured CO or NO_x from the mobile laboratory can be used to estimate the hydrocarbon level at the mobile laboratory. The standard deviations of the measured ratios in each wind sector provide input for a sensitivity analysis. These calculations are complete. An additional method through which Moody Tower data are being used is to perform regressions between hydrocarbon to CO or NO_x ratios and the CO or NO_x mixing ratios themselves within the identified wind sectors. This allows the variation of the ratio within the wind sector based on pollution levels. The regression used within each sector will be determined by regression parameters (i.e., that with the strongest correlation). This regression analysis is in progress. Combination of these methods will provide a range of hydrocarbon inputs to the zero-dimensional model that will allow estimation of both ozone and radical production for all sampling locations and times.

Preliminary Analysis

No additional analysis beyond that described above has been performed.

Data Collected

No new data has been collected as part of this project as it is purely a data analysis project.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

No significant problems have been identified beyond those described in previous reports. Work is proceeding as would be expected.

Goals and Anticipated Issues for the Succeeding Reporting Period

Tasks 6 and 9 are nearly complete and should be finished by the end of the next reporting period. Significant progress is expected for Tasks 7 (inorganic modeling and continued PMF analyses) and 8 (comparison of modeled biogenic hydrocarbon levels to observed OA) and Tasks 10 and 11 (generation of model input files). No major issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

Tasks 1-5 are considered complete. Although we are slated to have completed Tasks 8 and 9 but have not, we are ahead on Tasks 7 and 11, as these activities started ahead of schedule. We believe the progress on Tasks 7 and 11 balances the delays in Tasks 8 and 9; therefore, we deem our progress appropriate.

Submitted to AQRP by: Robert J. Griffin

Principal Investigator: Robert J. Griffin