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**	3/9/2015
REPORTING PERIOD	**From:** February 1, 2015 **To:** February 28, 2015	**REPORT #**	8

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 6, 8, and 9 should be complete, and the work for Task 10 should have begun. Tasks 1 through 5 and 9 are considered complete; this work was described in previous monthly technical reports, and no further information will be given here. Progress on Tasks 6-8, 10, and 11 is described here despite Tasks 7 and 11 being scheduled to begin 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 including the 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 ($\overline{OSc}$). These were all discussed in the previous monthly report. In addition, during the last reporting period, these metrics were investigated in “zones” of Houston (as opposed to at individual locations) to improve data statistics because of an increased number of data points; zones were based on a statistical cluster analysis. These metrics indicate a relatively high level of oxidation to the southeast of the city, a relatively low level of oxidation in the downtown area, and the highest level of oxidation to the northwest of the city.

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 submicron particulate matter concentrations were observed). These represent proxies for primary organic aerosol and two types of secondary organic aerosol (SOA; one fresh and one aged). However, when applied to the entire DISCOVER-AQ dataset, PMF yields too large of a residual error to be acceptable; therefore, work continues to attempt to identify the source of the error. Once complete, a more detailed analysis based on the variation of the PMF factors will be necessary to better understand the dynamics of the organic fraction of submicron particles in Houston. In addition, once this issue is resolved it will be possible to apply PARAFAC (a multi-dimensional version of PMF) that will allow consideration of particle size in the results found through PMF.

Task 7 – Importance of Secondary Processes

There is some overlap between Tasks 6 and 7 as the OOA components discussed above often are used as a proxy for SOA; further information on SOA requires completion of the PMF, however. Regardless, additional efforts are being made to identify secondary processes of relevance to the particulate matter measured as part of DISCOVER-AQ. Current efforts in this regard are focusing on the inorganic aerosol constituents.

The ISORROPIA-I thermodynamic equilibrium model was used with the submicron aerosol data (sulfate, nitrate, and ammonium) collected during DISCOVER-AQ. The model determined the concentrations of the inorganic species in the aerosol (solid/liquid) phase at chemical equilibrium; output included hydrogen ion concentration ($[H^+]$) and aerosol liquid water concentration. Simulations indicated that the aerosol was slightly acidic throughout the DISCOVER-AQ campaign, with slightly more acidity in southeast Houston.

Correlations between aqueous-phase $[H^+]$ and organic aerosol concentrations and the H:C and O:C ratios described previous were performed. These correlations were performed for specific locations when the UH-Rice mobile laboratory was stationary (i.e., Conroe, Spring Creek Park, Manvel Croix, Galveston, and San Jacinto) and for a specific time period (22-28 September 2013, the most polluted period of the campaign). Results indicate that organic concentrations had very strong, positive correlation with $[H^+]$ in all locations between 22-28 September ($R=0.80$) and specifically in Manvel Croix and Galveston for the entire campaign ($R=0.86$ and 0.94, respectively). Additional correlations will be performed between PMF output and ISORROPIA variables (including aerosol liquid water content). Future work also will include aggregation of ISORROPIA output into the zones described in Task 6. Other tasks will consider ammonia data when the UH-Rice mobile laboratory was co-located with the Princeton mobile laboratory and sulfate data in relation to sulfur dioxide.

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. This effort is complete, and the time series are ready for use. Using output from Task 6, biogenic time series will be considered versus time series of proxies for SOA. Thus, completion of Task 8 now depends on completion of Task 6. In addition, biogenic time series will be provided for use in Tasks 10 and 11 described below; these efforts will quantify biogenic influence on ozone and radical production.

Tasks 10 and 11 – Ozone and radical production rate calculations

Efforts on these tasks were focused on preparation of input files for photochemical modeling of ozone and radical production. The model to be used (LaRC) requires inputs of time, location, solar zenith angle, meteorology (temperature, dew point, and pressure), trace gas mixing ratios, and the photolysis rate of nitrogen dioxide. All of these data are available from the UH-Rice mobile laboratory, with the exception of the main hydrocarbons important for ozone and radical production (discussed below). Three-dimensional model output (described above) will be used for biogenic species. In addition, the model requires an estimate of the ozone column density, which was derived from NASA satellite measurements. Preliminary LaRC input files, except for the hydrocarbons, have been generated for all times in the data series associated with the UH-Rice mobile laboratory.

For other species, relationships between measured hydrocarbons and either carbon monoxide or nitric oxide (whichever yields the strongest correlation) at Moody Tower or on the NASA P-3B aircraft will be used to estimate hydrocarbon concentrations. Moody Tower will be used for ethane, propane, and other alkanes. The aircraft will be used for formaldehyde, propene, benzene, and toluene. The relationships are often dependent on wind direction (confirmed using back trajectory analysis) due to different sources, and the correlation is quantified for each spiral site or Moody Tower with varying wind directions. Thus, for a given time, location, and wind direction, relationships to determine alkane, alkene, formaldehyde, and aromatic mixing ratios have been determined. With these relationships now in hand, it will be possible to generate the necessary mixing ratios, complete the input files, and run the LaRC model.

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

The only minor problem identified is the continued issue with the error associated with the PMF modeling. It is expected that this issue will be resolved in the near term, allowing further analyses that depends on the OOA time series.

Goals and Anticipated Issues for the Succeeding Reporting Period

The primary goal for the upcoming reporting period is solution of the error issue in PMF. Once that is complete, it will be possible to complete Task 6, Task 7, and the aerosol focused efforts of Task 8. Progress on Tasks 10 and 11 also are expected. No other issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

Tasks 1-5 and 9 are considered complete. Although we are slated to have completed Tasks 6 and 8 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 6 and 8; therefore, we deem our progress appropriate.

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