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**	11/10/2014
REPORTING PERIOD	**From:** October 1, 2014 **To:** October 31, 2014	**REPORT #**	4

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 4 and 8 should be complete, and the work for Task 9 should have begun. Tasks 1 and 2 are considered complete; this work was described in the previous monthly technical report, and no further information will be given here. Progress on Tasks 3, 4, and 8-11 also is described here. Please note that work on Task 6 (detailed characterization of the oxidation state and other related parameters for OA using Positive Matrix Factorization or PMF) was initiated in August, but little to no progress on this Task was made in October, except in the context of other Tasks. Therefore, no additional progress is described here. Tasks 5 and 7 are not yet considered.

Task 3 necessitates sharing of data with collaborators from The University of Texas (UT) at Austin (Hildebrandt-Ruiz) and Baylor University (Sheesley); comparison of data also is part of this task. Rice high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) data were supplied to collaborators at the end of the previous reporting period. The slight delay was caused by an issue with the location flag in the data file being “smeared” due to the temporal averaging used. This issue was corrected prior to provision of the data. Data were received from collaborators at the end of the previous reporting period as well. As such, comparison of the data was performed during the current reporting period. The focus of this comparison was between the HR-ToF-AMS being operated by the Rice group using the mobile laboratory (ML) and the aerosol chemical speciation monitor (ACSM) data from UT at times when the ML was co-located with the UT measurements. Three particulate matter (PM) species were considered: bulk organic aerosol (OA), nitrate aerosol, and sulfate aerosol. For all three species, regression of the HR-ToF-AMS (y-variable) and the ACSM (x-variable) data shows a high degree of linearity. Slopes of 1.17 for OA and 0.89 for nitrate aerosol are well within the uncertainties associated with each instrument. However, the slope of 1.61 for sulfate is higher than what would be deemed acceptable (at least not without further investigation) so current efforts that will continue into the next reporting period will focus on rectifying this difference in the sulfate aerosol measurements.

In Task 4, the spatial and temporal variation of the submicron PM concentration in Houston during the DISCOVER-AQ field campaign was studied using the data obtained during stationary and mobile operations of the ML. Note that the protocol for this analysis now exists and can be updated easily as data change slightly based on Task 3. Stationary operation of the ML was mainly conducted at five different field sites: Conroe (with UT), Spring Creek Park, Manvel-Croix (with Baylor), San Jacinto and Galveston. The length of the ML operation at each location varied among sites (typical deployment periods comprised several hours during different days).

The diurnal character of different PM constituents at Conroe, Spring Creek Park, and Manvel Croix during DISCOVER-AQ has been evaluated. The limited size of the PM particle composition datasets collected at the San Jacinto and Galveston locations prevent the analysis of the diurnal variations of OA, sulfate, and nitrate at these sites. In addition to considering the diurnal profile of specific PM constituents, the diurnal profiles of various low-resolution markers of the extent of oxidation are considered for these same locations. These markers include the average carbon oxidation state (OSc) and the ratios of hydrogen (H) to carbon (C) (H:C) and oxygen (O) to C (O:C). All diurnal profiles are strongly location dependent and show considerable variability, likely due to the non-consecutive nature of the datasets that are being used to generate the diurnal profiles from the HR-ToF-AMS. Although a more rigorous analysis of the results is being conducted currently and will be included in the next monthly report, some general observations are stated here:

- Particulate nitrate concentrations at Conroe and Spring Creek Park exhibit a similar diurnal pattern with a marked decrease of concentration during the day and increasing concentration during the night, as typically observed for this species during summer time. Concentrations of this PM constituent at Manvel Croix differ from this pattern, with moderate daytime decreases and nighttime increases.
- Diurnal profiles of OA concentration show different trends at these three field sites. However, a common moderate peak of concentration is observed at ~8:00 to 10:00 CDT corresponding with the period of traffic emissions during rush hour. A pronounced broad peak in OA concentrations in the afternoon hours is observed at Manvel Croix field site, while a more moderate peak is observed at Conroe during the same period of time. This peak is likely associated with formation of secondary organic aerosol (SOA) as indicated by the corresponding peaks in O:C and OSc, particularly at Manvel Croix.
- Reductions in H:C and increases in O:C and OSc are observed during daytime (~8:00 and 20:00 CDT) at the Conroe and Spring Creek Park locations, indicating the prevalence of SOA during this period. A peak in OSc is observed at ~13:00 CDT at the Conroe site, while a double peak earlier in the morning (9:00-10:00 CDT) and between ~13:00 to 16:00 CDT is observed for this metric at Spring Creek Park.
- The diurnal profiles of H:C, O:C and OSc at Manvel Croix site exhibit an increase in H:C during the morning hours (~6:00-13:00 CDT), indicating the predominance of primary organic aerosol. This increase is followed by a reduction during the afternoon hours (13:00-18:00 CDT) and a corresponding increase in O:C and OSc during this period of time, indicating the formation of SOA.

- Concentrations of particulate sulfate at the Conroe and Spring Creek Park sites exhibit a characteristic peak at ~10:00-12:00 CDT associated with early emissions of sulfur dioxide, potentially related to traffic activity. An atypical peak of sulfate concentration is observed at ~18:00-20:00 CDT at the three monitoring locations with more pronounced increases occurring at Conroe. These will be investigated in the context of Task 3.
- The diurnal variations of sulfate and ammonium concentrations show a similar pattern at each sampling site, indicating as previously reported, that ammonium is predominantly associated with sulfate in the aerosol.

Task 8 evaluates the influence of biogenic volatile organic compounds (BVOCs) on ozone and PM formation. Here, the research team will depend on the use of the FACSIMILE model, which was purchased using funds for this project. It has been installed, and staff members continue to work to understand its operation. This model will require data inputs for BVOCs. Because data are not available for all periods of the mobile laboratory operation, alternative data sources have been identified. Community Multi-scale Air Quality (CMAQ) model output has been requested for the DISCOVER-AQ period; this will provide temporal and spatial distributions of isoprene, isoprene oxidation products, and monoterpenes. The CMAQ output will be used as input for this evaluation. The FACSIMILE model will calculate ozone production rates and reactivities for specific hydrocarbons. The influence of biogenic hydrocarbons for PM formation will be evaluated statistically. Current preliminary data indicate that biogenic hydrocarbon oxidation by nitrate radical constitutes a significant fraction of nocturnal PM formation.

In Task 9, NO_2 data from the Pandora spectrometer instrument are compared to OMI satellite measurements during DISCOVER-AQ Texas 2013. Cloudy conditions during this time period (September 2013) led to fewer data points for comparison than expected. OMI data were filtered by the row anomaly and cloud fractions greater than 20%. As recommended by Jay Herman (Pandora PI), Pandora data were only considered valid for clear sky direct-sun measurements, if normalized root mean squared values of the spectral fit were less than 0.01, and if NO_2 column measurement errors were less than 0.05 DU. Based on the valid data, the relationship between Pandora and OMI changes spatially in Houston. In some locations, the data cluster around the 1:1 line; in others, one technique consistently outputs larger column concentrations than the other, with southern locations exhibiting higher OMI values and northern locations exhibiting higher Pandora values. These data need to be investigated in the context of relative levels of pollution based on the following. Long-term Pandora data from the Moody Tower at the University of Houston gives a larger dataset with which to compare to OMI. From March 2012 until August 2013, 86 valid comparisons show that Pandora measures larger vertical column densities on more polluted days. However, on cleaner days, the relationship seems to be scattered around the 1:1 relationship.

The differences in measurements are likely due to the spatial scale differences between the two measurements because Pandora is a local vertical column measurement and OMI measures over a large area (13x24 km^2 at nadir). In the future, these data will be analyzed by taking into consideration the pixel area coverage and how pollution levels may change at a sub-pixel level. In the next month, Pandora data will be compared to a second OMI product as well as to aircraft-derived NO_2 columns during DISCOVER-AQ Texas.

Tasks 10 and 11 use zero-dimensional computer modeling to evaluate ozone production rates and radical sources. To start, a project scientist associated has obtained the NASA Langley photochemical model (LaRC) and has run it with data from previous field campaigns to ensure it is operating appropriately on the new computational platform. The scientist is currently working to generate appropriate input files based on the mobile laboratory data from DISCOVER-AQ. All input data for the model are available from the mobile laboratory, except, as above, the full suite of VOCs. Efforts continue to use regression analyses from VOCs measured on the Moody Tower to estimate VOCs for the ML (e.g., a relationship between a VOC and NO at Moody Tower is assumed to also hold for the ML). Output from the LaRC will include ozone production rate and concentrations of species necessary to estimate radical sources. The FACSIMILE model described above also will be utilized with multiple chemical mechanisms to evaluate these parameters and provide an estimate of the uncertainty of the calculations.

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

The goals for the next period are to resolve the issues identified in Task 3 (data comparison between all collaborators), update and complete Task 4 (diurnal profile of PM in Houston) once Task 3 is complete, and complete Task 5 (spatial analysis of PM in Houston). Work will continue on Tasks 6 (characterization of oxidation state and similar metrics for OA using PMF), 8 (characterization of biogenic influence), 9 (column versus *in situ* NO_2 measurements), 10 (modeling of ozone production rate), and 11 (modeling of radical sources). According to the project plan, Tasks 1-5 and 8 should be complete as of the end of November.

Detailed Analysis of the Progress of the Task Order to Date

Tasks 1 and 2 are considered complete. Although we are slated to have completed Tasks 3, 4, and 8 but have not, we are ahead on Tasks 6, 10, and 11, as these activities have started ahead of schedule. We believe the progress on Tasks 6, 10, and 11 balances the delays in Tasks 3, 4 and 8; therefore, we deem our progress appropriate. Task 9 is currently adhering to the planned schedule. Tasks 3, 4, and 5 should be complete by the end of the next reporting period.

Submitted to AQRP by: Robert J. Griffin

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