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**	12/8/2014
REPORTING PERIOD	**From:** November 1, 2014 **To:** November 30, 2014	**REPORT #**	5

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 and 8 should be complete, and the work for Task 9 should have begun. Tasks 1 and 2 and 4 are considered complete; this work was described in previous monthly technical reports, and no further information will be given here. Progress on Tasks 3, 5, 6, and 8-11 also is described here. Task 7 is not yet considered.

Task 3 necessitated 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 beginning of October. Data were received from collaborators as well. The focus of the resulting data 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 (NO_3^-) aerosol, and sulfate (SO_4^{2-}) 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. The research teams have been in communication with each other to determine the cause of this discrepancy. At first, particle collection efficiencies and sampling differences were discussed, but these were eliminated as probable causes. The current thought is that the ACSM data might have problems with the relative ionization efficiency used for sulfate; the team from UT is investigating.

In Task 5, the spatial variation of the submicron PM (PM_1) composition across 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 results from Task 3.

First, the relative contribution of OA, SO_4^{-2}, NO_3^-, ammonium (NH_4^+), and chloride to PM_1 at five selected field sites where the ML operated in stationary mode was considered. On a mass basis, OA was the predominant species at the Conroe, Spring Creek Park, Manvel-Croix and San Jacinto locations, followed by SO_4^{-2}, NH_4^+, NO_3^-, and chloride. The average contribution of OA ranged between 50.7 and 71.9 %, with highest and lowest percentages observed at the Conroe and San Jacinto sites, respectively. Sulfate concentrations constituted between 20.2 and 39.1% of the PM_1 at these four locations, with highest and lowest percentages observed at San Jacinto and Conroe, respectively. Ammonium contribution to PM_1 varied between 4.5 and 8.9%, while nitrate and chloride constituted between 1.1 and 3.2% and between 0.1 and 0.3% of PM_1, respectively. In contrast, SO_4^{-2} was the predominant PM_1 species at Galveston (47.8%), followed by OA, NH_4^+, NO_3^-, and chloride. Based on mobile sampling across several locations in Houston with varying concentration of PM, OA and sulfate are the predominant constituents of the submicron aerosol. Percentage contributions of OA as high as ~81% were detected in locations influenced by high traffic activity in south Houston (Sam Houston Parkway, SHP), while smaller contributions of OA were observed on the west side of Houston near SHP (55-60%). A more comprehensive analysis of the spatial distribution of PM_1 constituents across Houston was conducted by partitioning the Houston area where the ML was located (both mobile and stationary-mode operations) during DISCOVER-AQ into grids of ~1 square kilometer. Calculation of the average concentrations of PM_1, OA, SO_4^{-2}, NO_3^-, NH_4^+ and chloride, along with the average contribution of OA and sulfate to PM_1, in each grid was performed. Patterns such as the consistent dominance of OA in PM_1 across Houston, largest contributions of OA and NO_3^- in downwind areas (in this case to the northwest of downtown Houston), and the presence of locations with percentage contributions of SO_4^{-2} above 50% (particularly in East Houston, which are tracked by NH_4^+ contributions) can be observed from the spatial segregation of the data.

Task 6 is scheduled to begin at the start of the next work period. However, initial progress has been made as described in previous reports. Additional effort was made during the current reporting period. Size-resolved components (factors) of the organic fraction of PM_1 in Houston during DISCOVER-AQ will be identified through parallel factor (PARAFAC) analysis. PARAFAC is a three-dimensional factorization technique that extends a two-dimensional positive matrix factorization (PMF) analysis by including information on the size distribution of the aerosol components. The PARAFAC analysis will be conducted based on the application of two different mathematical algorithms: PMF3 and Multilinear Engine 2 (ME-2). Preliminary steps for application of PARAFAC to the HR-ToF-AMS data set collected during DISCOVER-AQ are being performed. As preliminary information on the character of the OA components is required for interpretation of the factors resulting from PARAFAC analysis, application of PMF to the corresponding data set is required at a preliminary stage. This task is being conducted currently using the PMF2 software coupled to a PMF Evaluation Tool on practice HR-ToF-AMS data collected during August 2014 in Houston.

Task 8 aims to evaluate 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 ML 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 BVOCs for PM formation will be evaluated statistically. The CMAQ data were obtained at the very end of the current reporting period.

In Task 9, additional analysis for the comparison between Pandora spectrometer measurements and the Ozone Monitoring Instrument (OMI) was performed. The Pandora was compared to two separate retrievals for OMI nitrogen dioxide (NO_2) total columns: NASA Standard Product level 2 v2.1and KNMI DOMINO level 2 v2.0. The OMI measurements include periods with cloud fractions less than 20% and without the row anomaly. Coincident Pandora measurements were averaged to ±30 minutes within the OMI overpass.

The spatial heterogeneity of NO_2 in Houston causes comparison mismatches due to the differences in spatial resolution of the measurements. Pandora is a local measurement, and OMI measures the average column over a large spatial area (13×24 km^2 at nadir and often much larger due to nadir pixels being compromised by the row anomaly). Both OMI retrievals are often lower than Pandora in more polluted regions and higher in more rural regions. More rural areas, such as northwest Harris County or Galveston, often have OMI values larger than comparable Pandora values due to the large spatial footprint of OMI encompassing portions of the urban plume not local to the site.

Channelview is in a nitrogen oxide source transition zone, with strong sources to the southwest but fewer strong sources to the northeast. Due to the placement of the Pandora, the comparison depends on local meteorological conditions. In easterly winds, the Pandora is located in the relatively unpolluted portion of the pixel, leading to OMI measuring higher than Pandora; with south-westerly winds, the large urban plume from Houston and the Houston Ship Channel is advected over the Channelview measurement site, leading to a Pandora measurement that indicates a higher local NO_2 column compared to OMI. In the future, a CMAQ-derived spatial weighting kernel representing the distribution of NO_2 over the OMI pixel footprint will be used to distribute the OMI measured NO_2 at a smaller spatial scale. The goal is to capture the spatial variability of NO_2 and validate this ‘downscaling’ with Pandora and possibly other NO_2 measurements.

Pandora measurements also were compared to ground *in situ* measurements. Pandora measurements are compared to derived boundary layer columns using estimated boundary layer height from a Vaisala ceilometer CL31 LIDAR and *in situ* surface NO_2 measured at two coincident locations: Moody Tower and Galveston. Hourly averaged surface NO_2 is integrated to the height of the boundary layer using two profile shape assumptions: well-mixed and linearly decreasing to zero at the top of the boundary layer. Monthly averaged OMI stratospheric NO_2 columns are subtracted from the Pandora measurements. Comparing ground concentration measurements to Pandora assists with algorithm development for inference of ground concentrations from space-based column measurements. The challenge lies in estimating the vertical distribution of NO_2 in the boundary layer and lower free troposphere.

In urban Houston, a well-mixed profile assumption overestimates the boundary layer column. However, a linearly profile decreasing to zero at the top of the boundary layer (a so-called half well-mixed column) improves this relationship. In less polluted Galveston, the error in boundary layer height and the stratospheric subtraction causes larger scatter and yield a relationship more difficult to distinguish. To finish this analysis, an in depth analysis of P-3B profile shapes, as well as other simplified profile shapes, will be used to assess further the relationship between column measurements and ground concentrations.

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 ML 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 ratio 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). Plots of the ratios of two compounds as a function of wind direction have been generated and are currently being used to generate corresponding appropriate values for the ML, which will allow generation of the necessary LaRC input files. 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), continue work on Tasks 6 (characterization of oxidation state and similar metrics for OA using PMF), 8 (characterization of biogenic influence), 10 (modeling of ozone production rate), and 11 (modeling of radical sources), and complete work on Task 9 (column versus *in situ* NO_2 measurements). According to the project plan, Tasks 1-5, 8, and 9 should be complete as of the end of December.

Detailed Analysis of the Progress of the Task Order to Date

Tasks 1, 2, 4, and 5 are considered complete. Although we are slated to have completed Tasks 3 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 and 8; therefore, we deem our progress appropriate. Task 9 is currently adhering to the planned schedule. Task 3 should be complete by the end of the next reporting period.

Submitted to AQRP by: Robert J. Griffin

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