

## AQRP Monthly Technical Report

<b>PROJECT TITLE</b>	ANALYSIS OF SURFACE PARTICULATE MATTER AND TRACE GAS DATA GENERATED DURING THE HOUSTON OPERATIONS OF DISCOVER-AQ	<b>PROJECT #</b>	14-009
<b>PROJECT PARTICIPANTS</b>	R.J. Griffin, B.L. Lefer, and group members	<b>DATE SUBMITTED</b>	10/8/2014
<b>REPORTING PERIOD</b>	<b>From:</b> September 1, 2014 <b>To:</b> September 30, 2014	<b>REPORT #</b>	3

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 15<sup>th</sup> of the month following the reporting period shown above.

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### 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, 2, 3, and 8 should be complete, and the work for Task 9 should have begun. Tasks 1 and 2 are considered complete. Progress on Task 3 is described here; it will be complete shortly. Because of delays in the availability of funds to the University of Houston and an associated delay in the ability to purchase a necessary computer model, Task 8 is not complete, though progress is described here. Initial progress on Tasks 9 through 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 September. Therefore, no additional progress is described here.

Task 1 quantifies particulate matter (PM) emission rates. The previous progress report for this project highlighted the identification of on-road events for use in evaluation of organic PM (also referred to as OA) emissions. After evaluation of the magnitude of enhanced OA concentrations (as a delta relative to background before and after the plume), enhancements in carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>) were calculated. The changes in CO and NO<sub>x</sub> in plumes are utilized to calculate relative emission factors (EF) for OA. It should be noted that  $\Delta\text{CO}/\Delta\text{NO}_x$  molar ratios from identified events do not appear to depend on fleet composition (percentage of diesel/heavy-duty vehicles). The bulk CO/NO<sub>x</sub> emission ratios calculated from the Motor Vehicle Emission Simulator (MOVES2014) emissions model from the United States Environmental Protection Agency for Houston/Harris County for the month of September 2013 are ~0.58 for diesel vehicles and ~7.75 for gasoline vehicles. However, emission ratios can vary significantly due to varying driving conditions, temperature, and other factors. For the conversion of measured OA/NO<sub>x</sub> or OA/CO ratios to EF of OA (g OA emitted per mile driven), weighted averages of EFs for CO and NO<sub>x</sub> were estimated based on fleet composition assuming

that all heavy-duty vehicles identified in the videos collected on the mobile laboratory have diesel engines and that all light-duty vehicles and motorcycles are gasoline-based. The EF of OA was then taken as the product of the EF for CO times the observed OA/CO ratio or as the EF for NO<sub>x</sub> times the observed OA/NO<sub>x</sub> ratio. These vehicle EFs for OA are rough estimates of how much OA is emitted per mile driven for the average fleet composition encountered by the mobile laboratory during the events. These values may not be representative of the OA EFs for the vehicle fleet in Houston/Harris County. Large inconsistencies exist between the EF of OA values predicted from CO and NO<sub>x</sub> measurements and between different vehicles (in some cases, up to more than an order of magnitude; the range of values obtained is 0.14 to 13.74 g per mile driven). To further characterize these differences, a targeted motor vehicle emissions study will be performed using the mobile laboratory in the near term (likely late 2014 or early 2015). Rather than relying on chance encounters with vehicles, as with the DISCOVER-AQ study, this new study will deploy the mobile laboratory at a specific site to measure vehicular emissions. The novel method presented here will be used for the new data, with the results determining the best method by which to estimate motor vehicle EF values for OA. Based on the September 2013 data, however, no additional progress can be made, and this task for now is considered complete.

Task 2 characterizes large PM concentration events that are short in temporal duration (order minutes). Analysis of the submicron PM peak events observed during the DISCOVER-AQ field campaign and identification of the sources responsible for these events were finalized during the current reporting period. Time and location were identified, and the increases in OA or sulfate concentration compared with local background levels were calculated. Based on video observations, the probable associated source for each of the observed events was determined. As previously reported, 26 PM statistically defined peak events were observed during the mobile-mode operation of the mobile laboratory. From these, 15, 6, and 4 episodes of high PM concentration were associated with traffic activity, industrial sources (specifically chemical and petrochemical facilities), and biomass burning (BB) activities respectively. The responsible source(s) for one of the observed PM peak events was not identified due to deficient light conditions and low resolution of the video records.

Average fleet composition during the PM peak events associated with mobile sources was analyzed. Light-duty vehicles were predominant in 50% of the traffic-related events, while heavy-duty vehicles and light-duty trucks were the main component of the fleet in 28.6 and 21.4% of the PM peak events associated with vehicle emissions, respectively. Four of the traffic-related PM peak events were connected with single vehicles from which plumes were clearly identified. OA was found to be the main constituent of the submicron PM in the traffic-related peaks, with a range of increase in concentration of 14 to 71 µg/m<sup>3</sup> compared with local background levels.

Sulfate was the largest component of the peak events identified in the perimeter of three industrial complexes, including those associated with petrochemical and refining activities. More moderate increases in the organic and ammonium fraction of PM compared with the specific background concentrations were also noticed in these peaks. Average sulfate levels in the identified industrial-related peaks ranged between 3 and 30 µg/m<sup>3</sup>.

Peak events associated with BB showed high concentrations of OA, indicating significant increases of this component compared with its local background levels. Average OA concentration in these peaks varied between 16 and 107 µg/m<sup>3</sup>.

Although comprehensive characterization of the organic fraction in the identified peaks will be conducted by application of PMF (Task 6), preliminary analysis of the character of the OA was performed based on (i) metrics related to the oxidation state of the constituents of this fraction and (ii) specific mass spectral tracers for hydrocarbon-like organic aerosols (HOA). The ratio of oxygen to carbon (O/C), hydrogen to carbon (H/C), and organic mass to organic carbon (OM/OC) of the organic fraction of PM are considered. For traffic activity, the average O/C, H/C, and OM/OC were  $0.11 \pm 0.04$ ,  $1.85 \pm 0.07$ , and  $1.32 \pm 0.08$ , respectively. The O/C and OM/OC values agree with previously reported ratios for emissions from diesel and gasoline vehicles (O/C between 0.06 and 0.1 and OM/OC ranging between 1.2 and 1.3). No specific correlation was observed between predominant vehicle type in the fleet and O/C, H/C, and OM/OC ratios. An observed decrease in O/C in the PM peaks when compared with the background levels (average background O/C of  $0.38 \pm 0.12$ ) indicates a lower oxidation state of the OA emitted by the vehicles, which concurs with the expected predominance of primary HOA in these peaks. This observation is supported by the increase in the H/C value for the selected events (average background H/C of  $1.59 \pm 0.15$ ). A strong correlation between OM/OC and O/C ( $R^2 = 0.994$ ) suggests very little contribution from nitrogen in these aerosols.

The average O/C, H/C, and OM/OC values for the peak events associated with BB are  $0.31 \pm 0.016$ ,  $1.63 \pm 0.04$ , and  $1.56 \pm 0.022$ , respectively. As with the traffic-related PM peaks, a decrease in the oxidation state of the OA compared with the background levels was noticed. This observation is consistent with the expected primary character of the aerosol in plumes generated by BB activities. Values for O/C between 0.3 and 0.4 have been reported previously for BB plumes, agreeing with these observations. The primary character of the organic aerosol in the BB-related events is confirmed by an increase in the H/C ratios.

More moderate differences between O/C in the background and peak event OA are noticed for peaks associated with BB plumes when compared to traffic-related peaks (average reduction ~ 30 and 70%, respectively). This observation indicates a highly reduced/primary character of the OA in the PM peaks from vehicle emissions. Average OM/OC for the PM peaks produced by traffic activity was lower than that observed for the BB events, agreeing with previous research reporting the trend HOA < BB OA < oxygenated OA (OOA) for this ratio.

In addition to the oxidation state of the OA as characterized by these ratios, the enhancement of specific mass spectrometer mass fragments associated with combustion emissions in the identified peak events was examined. The signals at mass-to-charge ratio (m/z) 43, 55, and 57 have been used as tracers for HOA, and it has been demonstrated that they exhibit strong correlation with markers of combustion emissions such as CO and NO<sub>x</sub>. As other oxygenated species may impact m/z 43 and 55, and their correlation with CO and NO<sub>x</sub> is usually weaker compared with that for m/z 57, m/z 57 has been considered as a more reliable tracer for HOA. An increase in the m/z 57 signal was observed for the entire set of peak events associated with vehicle emissions. The increase relative to background ranged between 0.32 and 2.34 equivalent mass units ( $\mu\text{g}/\text{m}^3$ ), with an average of  $0.79 \pm 0.63$ . The highest value was observed for an event in which two diesel light duty trucks were identified as the responsible sources of the increase in the PM concentration. These results are consistent with observations obtained from analysis of the O/C, H/C, and OM/OC ratios and confirm the primary character of the OA present in the traffic-related PM peaks observed during the DISCOVER-AQ field campaign.

To summarize, PM enhancement events were characterized in detail based on their mass spectrometric characteristics. Task 2 is now considered complete.

Task 3 necessitates sharing of data with collaborators from The University of Texas at Austin (Hildebrandt-Ruiz) and Baylor University (Sheesley); comparison of data also is part of this task. Rice aerosol mass spectrometer data were supplied to collaborators at the end of the 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 reporting period as well, leaving no time to compare between groups and instruments in this time. This comparison will be performed early in the next reporting period.

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 are currently working 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 (model output, airplane data, and state auto-gas-chromatograph data) currently are being considered and evaluated for use. 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.

Task 9 compares *in situ* nitrogen dioxide (NO<sub>2</sub>) measurements with available column measurements. During this reporting period, Pandora NO<sub>2</sub> column retrievals and *in situ* surface data were compared. Directly comparing surface concentrations (*x*-axis) to Pandora column measurements (*y*-axis) indicates a time-dependent relationship, with a larger slope during the middle of the day during peak periods of photochemistry. However, if the *in situ* NO<sub>2</sub> mixing ratio is integrated over the height of the boundary layer, the time dependence disappears, and the strength of this linear relationship improves ( $R^2 = 0.53$ ), though the resulting slope of 0.41 indicates that assuming the NO<sub>2</sub> mixing ratio is constant up the boundary layer height is inappropriate. This relationship will be improved in the future by considering more accurately a realistic vertical distribution of NO<sub>2</sub> in the boundary layer. In the next month, Pandora retrievals will be compared to satellite-based OMI total column during the month of September 2013.

Tasks 10 and 11 use zero-dimensional computer modeling to evaluate ozone production rates and radical sources. To start, a project scientist associated with this project has succeeded in obtaining the NASA Langley photochemical model and running it with data from previous field campaigns to ensure it is operating appropriately on the new computational platform. The next step is 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. Over the next month, efforts will be made to estimate VOC mixing ratios for the mobile laboratory. Output from this model 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**

The only significant problem beyond those associated with the delay in funding is related to the need for more data for continued evaluation of primary particle emissions from mobile sources, as described above. These measurements will be funded by other sources but will be described in a subsequent report as they will complement the efforts described here. The measurements are likely to occur late in 2014 or early in 2015. Other delays (for example, in sharing data) are minor and can be compensated for over the next several weeks.

### **Goals and Anticipated Issues for the Succeeding Reporting Period**

The goals for the next period are to finish Task 3 (data comparison between all collaborators), initiate and complete Task 4 (diurnal profile of PM in Houston), and continue Tasks 6 (characterization of oxidation state and similar metrics for OA using PMF), 8 (characterization of biogenic influence), 9 (column versus *in situ* NO<sub>2</sub> measurements), 10 (modeling of ozone production rate), and 11 (modeling of radical sources).

### **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 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 will be complete by the end of the next reporting period.

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