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**	5/8/2015
REPORTING PERIOD	**From:** April 1, 2015 **To:** April 30, 2015	**REPORT #**	10

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 and 8 through 10 should be complete, and the work for Tasks 7 and 11 should have begun. Tasks 1 through 6 and 9 previously were considered complete; this work was described in previous monthly technical reports. Some further information will be given here for Task 9. Progress on Tasks 7, 8, 10, and 11 also is described here.

Task 7 – Importance of Secondary Processes

The association between ammonia concentration and the levels of sulfate and ammonium in sub-micron particulate matter during DISCOVER-AQ were examined based on ammonia data provided by Dr. Mark Zondlo's group (Princeton University). Periods when the University of Houston (UH)/Rice University mobile air quality laboratory (MAQL) and the Princeton University mobile platform (PU-MP) were co-located were identified, and the spatial variation of the ammonia, ammonium, and sulfate concentrations during these periods were investigated. Expected similar trends for sulfate and ammonium levels are observed, but the association between ammonia and these constituents is not clearly identified due in part to the short period for which the mobile facilities were co-located. As a result, no conclusions can be drawn regarding ammonia impacts from these data.

However, the average spatial variation of the ammonia concentrations collected by the PU-MP during DISCOVER-AQ, and the spatial distribution of the ammonium, sulfate, and sulfur dioxide concentrations obtained by the MAQL can be considered despite periods when the instruments were not co-located. In general, zones with high levels of ammonium and sulfate in particulate matter do not correspond well to zones with particularly high levels of ammonia or sulfur dioxide. However, it is worth mentioning that the instrumentation also had different averaging times.

Further analysis on the degree of association between different trace gases, meteorological variables, and particulate matter constituents was performed through generation of a correlation matrix. The weak resulting correlation between sulfur dioxide and sulfate levels suggests a significant influence of regional transport on the observed sulfate concentrations.

The analysis of correlation described above shows statistically significant association (though not always strong) between most of the aerosol constituents and trace gases; therefore, a preliminary principal component analysis (PCA) was conducted in order to determine independent factors that contribute to the variance in this data set. In addition to examining the correlation between the variables, the feasibility of PCA application on this data set was evaluated by the Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and the Bartlett's test of sphericity. A KMO of approximately 0.7 and a rejected null hypothesis for the Bartlett's test indicated the feasibility of PCA application. Examination of the results indicates that the four first factors should be retained in order to explain approximately 70% of the variability in the data set. The first factor mostly represents sulfate and ammonium concentrations, and the second factor is associated with anthropogenic emissions (significant weights of carbon monoxide, sulfur dioxide, and nitric oxide). The third factor is related to biogenic emissions (isoprene and terpene concentrations from three-dimensional model output (CMAQ) highly influence this factor), and the fourth factor is linked to meteorological conditions. These results indicate that biogenic species influence particulate matter in Houston (12.6% of variance of the third factor) but that anthropogenic species appear to be more significant (combined 45.6% of variance of the first two factors). Both the first and third factors show significant loadings of organic aerosol and nitrate.

This and previous reports have evaluated the importance of secondary organic aerosol (SOA), ammonia to ammonium conversion, nitric oxide to nitrate conversion, and sulfur dioxide to sulfate conversion. The remaining work for Task 7 is to evaluate the relative importance of aerosol liquid water (ALW), values for which have been estimated in previous work. Upon evaluation, the two thermodynamic models used yield similar predictions of ALW but vastly different estimates of aerosol pH; based on recent literature, this work is not the first to observe this. Therefore, remaining work will focus only on the influence of ALW, not on the influence of pH.

Task 8 – Biogenic Influence

The relative influence of biogenic volatile organic compounds on SOA has been evaluated based on location of the MAQL (previous reports) and on PCA, as described in Task 7 above. The relative influence of isoprene on ozone formation is described in the work associated with Task 10 below. Task 8 is now considered complete.

Task 9 – Nitrogen Dioxide Columns

Although this work had been considered complete in previous reports, additional effort was placed on this task in preparation for the DISCOVER-AQ science meeting held in Boulder, CO, in the first week of May 2015. It is still considered complete. One of the students on this project presented work associated with the nitrogen dioxide columns at the science meeting.

Because previous work showed that the OMI satellite has a hard time capturing the spatial variability of nitrogen dioxide in an urban region, a new technique was applied to downscale

OMI data to a finer resolution. This downscaling takes the OMI nitrogen dioxide mass for each pixel and uses CMAQ model output to derive a spatial weighting kernel. Although CMAQ can often over estimate nitrogen dioxide concentrations, it is the relative distribution that matters. The spatial weighting is then used to distribute the nitrogen dioxide measured by OMI at the CMAQ scale. The technique conserves nitrogen dioxide from OMI and does not distribute the mass outside the OMI pixel area.

This technique has been applied in Houston and compared to DISCOVER-AQ Pandora and P-3B measurements. The CMAQ models used include the 4-kilometer UH Air Quality Forecasting (AQF) model and the national AQF center 12-kilometer model. The goal was to improve the Pandora to OMI comparisons. The spatial heterogeneity of nitrogen dioxide in Houston causes comparison mismatches due to the differences in spatial resolution of the measurements. Pandora measures a cone between the sensor and the sun, covering the spatial area of a few kilometers in the early afternoon; OMI measures the average column over a much larger spatial area. This often leads to OMI underestimations in polluted areas and over estimations in rural regions.

To compare to the P-3B spirals, a weighted average of the OMI pixel or downscale grid boxes was taken, depending on how long the aircraft was located within each polygon. Only spirals within two hours of the OMI overpass are considered. Each Pandora was matched to the OMI or downscale polygon in which it was located during that day. Pandora data were averaged ±30 minutes from the OMI overpass

Clouds and the row anomaly from the OMI retrieval drastically limited data during the campaign, especially as flight days were not necessarily correlated with clear OMI retrievals. Most pixels from OMI were located on the edge of the swath.

Improvements observed in the ship channel area (Channelview and Deer Park from the P-3B comparison) were expected, as OMI generally underestimated the nitrogen dioxide in that region. The downscale distributed the expected nitrogen dioxide from the coincident pixels to bring the measurements from the P-3B into better agreement. The Pandora instruments did not observe this improvement. The different footprints of the two measurements make a big difference in the result. Just one Pandora does not capture spatial variability, whereas the P-3B can measure the varying environments within the spiral area.

The results in Conroe show a clear example where errors in model transport also can lead to a huge difference in the result. When modeled and measured winds agree, all aircraft, OMI, and downscale data are in good agreement. However, if model meteorology erroneously transports the Houston urban plume to the Conroe region, the redistribution was significantly incorrect.

Tasks 10 and 11 – Ozone and radical production rate calculations

To summarize previous efforts on these tasks, the MAQL data have been evaluated using the Langley Research Center (LaRC) photochemical zero-dimensional model. The LaRC model is run in a diurnal, steady-state, time-dependent mode. To solve for instantaneous values for ozone formation and destruction, the model takes each time step and runs input data through a diurnal cycle, holding all constraints steady except for photolysis rate constants and nitric oxide, which both change diurnally. Calculated values are accepted if convergence is within 0.5-1% of the initial starting values; from these values, production (F), destruction (D), and net production (P) of ozone are calculated. All chemical reaction kinetic values are taken from published literature.

At a minimum, the model is constrained to ozone, carbon monoxide, nitrogen oxides, methane, and non-methane hydrocarbons. All constraints were measured aboard the MAQL, with the exception of non-methane hydrocarbons. Hydrocarbons were estimated using NASA P-3B data (benzene, formaldehyde, aromatics, and alkenes) and Moody Tower hydrocarbon data (ethane, propane, ethene, alkanes, and ethyne) based on their relationships with nitrogen oxides and carbon monoxide lumped by wind direction quadrants. Isoprene values are not expected to have a relationship with carbon monoxide or nitrogen oxides. Therefore, isoprene inputs were initially taken from CMAQ. In this scenario, isoprene was interpolated in time and space from the hourly CMAQ output files so that input was matched at each location to the closest hour. This scenario is called the CMAQ scenario. A second scenario (ZERO) was investigated in which isoprene mixing ratios were set to zero. A final scenario (P3B) was investigated by making any CMAQ value larger than the maximum value observed by the P3-B equal to the P3-B value at that location. Based on availability of continuous data, the Conroe and Manvel Croix regions have been selected. Data were filtered to consider only times when nitrogen oxides were less than 100 ppbv in order to minimize interference from fresh motor vehicular exhaust plumes while in motion.

The output from the ZERO scenario was shown in the previous progress report and showed values that were consistently too small, despite showing the appropriate diurnal profile. Results for the CMAQ case indicate that F and D rates for ozone (and its individual components) peak just before noon at Conroe but show a significant drop around noon at Manvel (related to meteorology on one of the days simulated). The values calculated (in excess of 100 ppbv per hour) are excessively large. Still, simulated ozone formation from the reaction between hydroperoxy radicals and nitric oxide accounts for roughly half of the overall formation rate, regardless of time of day or location. Non-methyl organic peroxy radical reactions with nitric oxide account for roughly 37%, with methyl peroxy radical reactions making up the remainder.

In general during the da, F exceeds D, indicating a net positive P. Unlike the ozone formation rates, however, the destruction rates of ozone illustrate that the relative contribution of the individual rate components are more variable. At Conroe, D is dominated by nitric acid formation, accounting for roughly 97% of the overall D rates. At Manvel, D is dominated by nitric acid formation only in the mornings, while losses due to specific ozone reactions become more important in the afternoon. Generally, predicted F, D, and P values at Conroe are much higher than that at Manvel.

When P values are compared to levels of nitrogen oxides, both locations show the typical ‘turnover’ of P at higher concentrations, potentially indicating a transition between sensitive and saturated regimes with respect to nitrogen oxides. However, this transition is at a higher concentration than previously modeled in Houston.

As a quick test of the sensitivity of the LaRC output to isoprene, the P3B scenario was run. In this case, more realistic values of F, D, and P (net 20 to 30 ppbv per hour) were found at each location diurnally. Interestingly, the relative importance of various contributors to F and D did not change. This indicates that ozone formation in the Houston region is influenced strongly by biogenic activity.

Now that model output has been defined (that is, the P3B scenario will be used as the base case) and simulation of ozone formation is complete (Task 10), it will be possible to investigate model output with regard to radical formation processes. Again, this will be done using the P3B scenario for the Conroe and Manvel Croix regions. This fulfills Task 11 and will be the focus of work during the next reporting period.

Preliminary Analysis

No additional analysis beyond that described above has been performed.

Data Collected

No new data have 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 major problems were encountered in performing work over this period.

Goals and Anticipated Issues for the Succeeding Reporting Period

Based on the information provided above, all Tasks except Tasks 7 and 11 are complete. Most effort will be placed in these areas. In addition, a draft final report will be submitted, as will a quarterly report. No issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

According to the project schedule, all projects except Task 7 and 11 should be complete (and are). Therefore, we deem our progress appropriate. There should be no problems to complete the work prior to the end of the project.

Submitted to AQRP by: Robert J. Griffin
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