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**	6/8/2015
REPORTING PERIOD	**From:** May 1, 2015 **To:** May 31, 2015	**REPORT #**	11

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, the work for the entire project should be complete. Tasks 1 through 6, 8, and 9 were considered complete previously; this work was described in previous monthly technical reports. Although considered complete previously, additional effort was put forth for Task 10 and is described here. Progress on Tasks 7 and 11 also is described here. During May 2015, considerable effort also was focused on completion of required reporting (monthly report for April 2015, quarterly report for March-May 2015, and draft final report).

Task 7 – Importance of Secondary Processes

Principal Component Analysis (PCA) was applied in order to determine independent factors that contribute to the variance of the data set comprised by aerosol constituents, meteorological variables, and concentration of different traces gases during DISCOVER-AQ. The PCA was applied on the entire data set collected for the Houston area (HA) during the field campaign and on sub-datasets corresponding to the analysis zones previously defined (Zone 1 - Northwest Houston; Zone 2 - Central Houston; Zone 3 - Southeast Houston). Following PCA application, multiple-linear regression analysis based on the absolute principal component scores of the retained PCA factors (APCS) was conducted in order to determine their relative importance in explaining the observed concentrations of particulate matter (PM) during DISCOVER-AQ. In order to remove the correlation between the independent variable in the regression analysis (PM) and the dependent variables included in PCA analysis, the concentration of organic aerosol was removed from the data set and a proxy for its oxidation state (O:C ratio) was included in the group of variables. Factors with eigenvalues in excess of one and jointly explaining at least 70% of the variance in each data set were selected during PCA application, leading to four main components retained in each sub-dataset.

Tables 1 to 4 present the loadings of the different variables in the retained components and the variance explained by each factor in each data set. The four retained factors explain around 70% of the variance in the HA and Zones 2 and 3 data sets, while approximately 78% of the variance in the data set corresponding to Zone 1 is explained by the selected PCA factors. Although the same number of factors was identified in each data set, some variation was observed in the predominant variables in each factor. Table 5 summarizes the variables with large weights in each retained factor for the different data sets under analysis.

Table 1.Rotated PCA factors retained in the entire data set (HA) collected during DISCOVER-AQ and percentage of variance explained by each factor (in parentheses).

Rotated Factor Matrix

	Factor			
	1 (24.7%)	2 (18.3%)	3 (14.4%)	4 (12.2%)
O:C	.088	-.309	.220	-.103
NO_3	.667	.185	-.380	.334
SO_4	.965	.022	.137	-.033
NH_4	.974	.059	.057	.023
T	-.108	.131	.732	-.192
RH	-.118	-.026	-.810	-.121
CO	.143	.681	.027	.217
SO_2	.113	.727	.266	-.162
NO	.029	.852	.033	-.019
Isoprene	.016	.049	.531	.752
Terpene	.094	.067	-.292	.822

Table 2.Rotated PCA factors retained in the data set corresponding to northwest Houston (Zone 1) and percentage of variance explained by each factor (in parentheses).

Rotated Factor Matrix

	Factor			
	1 (29.3%)	2 (21.7%)	3 (19.1%)	4 (8.3%)
O:C	-.562	-.019	-.412	-.268
NO_3	.665	.493	.191	.077
SO_4	-.088	.961	.015	-.080
NH_4	.105	.962	.049	-.032
T	-.883	-.106	.097	.182
RH	.869	.061	-.060	-.251
CO	.209	.237	.399	.586
SO_2	-.248	.073	.890	.091
NO	.118	.003	.910	.083
Isoprene	-.220	-.236	.033	.848
Terpene	.727	-.281	-.083	.206

Table 3.Rotated PCA factors retained in the data set corresponding to central Houston (Zone 2) and percentage of variance explained by each factor (in parentheses).

Rotated Factor Matrix

	Factor			
	1 (32.6%)	2 (16.0%)	3 (11.9%)	4 (9.3%)
O:C	-.102	.083	.018	.851
NO_3	.053	.703	.435	-.144
SO_4	.278	.919	.032	.144
NH_4	.231	.938	.013	.108
T	.632	.138	-.115	.253
RH	-.540	-.151	-.502	-.296
CO	.734	.074	.028	-.083
SO_2	.699	.210	.075	-.070
NO	.790	.112	.009	-.145
Isoprene	.109	-.011	.871	.154
Terpene	-.193	.243	.686	-.272

Table 4.Rotated PCA factors retained in the data set corresponding to southeast Houston (zone 3) and percentage of variance explained by each factor (in parentheses)

Rotated Factor Matrix

	Factor			
	1 (21.0%)	2 (17.2%)	3 (13.8%)	4 (12.2%)
O:C	-.343	-.070	-.582	-.073
NO_3	.729	.199	.034	.458
SO_4	.017	.988	.030	.081
NH_4	.041	.983	.034	.083
T	-.927	.088	.102	.071
RH	.127	-.118	-.032	-.917
CO	-.054	-.013	.619	.225
SO_2	.253	.269	.425	-.122
NO	-.111	-.053	.840	-.002
Isoprene	.430	-.003	.201	.741
Terpene	.564	.077	.418	.011

Variable definitions for Tables 1-4: NO_3 = nitrate, SO_4 = sulfate, NH_4 = ammonium, T = temperature, RH = relative humidity, CO = carbon monoxide, SO_2 = sulfur dioxide, NO = nitric oxide

Table 5. Dominant variables in the retained PCA factors for the different datasets.

Zone	F1	F2	F3	F4
Houston (HA)	SO_4 and NH_4	CO, SO_2 and NO	T, RH	Isoprene and terpene
1-Northwest Houston	T, RH and terpene	SO_4 and NH_4	SO_2 and NO	Isoprene
2-Central Houston	CO, SO_2 and NO	SO_4 and NH_4	Isoprene and terpene	O:C ratio
3-Southeast Houston	T and NO_3	SO_4 and NH_4	CO and NO	RH and isoprene

According to these Tables, Factor 1 in HA exhibits high loadings of sulfate and ammonium (secondary processes leading to PM formation), Factor 2 is dominated by CO, SO_2 and NO concentrations (anthropogenic emissions), Factor 3 is influenced strongly by temperature and relative humidity (meteorology), and Factor 4 exhibits high loadings of isoprene and terpene concentrations (biogenic emissions). The PCA factors in northwest Houston are related to biogenic emissions (Factors 1 and 4), with Factor 1 being influenced by meteorological conditions, secondary processes relevant to PM formation (Factor 2) and anthropogenic emissions (Factor 3). Retained factors in central Houston exhibit high loadings of CO, SO_2 and NO concentrations (Factor 1), sulfate and ammonium (Factor 2) and isoprene and terpene (Factor 3). Factor 4 in Zone 2, which explains ~9% of the variance in the data set (Table 3), exhibits a high loading of O:C ratio and is the only variable with a significant weight in this factor. The PCA factors in southeast Houston exhibit high loadings of NO_3 (Factor 1, which captures the NO_3 dependence on temperature), sulfate and ammonium (Factor 2), and CO and NO (Factor 3). The factors in Zone 3 seem to be less influenced by biogenic emissions as only isoprene is dominant in Factor 4, though it should be noted that the Ship Channel area can be influenced by anthropogenic sources of isoprene.

The coefficients of correlation for multiple-linear regression analysis conducted based on APCS for the different data sets are presented in Table 6. Associated regression coefficients (r) for each retained factor are also included in Table 6. Coefficients of correlation above 0.8 were observed for each data set, indicating that APCS are suitable predictors of the PM levels. As the PCA factors are orthogonal (independent), the relative value of their regression coefficients provides an estimate of their importance explaining the observed PM concentrations in each data set. According to this, the influence of factors in PM concentrations in northwest Houston follows the order secondary processes (SO_2 to SO_4, NH_3 to NH_4) > biogenic emissions > anthropogenic emissions. Relative importance of factors in central Houston follows the order: secondary processes (SO_2 to SO_4, NH_3 to NH_4) > anthropogenic emissions > biogenic emissions. The relative importance of PCA factors in southeast Houston follows the sequence: secondary processes (SO_2 to SO_4, NH_3 to NH_4) > NO_3-related factor > anthropogenic emissions > biogenic emissions.

Table 6. Results of regression analysis based on APCS for the different data sets.

Zone	F1	F2	F3	F4	Constant	r
Houston	4.56	1.49	-0.219	2.41	4.012	0.86
1-Northwest Houston	2.42	3.01	1.45	1.92	8.011	0.80
2-Central Houston	1.51	3.45	1.19	0.17	0.48	0.91
3-Southeast Houston	1.83	1.93	0.32	1.04	10.1	0.93

In addition, as discussed in previous reports, the ISORROPIA-I thermodynamic equilibrium model was used with meteorological and HR-ToF-AMS inorganic PM data collected on the mobile laboratory to estimate aerosol liquid water content (LWC). The three zones described above have been used for comparison of ISORROPIA model output to aerosol constituent concentrations and metrics (for example, atomic ratios such as O:C or hydrogen to carbon (H:C)) from the HR-ToF-AMS by aggregating all available data by zone.

Some chemical constituents of the aerosol had strong correlations with LWC in Zones 2 and 3. Specifically, sulfate and ammonium in Zones 2 and 3 are well correlated with the corresponding LWC (R values between 0.63 and 0.81). It is expected that sulfate and ammonium would have similar relationships given the dependence of ammonium on sulfate. However, none of the chemical constituents correlated well with LWC in Zone 1, despite a larger dataset. The relatively higher chemical mass concentrations in Zone 1 may have contributed to the poorer correlations between chemical constituent concentrations and LWC. Interestingly, bulk organic aerosol concentration is most highly correlated with LWC in Zone 2 ($R = 0.49$), where organic aerosol is, on a relative scale, the least oxidized. No correlations between O:C or H:C and LWC are observed in any of the zones when all data are included. However, the scatter plots indicate that there are subsets of data for which correlations can be observed. Therefore, regressions will be considered for smaller sets of data based on date and hour of day within each zone.

Based on the information provided here, Task 7 is not yet considered complete. All that remains however is to investigate the relationship between organic aerosol factors and LWC and the temporal dependences (date or time of day) of the water-aerosol constituent regressions.

Tasks 10 and 11 – Ozone and radical production rate calculations

Although considered complete previously, the estimation of volatile organic compound (VOC) mixing ratios for the mobile laboratory locations and times was re-evaluated. Previous scenarios included a case in which isoprene was taken from model output (CMAQ), isoprene was set to zero (ZERO), and isoprene was determined based on the P3-B flights (P3-B). Other VOC mixing ratios were determined based on wind direction and other measurements on the mobile laboratory. However, a fourth case was considered in which all VOC mixing ratios were corrected by P3-B data. This case is referred to as the P3B-all scenario and will serve as the base case for the radical production investigation. Data have been segmented by "traffic" and "non-traffic" periods based on location flags for the mobile laboratory. Again, modeling is performed for the Conroe and Manvel Croix areas using the Langley photochemical zero-dimensional model (LARC).

Illustrative model output for Conroe is included here. The P3-B-all scenario leads to an expected diurnal profile for ozone formation, with values for net ozone production on the order of 20 to 40 ppbv per hour when away from periods associated with sunrise and sunset. These values are slightly higher when considering the traffic periods. The formation of ozone is dominated by the reaction of nitric oxide with hydroperoxy radicals and organic peroxy radicals with more than one carbon atom. The loss of ozone is dominated by the reaction of nitrogen dioxide with the hydroxyl radical to form nitric acid.

Now that model input has been defined (that is, the P3B-all scenario will be used as the base case) and simulation of ozone formation metrics is complete, LARC model output with regard to radical formation processes will be investigated. Again, this will be done using the P3B-all scenario for the Conroe and Manvel Croix regions. This fulfills Task 11 and will be complete prior to the end of the project 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. Tasks 7 and 11 will be complete prior to the project's end. A final report will be submitted at the end of the reporting period (June 30, 2015). No issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

According to the project schedule, all tasks should be complete. Nine out of eleven are complete, and the last two will be done prior to project's end. Therefore, we deem our progress appropriate. There should be no problems to complete the work prior to the end of the project.

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