

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
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REPORTING PERIOD	From: March 1, 2015 To: March 31, 2015	REPORT #	9

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 are considered complete; this work was described in previous monthly technical reports, and no further information will be given here. Progress on Tasks 7, 8, 10, and 11 is described here.

Task 7 – Importance of Secondary Processes

The original positive matrix factorization (PMF) analysis of organic aerosol (OA) mass spectral (MS) data collected by an aerosol mass spectrometer (AMS) during DISCOVER-AQ 2013 was expanded to cover approximately the last two weeks of data. Using PMF2 (v. 4.2) and following standard AMS data processing, three-factor solutions were resolved for the periods Week 3 and Week 4 separately (as defined by September 17-21 and September 21-28, respectively). Both three-factor solutions were identified successfully as hydrocarbon-like OA (HOA), semi-volatile oxygenated OA (SV-OOA), and low-volatility oxygenated OA (LV-OOA). Each factor was identified based on their distinct MS patterns and elemental analysis (EA). For example, the primary combustion HOA factor shows characteristic enhancements at mass-to-charge (m/z) of 43 and 57 and at larger alkane fragments. The EA on each PMF factor provides information on its relative oxidation state and chemical composition. Hydrogen-to-carbon ratios (H:C) are inversely proportional to photochemical age, while carbon oxidation state (OSc), oxygen-to-carbon ratios (O:C) and organic-matter-to-organic-carbon (OM:OC) increase proportionately with OA age. The secondary factors SV-OOA (freshly produced, less aged) and LV-OOA (from regional transport, highly aged) exhibit lower H:C and higher oxygen content (OSc, O:C, and OM:OC) than the HOA factor. Volatility decreases with increasing age, which explains the definition of LV-OOA (highest OSc) and SV-OOA (lower OSc). These results indicate successful separation of bulk OA that were sampled on-road and at stationary background sites

into primary OA (POA) and secondary OA (SOA) sources. The average relative contribution of these factors to total OA mass during Week 3 and 4 are 18% (HOA), 63% (SV-OOA), and 19% (LV-OOA), indicating that locally produced SOA contributes a significant fraction to PM₁ OA mass in Houston.

Several standard quality control checks were performed on the PMF solution. Fitting residuals were reasonable based on final fitting parameters and convergence criteria. The time series of the concentrations of each PMF factor were compared against internal (AMS) and external (trace gas) tracers for reality checks. It was found that the HOA factor co-varied with primary combustion tracers such as carbon monoxide (CO) and nitrogen oxides (NO_x) (Pearson R values of 0.45 and 0.44, respectively). Co-variance also was observed between the locally produced, secondary SV-OOA factor and AMS nitrate (NO₃) signal (R = 0.79). As reported previously, the NO₃ signal has been related to organic nitrates. This also is supported by reasonable correlation between SV-OOA and an AMS nitrogen-containing organic fragment (R = 0.37). As such, there is reasonable evidence that SV-OOA in Houston is at least partially associated with organic nitrogen-containing particles generated from nitrate radical or hydroxyl radical/NO_x-initiated chemistry. Finally, the LV-OOA signal shows weak but possible co-variance with 'aged' parameters such as odd oxygen and AMS sulfate (SO₄) (R of 0.53 and 0.67, respectively). The data will likely show better correlation when segregated by space, time, and other parameters; further correlations will be investigated using a three-dimensional PMF that includes particle size.

The PMF model assumes that MS patterns for each physical factor remain constant with time. One of the goals of this factor analysis is to test the validity of this assumption, especially with respect to the spatially and temporally diverse DISCOVER-AQ dataset. The MS patterns for the 3-factor solutions in Week 3 and Week 4 show similar MS patterns as well as similar values and consistent trends in EA parameters (e.g. H:C and O:Sc). The differences between the two sets of PMF solutions at each m/z are relatively small. However, slight differences do exist and will be investigated further.

Diurnal concentration profiles of these PMF factors provide broad information about the characteristics and sources of each factor in Houston. The HOA factor exhibits a strong morning rush hour (7:00-10:00 local) peak and several weaker peaks at approximately 4:00-6:00, 14:00-16:00, and 20:00-23:00 local, indicating significant sources of fresh POA throughout the day in Houston. On the other hand, the more locally produced SOA factor (SV-OOA) shows strong diurnal character, with elevated concentrations during night time. This diurnal profile suggests that a large portion of the less-aged SOA factor is produced by nitrate radical oxidation of volatile organic compounds (VOCs) and is less dependent on photochemistry. The proposed nitrate radical chemistry source of SV-OOA is supported by a similar diurnal night time enhancement in NO₃. The elevated night-time concentrations could also be due to lower temperatures and the semi-volatile nature of the SV-OOA factor. Not only do low temperatures allow the partitioning of SV species into the particle phase, the produced SOA is also less likely to evaporate and decrease in mass. The LV-OOA factor, however, shows strong enhancement during daytime hours, likely due to the dependence of aging and growth processes on photochemistry. The diurnal characteristics described here provide strong validation of the PMF factors resolved from AMS OA measurements, allowing further characterization of both primary and secondary sources of OA in Houston. It should be noted that a combination of stationary and mobile measurements were included in the PMF analysis and that the method is still capable of separating the primary and secondary OA factors with reasonable fit residuals. The evaluation

of co-variance with external tracers, diurnal variation, and spatial variation of the PMF factors help validate this method of combining both stationary and mobile datapoints.

Mean and median values follow similar trends in the diurnal profiles of the factors; thus, spatial diversity in the dataset (for both mobile and stationary measurements) is not expected to greatly bias the qualitative diurnal interpretations. Analysis of the spatial distribution and relative contributions of these PMF factors is presented below. Furthermore, boundary layer heights and other meteorological factors that could bias concentration gradients will be taken into consideration in future analyses.

The spatially based average concentrations of each PMF factor in Houston can be found for Weeks 3 and 4 by dividing and averaging into 1-km x 1-km cells. Average HOA fractions were elevated on major freeways travelled by the mobile laboratory (e.g. Interstate-10, Interstate-45, and TX-1488) and near point source industrial emitters. There are two regions in Houston where the SV-OOA signal is relatively high: 1) in northwestern Houston where significant biogenic VOCs could contribute to SOA production and 2) in southeastern Houston where elevated concentrations of reactive anthropogenic VOCs are expected to produce SOA. The distribution of LV-OOA concentrations in Houston indicates that aged OA is elevated in the northwestern part of Houston and parts of central Houston, both of which are likely due to aged outflow from the city and industrial areas. Detailed back-trajectory analysis will be performed to confirm this hypothesis, especially because aged OA can be transported from regional aged air masses.

Similar methods can be used to determine the spatial distribution of the relative contribution of these PMF factors (that is, a fractional value after normalization by total OA). The HOA signal dominates on most freeways, while the locally formed SV-OOA factor is ubiquitous (on average 53% of total signal) throughout Houston, except regions where primary HOA dominates. Finally, LV-OOA contributions to total OA are important only in regions where both HOA and SV-OOA concentrations are low. These observations indicate that all three PMF have distinct sources that are spatially variable in Houston. The distribution of the fractions of POA (HOA as proxy) and SOA (sum of LV-OOA SV-OOA as proxy) to total OA mass has been analyzed similarly. It should also be noted that identical analyses performed using median values instead of mean values produced similar patterns, indicating that the observed concentration patterns are not greatly biased by extreme events and vehicular plumes.

The analyses presented here help validate the PMF factorization of OA mass spectra into three distinct factors and prove that PMF is a useful tool to help characterize primary and secondary processes contributing to OA in Houston. However, ongoing analysis will be conducted to improve PMF fitting residuals, to potentially resolve more factors (e.g. a biomass-burning factor, an isoprene oxidation factor, etc.), and to rule out rotational ambiguity in PMF solutions.

The specific character (i.e., primary vs. secondary) of the OA and its diurnal variation in the analysis zones defined previously for the Houston area (Zone 1- northwest Houston; Zone 2 - greater central Houston; Zone 3 - east and southeast Houston) was examined based exclusively on stationary-mode measurements collected using the AMS. The zone-based variation of the fraction of POA and SOA represented by the HOA and the sum of the SV-OOA and LV-OOA factors obtained by preliminary PMF analysis has been calculated. The dominant secondary character of OA in northwest and southeast Houston (Zones 1 and 3) is observed, with SOA representing an average of ~93% of OA. The SV-OOA factor is more important than the LV-OOA factor in these zones (62 and 57% of SOA for Zone 1 and 3, respectively). The organic

aerosol in central Houston has a more primary character compared with Zones 1 and 3, although the average composition of OA in this zone still indicates dominant the contribution of SOA (67.1%). The variation of the character of OA in Zones 1 to 3 suggests that different sources and processes are determining the levels of organic PM₁ across Houston, with the central part of the Houston area being more impacted by sources of primary aerosol (e.g., traffic activity) and northwest and east/southeast Houston being influenced by regional transport and VOC emissions (from biogenic and anthropogenic origin) leading to the formation of SOA. Though Zones 1 and 3 exhibit a similar apportionment of the OA, the source of the VOCs participating in the formation of this aerosol fraction is likely different and needs further study.

The diurnal variation of the HOA, SV-OOA and LV-OOA fractions in Zones 1 and 2 has been evaluated. The diurnal variation of PMF fractions in Zone 3 was not considered due to limited data availability for this zone. The fraction of POA in northwest Houston peaks at ~8:00 local time (~23% of OA) during rush hour and remains below 10% during most of the day and nighttime. The SV-OOA fraction exhibits the highest levels at night and in the early morning, reflecting the trends for nitrate observed at the field sites during DISCOVER-AQ (as presented in a previous report), supporting the idea of significant association between this fraction and organic nitrates. The LV-OOA fraction shows a peak during the afternoon hours (~ 13:00 to 18:00 local) corresponding to the period of increased photochemical activity. The fraction of POA in the central part of Houston exhibits two clear peaks corresponding to the morning and evening periods of high traffic activity, during which POA constitutes ~ 30% of the observed concentrations of OA. The SV-OOA fraction in central Houston shows a different trend than that exhibited in the northwest part of Houston, with less marked increase during nighttime. The LV-OOA fraction displays two clear peaks at ~ 11:00 and 13:00 local time with increasing levels at nighttime followed by a decrease in the early morning.

In a previous report, use of the ISORROPIA-I thermodynamic equilibrium model with PM₁ data (SO₄, NO₃, ammonium, and chloride), temperature, and relative humidity to predict aerosol liquid water content (LWC) and hydrogen ion (H⁺) concentration was described. ISORROPIA model output indicates that the median pH (determined from LWC and H⁺) over the entire DISCOVER-AQ campaign was approximately 0.80. This seems exceedingly low, so different methods of thermodynamic equilibrium modeling have been explored by using the Extended Aerosol Inorganics Model (EAIM). Preliminary results from the EAIM model indicate that the median pH over the entire campaign was approximately 1.62. Further analysis of both ISORROPIA and EAIM outputs is being conducted to understand this difference. It will be critical to determine the optimal way of estimating LWC and pH so that such data can be investigated in terms of their effects on partitioning of both inorganic and organic aerosol constituents.

Task 8 – Biogenic Influence

To further investigate the processes leading to the formation of SOA in Houston, the association between biogenic VOC levels and SOA concentration during DISCOVER-AQ was examined. The spatial and temporal distributions of isoprene and terpenes concentrations in Houston were obtained from the Community Multi-scale Air Quality (CMAQ) model. Predicted levels of isoprene and terpenes were below 3 ppbv for the majority of the Houston area. Higher levels of these species were observed in northwest Houston, with concentrations between ~ 5 and 12 ppb. Based on the entire dataset, there were no statistically significant correlations between isoprene concentrations and SOA, SV-OOA, and LV-OOA levels. A moderate degree of correlation was

observed between terpenes concentrations and SOA and SV-OOA levels ($r = 0.60$ and 0.65 , respectively), while only a weak correlation was noted between terpenes concentration and LV-OOA levels.

Considering the high levels of isoprene and terpenes predicted for northwest Houston, specific correlations between concentrations of these species and SOA and SV-OOA concentrations in Zone 1 were examined (focusing only on stationary data). Terpenes concentrations exhibit statistically significant moderate correlation with levels of SOA and SV-OOA ($r = 0.50$ and 0.58 , respectively). Correlation between isoprene concentrations and SOA, LV-OOA, and SV-OOA concentrations was not statistically significant. According to these results, terpenes levels are more likely to impact the formation of SOA in Houston (compared with isoprene concentrations) and might particularly impact the formation of the SV-OOA fraction. This corroborates the theory presented in both earlier reports and this report regarding the impact of monoterpenes on SOA formation through oxidation by nitrate radical. Ozone production from biogenic VOCs is addressed in the next task.

Tasks 10 and 11 – Ozone and radical production rate calculations

The mobile laboratory data were incorporated into the Langley Research Center (LaRC) Photochemical Box Model. The LaRC model was run in a diurnal, steady-state, time-dependent mode. To solve for instantaneous values for ozone formation (PO_3) and destruction, the model takes each time-step and runs input data through a diurnal cycle holding all constraints steady except for the photolysis rate constants (j -values) and nitric oxide (NO) mixing ratio, which both change diurnally. Calculated values are accepted if convergence is within 0.5-1% of the initial starting point. Previously published reaction mechanisms and kinetics are used. At a minimum, the model is constrained to ozone, CO, NO_x , methane, and non-methane hydrocarbons.

All constraints were measured aboard the mobile laboratory 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) and their relationships with NO_x or CO binned by wind direction quadrants. Currently, we have modeled the Conroe and Manvel Croix regions.

The P-3B collected data by spiraling over eight points of interest in the Houston region. P-3B spiral data were subset by point of interest, and each spiral was assigned a wind direction according to the hourly data from TCEQ at the nearest location. Subsetting the data by wind quadrant improves the relationships from CO and NO_x , and the best correlation is chosen for each source region (rural, urban, or industrial/urban).

At Moody Tower, there was an auto-GC running continuously during the DISCOVER-AQ Texas campaign. Similar to the P-3B data, the relationships between hydrocarbons needed for the model were related to the local wind direction. Matching Moody Tower relationships to the points of interest (Conroe and Manvel Croix) was difficult, but the source regions considered were generally the industrial/urban ship channel area, urban Houston (not industrial), and rural. For example, at Conroe, air coming from the ship channel is from a southeasterly quadrant, but at Moody Tower this source region would be classified from northeast-easterly winds. The same logic was applied to Manvel Croix.

Isoprene values are not expected to have a relationship with CO or NO_x as they have different sources. Therefore isoprene inputs are taken from the UH Air Quality Forecast for that time period, which was run using CMAQ, as described above.

In the model, ethane, propane, ethene, benzene, ethyne, and isoprene are all treated explicitly. The rest of the alkenes, alkanes, and aromatics are lumped together into the three groups. Data from Moody Tower in 2010 was used to estimate the fraction of alkenes (propene), alkanes (butane, pentane, hexane), and aromatics (toluene) measured. When looking at Moody Tower data from 2010 with respect to the data measured during DISCOVER-AQ Texas, 66% of alkanes were measured at Moody Tower, 55% of aromatics were toluene, and 48% of alkenes were propene. These ratios were applied to the estimations for alkanes, propene, and toluene determined as described above.

Other inputs to the model include latitude, longitude, time of day, temperature, dew point, pressure, j_{NO2} at nadir and zenith, and ozone column. Only j_{NO2} zenith was measured, and it was assumed that j_{NO2} nadir is 10% of j_{NO2} zenith. Ozone column was taken from the OMPS satellite overpass over the center of Houston.

As stated above, the model was run for Conroe and Manvel Croix data. Data were filtered by NO_x being less than 100 ppbv to minimize interference from fresh car exhaust plumes while in motion. The mobile laboratory sampled for ~3 days at Manvel Croix, collecting 1081 data points for the model. At Conroe, the mobile laboratory sampled for ~10 days, gathering 4988 data points. Conroe has a typical upwind diurnal pattern for ozone formation, destruction, and net production. The peak around solar noon indicates that solar radiation is the driver for the diurnal pattern. In contrast, Manvel has a peak in the late morning due to its closer proximity to the urban and industrial source regions. This shows that the pattern in Manvel is indicative of a balance between the NO_x and VOC morning emissions from rush hour and the increasing solar radiation later in the day. There is an exception around 1pm at Manvel Croix, which is caused by a decrease in solar radiation during one out of the three days measured there (most likely clouds).

Both locations exhibit the typical turnover of PO₃ at higher concentrations of NO_x, indicating a transition between NO_x-sensitive and VOC-sensitive regimes. This transition is at a higher concentration than previously modeled in Houston. Manvel Croix also demonstrates how the pollution environment for ozone production can change from day to day but seems to be mostly dependent on time of day.

Future work will include investigating better hydrocarbon estimations from the ship channel source region, sensitivity analysis of the hydrocarbon estimations (particularly biogenic VOCs to contribute to Task 8), and modeling of additional areas from the mobile laboratory sampling spatial distribution. In addition, we will use these model runs to evaluate radical sources for the same times and locations.

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 major problems for this period have been identified. We are behind on Tasks 8 and 10 but ahead on Tasks 7 and 11 so this balances out. The uncertainty in the calculations of LWC and pH needs to be understood and will be addressed moving forward.

Goals and Anticipated Issues for the Succeeding Reporting Period

Goals include participation in an air quality symposium at the University of Texas in April. In addition, significant progress on Tasks 7, 8, 10, and 11 should be made in April. No issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

Tasks 1-6 and 9 are considered complete. Although we are slated to have completed Tasks 8 and 10 but have not, we are ahead on Tasks 7 and 11, as these activities started ahead of schedule. We believe the progress on Tasks 7 and 11 balances the delays in Tasks 8 and 10; therefore, we deem our progress appropriate.

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