AQRP Monthly Technical Report

PROJECT TITLE	**Sources of Organic Particulate Matter in Houston: Evidence from DISCOVER-AQ data Modeling and Experiments**	**PROJECT #**	Choose an item. 14-024
PROJECT PARTICIPANTS	Lea Hildebrandt Ruiz and Ying Xu (The University of Texas at Austin) Greg Yarwood Bonyoung Koo (ENVIRON) Gookyoung Heo (University of California, Riverside)	**DATE SUBMITTED**	4/8/2015
REPORTING PERIOD	**From:** March 9, 2015 **To:** April 8, 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. I 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

Task 4. Photochemical Modeling

IVOC emissions for the CAMx base case simulation were estimated based on the source-specific emissions data for the 2012 Texas ozone modeling provided by TCEQ and unspeciated fractions of total non-methane organic gas (NMOG) emissions estimated by Jathar et al. (2014).

Table 1 shows NMOG fractions of 3 different combustion source types (gasoline, diesel, and biomass burning) by source sector. These fractions were estimated based on the TCEQ inventory data of the 8 HGB-area counties.

Table 1. Fractions of NMOG emissions by combustion source type

	Onroad	Nonroad	Offroad	Area	O&G	Fires[1]	Unspeciated fraction[2]
Gasoline	88.6%	80.9%	1.7%	-	-	-	25%
Diesel	11.4%	10.1%	40.8%	-	-	-	20%
Biomass burning	-	-	-	1.9%	-	100%	20%

[1] Open burning emission based on NCAR's fire inventory data (FINN)
[2] Unspeciated fraction of NMOG emission (Jathar et al., 2014)

Unspeciated NMOG emissions for these combustion sources were assumed to be IVOC emissions. Since the current speciation profiles were normalized to the sum of the speciated compounds rather than the total NMOG emissions in order to include all of the organic mass in the model, the updated emissions renormalized the speciation profiles to account for unspeciated organics, resulting in reduced emissions of speciated organics (Jathar et al., 2014). Note that NMOG emissions of the area and oil & gas (O&G) sectors are predominantly from fugitive or natural gas combustion sources, which we didn't include in our IVOC estimation due to lack of data. We will conduct sensitivity tests to assess impact of IVOC emissions for these sources.

Figure 1 compares the current vs. updated emissions of the traditional VOC precursors (toluene, xylene, benzene, isoprene, and monoterpenes) and IVOC for the 4-km HGB modeling domain.

Jathar, S.H., Gordon, T.D., Hennigan, C.J., Pye, H.O.T., Pouliot, G., Adams, P.J., Donahue, N.M., Robinson, A.L., 2014, Unspeciated organic emissions from combustion sources and their influence on the econdary organic aerosol budget in the United States, Proc. Natl. Acad. Sci., 111, 10473-10478.

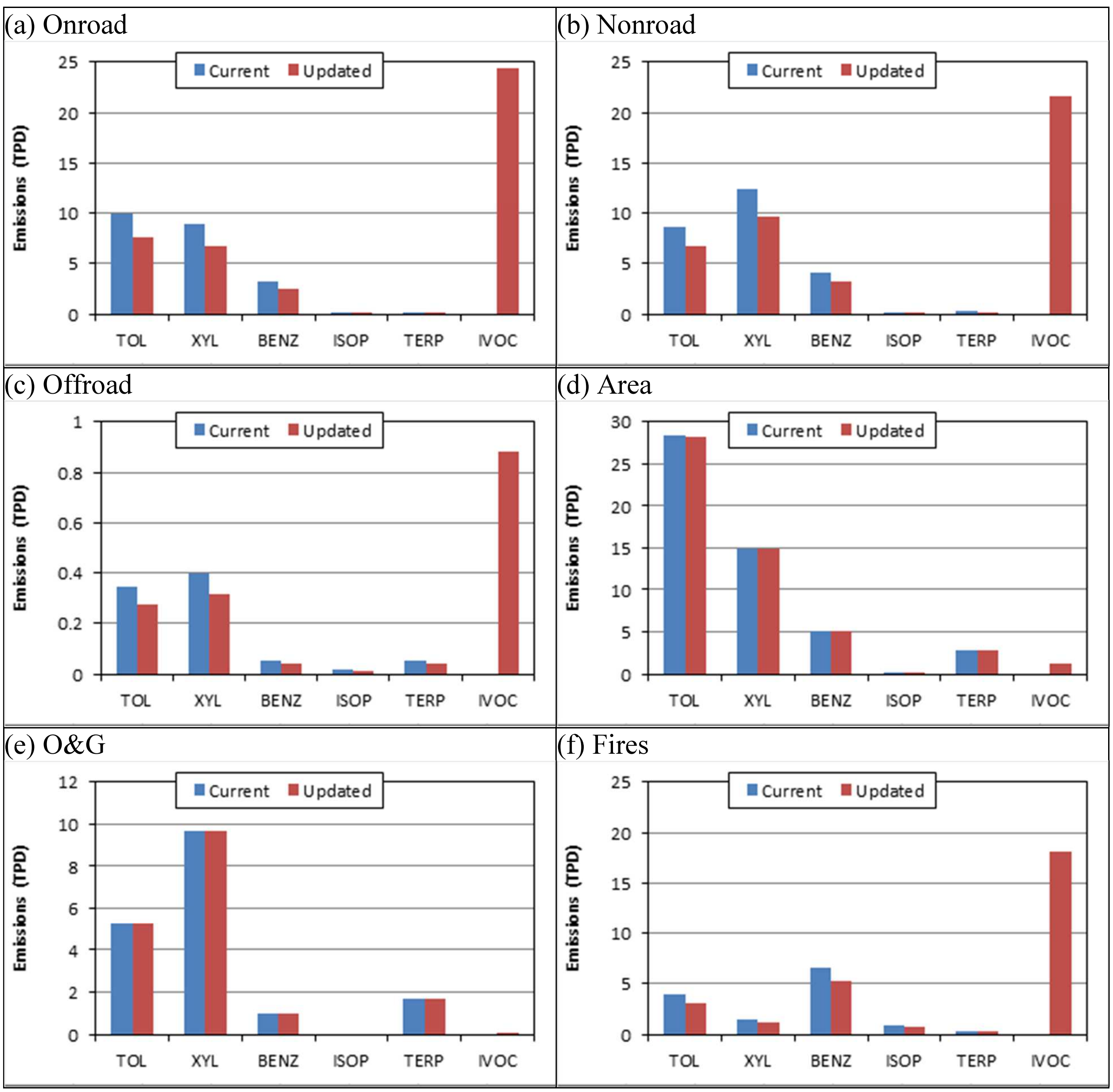
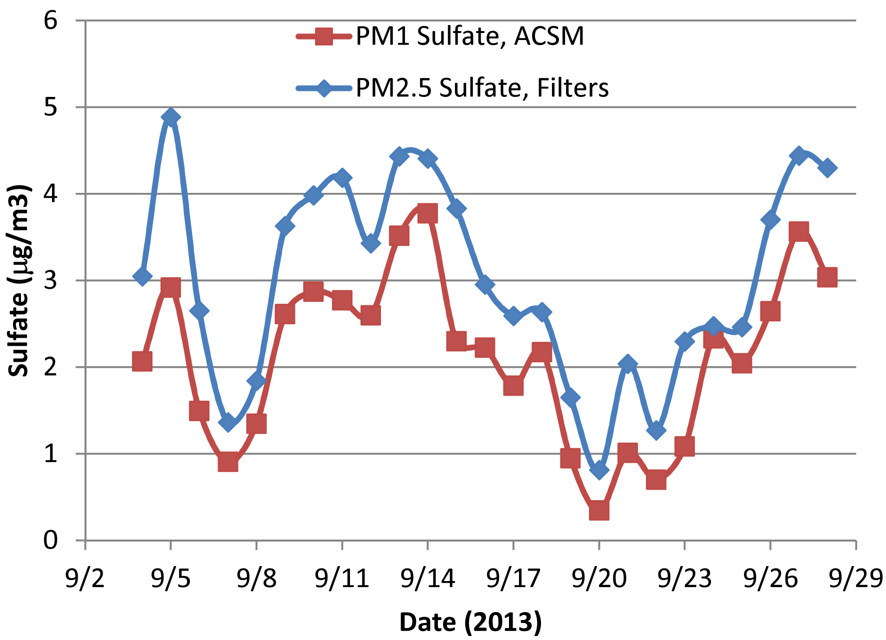


Figure 1. Daily total emissions in the 4-km modeling domain (averaged over September).

Task 5. Discover-AQ Data Analysis

Results from inorganic ion analysis performed by the Dessert Research Institute (DRI) were obtained on April 7. More detailed analysis is undergoing, but Figure 2 below shows two interesting results. In the top panel, the comparison of PM2.5 sulfate concentrations (from inorganic ion analysis) and PM1 sulfate concentration (from the UT Austin ACSM) suggests that concentrations followed the same trend. The higher concentrations from inorganic ion analysis are most likely due to a large size-cut-off (PM2.5) in the filter data. In the bottom panel, a comparison of the "nitrate" data confirms our initial interpretation of the ACMS data that the "nitrate" seen in the ACMS is due to organic; there was very little inorganic nitrate present in these particles.



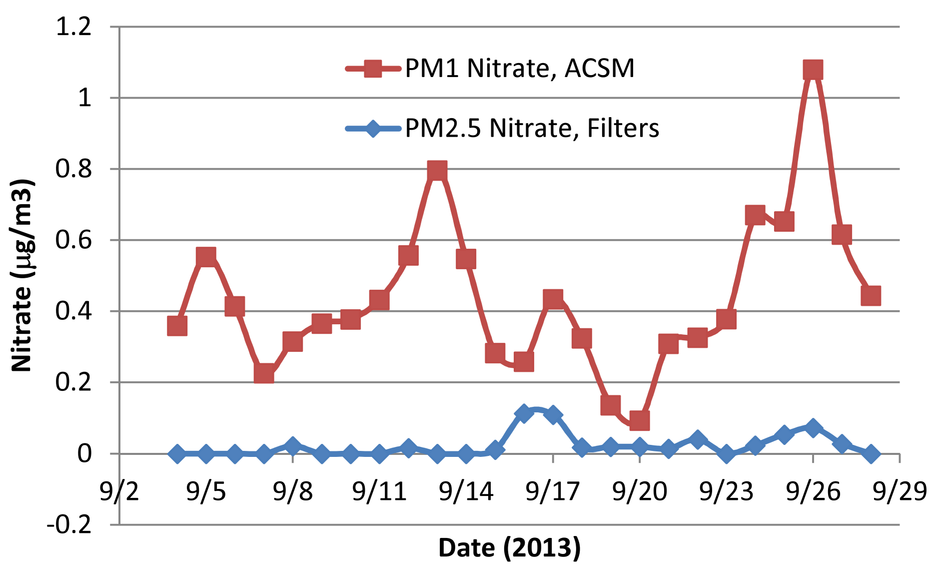


Figure 2. Comparison of PM2.5 filter and PM1 ACSM measurements for sulfate and nitrate (preliminary data)

Analysis of gas-phase data from the High Resolution Time – of – Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) was continued. In order to condense and summarize the information in these data, ions were organized into the following groups: monoacids, diacids, species with 1, 2 or 3 oxygens (but no nitrogen), species with more than 3 oxygen atoms, C5 compounds (no nitrogen), C5 compounds (with nitrogen), C6-C10 (no nitrogen), C6-C10 (with nitrogen). Time series and diurnal cycles of these grouped compounds can now be analyzed. In addition, we intend to perform positive matrix factorization (PMF) on the HR-ToF-CIMS data.

Task 6. Positive Matrix factorization

Positive matrix factorization (PMF) analysis of the ACSM data was completed and revealed contributions from two different types of oxygenated organic aerosol (OOA) : less and more highly oxidized OOA, hydrocarbon-like organic aerosol (HOA), and possibly organic aerosol associated with oxidation of isoprene. Detailed analysis of the results revealed that low signal to noise (S/N) at high mass-to-charge ratios (*m/z*) may dominate the error minimization in the optimization routine. Hence, before quantitative results are reported, the analysis will be repeated removing data at high *m/z* which are anyways subject to low S/N and therefore did not appear to provide useful information.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Task 0. Data Sharing

Dr. Sheesley has informed us of a delay in analysis of the radiocarbon data for collected filters. She now intends to share those data with us towards the end of May. We intend to complete PMF analysis and share results by the end of May.

Task 2. Environmental Chamber Experiments and Box Modeling

Before commencing high NOx experiments we wanted to calibrate our NOx monitor and discovered that it was not performing to specifications. After some trouble shooting with Teledyne API tech support a decision was made to send the instrument to Teledyne for repair. The instrument is now repaired and on its way back to Austin and once it arrives high NOx experiments can commence.

This delay due to the NOx monitor repair is one of the reasons why we requested a no-cost extension of the project until August 31, 2015, which has been approved.

Task 6. Positive Matrix factorization

Detailed analysis of the results revealed that low signal to noise (S/N) at high mass-to-charge ratios (*m/z*) may dominate the error minimization in the optimization routine. Hence, before quantitative results are reported, the analysis will be repeated removing data at high *m/z* which are anyways subject to low S/N and therefore did not appear to provide useful information.

Goals and Anticipated Issues for the Succeeding Reporting Period

Task 2. Environmental Chamber Experiments and Box Modeling

The focus over the next month will be to continue to conduct 2-3 experiments every week in order to evaluate the SOA yields of the IVOCs of interest. The thermodenuder will be operated during some of these experiments to evaluate the vapor pressure of the organic aerosol formed.

Task 5. Discover-AQ Data Analysis

Analysis of the complex data from the HR-ToF-CIMS will be continued. Positive matrix factorization analysis will be attempted.

Task 6. Positive Matrix factorization

Positive matrix factorization of ACSM data will be continued. We anticipate that this analysis will be completed by the end of May.

Detailed Analysis of the Progress of the Task Order to Date

There have been a few delays in the project, primarily due to instruments which needed to be repaired. The recent need to repair our NOx monitor prompted us to request a no-cost extension through August 31, 2015, which has been granted. We do not anticipate problems completing all project tasks and spending all funds by the end of the project period (August 31, 2015).

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