

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	6/8/2015
REPORTING PERIOD	From: May 9, 2015 To: June 8, 2015	REPORT #	12

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 2. Environmental Chamber Experiments and Box Modeling

UT Austin conducted additional environmental chamber experiments to form secondary organic aerosol (SOA) from the photo-oxidation of linear and branched pentadecane using H₂O₂ as OH radical precursor, with and without added NO_x. Tenax sorbent tubes were collected several times during each experiment for quantification of the IVOC concentration. With these data aerosol mass yields can be calculated for these two different IVOCs, but the data are awaiting quality assurance.

Task 4. Photochemical Modeling

Rambol Environ conducted a preliminary model performance evaluation for the CAMx base case simulation of the 2013 DISCOVER-AQ period. Scatter plot of observed vs. predicted hourly ozone concentrations at CAMS sites shows underestimation biases at high observed ozone (> ~70 ppb) while the model tends to overestimate at lower ozone levels (Figure 1). Figure 2 shows an example time series plot of observed and predicted hourly ozone at the Conroe site: The model mostly overestimated observed ozone but underpredicted ozone peaks on September 25 and 26. We are currently preparing a revised base case with adjusted cloud fractions at the 4-km grid cells to improve the model performance. We also evaluated model-predicted inorganic PM_{2.5} components (sulfate, nitrate, and ammonium) using the filter measurement data provided by Dr. Sheesley (Figure 3). The model tends to underestimate PM_{2.5} sulfate and ammonium while predicting much higher PM_{2.5} nitrate than observations. ACSM data (PM₁) implies significant fraction of organic nitrates which is not observed by the filter measurement. We will evaluate model predictions of organic aerosols once organic compound measurement data from UT Austin and Baylor University are available.

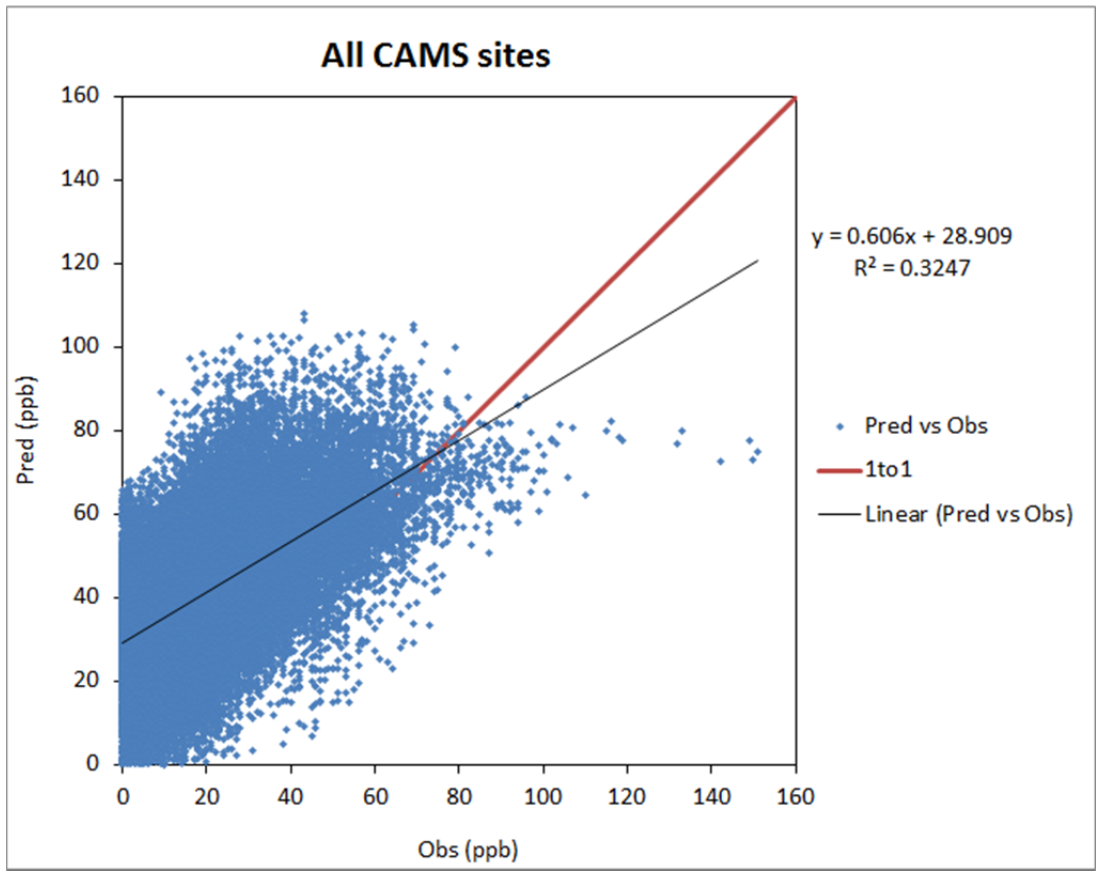


Figure 1. Scatter plot of observed vs. predicted hourly ozone concentrations at the CAMS sites within the 4-km modeling grid.

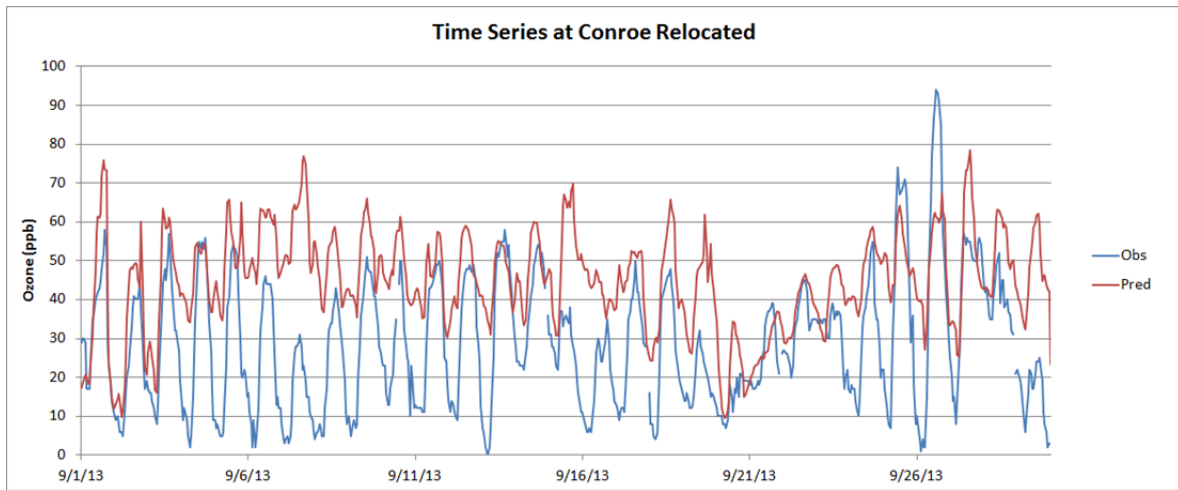
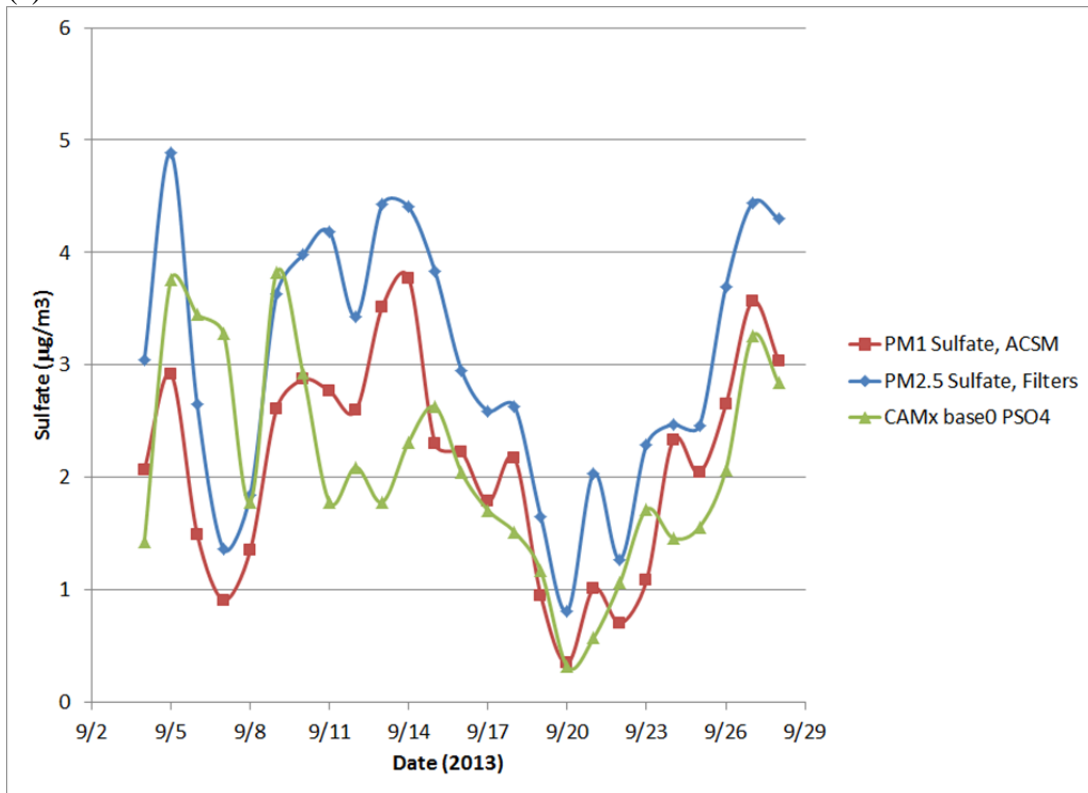
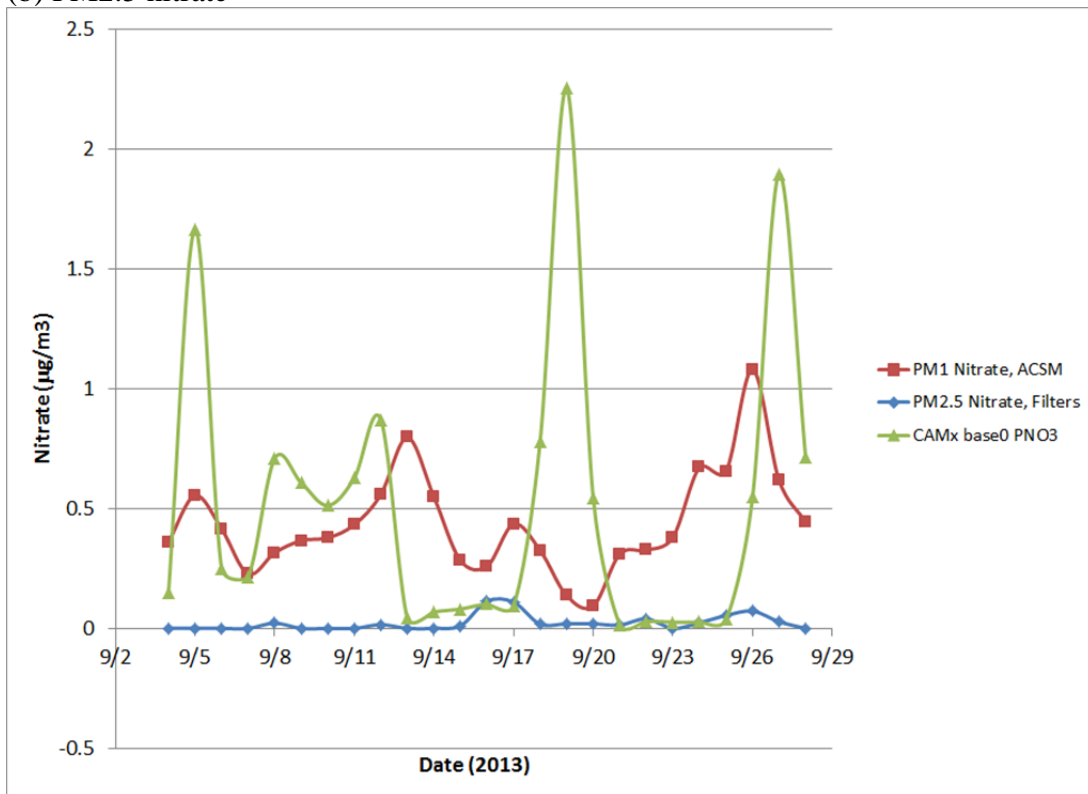


Figure 2. Time-series plot of observed and predicted hourly ozone concentrations at the Conroe site.

(a) PM2.5 sulfate



(b) PM2.5 nitrate



(c) PM_{2.5} ammonium

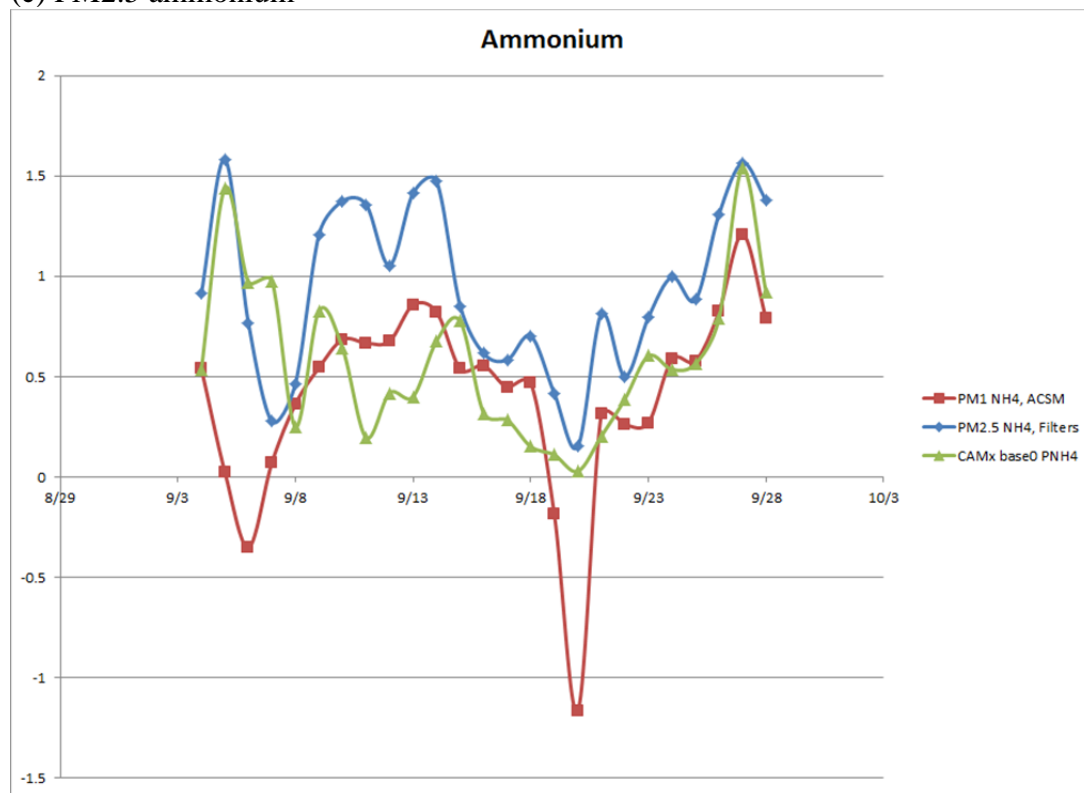


Figure 3. Observed (filter measurement) and predicted (CAMx) 24-hr average concentrations of PM_{2.5} sulfate, nitrate, and ammonium at the Conroe site. Preliminary PM₁ concentrations measured by ACSM are also shown for comparison.

Task 5. Discover-AQ Data Analysis

Quality assurance of the bulk composition and concentrations of PM₁ measured by the ACSM was completed. On average, 72 percent of non-refractory PM₁ (particulate matter smaller than 1 μm in diameter) was organic material, including a high fraction of organic nitrates. There was little diurnal variation in the concentrations of ammonium sulfate; however, concentrations of organic and organic nitrate aerosol were consistently higher at night than during the day. Concentrations of inorganic ions in PM_{2.5} filters collected at Conroe were quantified by the Desert Research Institute (DRI). In general, results from the filter analysis agreed well with concentrations measured by the ACSM (see results in Figure 3 above). Filter analysis results also confirmed that concentrations of inorganic nitrate were very low during the measurement campaign and that nitrate observed by the ACSM was due to organic nitrate species. Final quality-assured data on PM₁ mass concentrations (from the ACSM) as well as results from the inorganic filter analysis were shared with investigators of AQRP projects 14-009 and 14-029.

Task 6. PMF Analysis

UT Austin also conducted positive matrix factorization (PMF) analysis on the aerosol mass spectrometer data collected by the ACSM and on the gas-phase data collected by the chemical ionization mass spectrometer (CIMS) operated with iodide-water cluster ionization. PMF analysis on the ACSM data suggests that the organic aerosol consisted mostly of oxygenated organic aerosol, as expected considering the distance of the measurement site from major

primary sources as well as the high level of photochemical activity throughout the measurement campaign. PMF analysis on CIMS data is ongoing.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

The SEMS instrument (used for measurements of particle size distributions and for quantification of ACSM data) needed to be sent to the manufacturer for repair and returned on June 8. The GC instrument continues to be down and is awaiting repair. Without the GC instrument we are unable to quantify the amount of IVOC consumed in the chamber experiments and therefore cannot quantify aerosol mass yields. We have some data on aerosol mass yields for two of the chosen IVOCs but need to await repair of the GC in order to continue with the laboratory chamber experiments. As soon as the GC is repaired we will make a detailed experimental plan until the end of the project period. Until then environmental chamber experiments will focus on characterizing the organic aerosol volatility using the thermodenuder we developed as part of this project.

Goals and Anticipated Issues for the Succeeding Reporting Period

Task 2. Environmental Chamber Experiments and Box Modeling

Several experiments will be conducted every week in order to evaluate the volatility (vapor pressure) of secondary organic aerosol formed from the photo-oxidation of the IVOCs. Experiments to quantify aerosol mass yields of IVOCs will be restarted as soon as the GC instrument is operating again.

Task 6. Positive Matrix factorization – ENVIRON and UT Austin

PMF analysis on organic aerosol mass spectra measured by the ACSM will be finalized and results will be shared with other AQRP investigators within the next week. PMF analysis on gas-phase data measured by the HR-ToF-CIMS will be continued.

Detailed Analysis of the Progress of the Task Order to Date

There continue to be delays due to instrument maintenance and repair. The project end date has been extended to August 31, 2015. We expect to spend all funds by the end of the project period (August 31, 2015).



Submitted to AQRP by: Lea Hildebrandt Ruiz

Principal Investigator: Lea Hildebrandt Ruiz