

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	7/8/2015
REPORTING PERIOD	From: June 9, 2015 To: July 8, 2015	REPORT #	13

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 IVOCs using H₂O₂ or HONO as OH radical precursor. Experiments were conducted in an excess of propene so that concentrations of OH can be estimated using either the box model or the observed propene decay. The thermodenuder was used in several experiments to measure the mass fraction remaining (MFR) of organic aerosol after heating and vaporization in the thermodenuder. These data can now be used in an evaporation model to quantify the volatility of the organic aerosol.

Task 4. Photochemical Modeling

Ramboll Environ evaluated model performance for the carbonaceous components of PM_{2.5} mass using the DISCOVER-AQ surface measurement data provided by Dr. Sheesley (Baylor Univ.). Figures 1 through 3 compare observed and modeled OC and EC concentrations at the Conroe, Moody Tower, and Manvel Croix monitoring stations. PM_{2.5} carbon mass was measured using the TISCH high volume sampler (HV2.5) and the URG medium volume sampler (MV2.5) at Moody Tower and Manvel Croix while only the high volume sampler data is available at Conroe. OC and EC concentrations were analyzed by the thermal optical transmittance (TOT) technique, which were corrected for positive and negative artifacts based on the Chemical Speciation Network (CSN) data analysis (Malm et al., 2011). Various sampling frequencies were used (3.5 to 24 hours) for the samplers and hourly modeled concentrations were averaged consistently with the measurements.

On average, CAMx overpredicts OC concentrations (mean bias (MB) = 0.03~0.7 $\mu\text{g}/\text{m}^3$) except for the MV2.5 data at Moody Tower (MB = -0.09 $\mu\text{g}/\text{m}^3$) although observed peaks are underpredicted in some cases (e.g., MV2.5 peaks in late September). The model tends to overpredict EC concentrations (MB = -0.003~0.7 $\mu\text{g}/\text{m}^3$).

Daily average fractions of modeled OA components (anthropogenic primary – PAP; biomass burning – PFP; anthropogenic secondary – PAS; biogenic secondary – PBS) are also shown in Figures 1 through 3. The model results indicate that majority of OA mass (60~70%) is oxygenated OA (PAS+PBS).

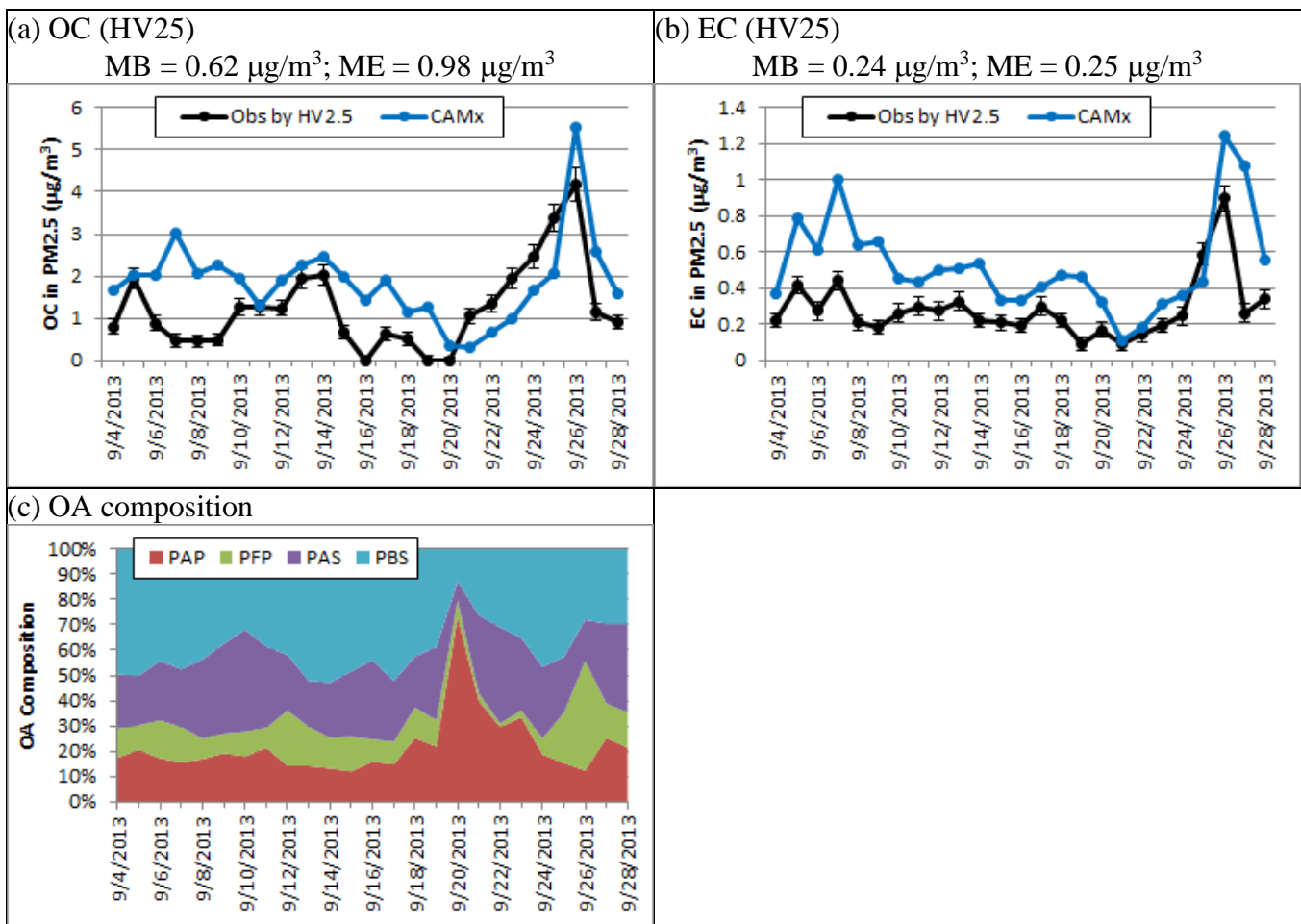


Figure 1. Modeled vs. observed OC (a) and EC (b) concentrations and modeled OA compositions (c) at Conroe during September 2013. Mean bias (MB) and mean error (ME) are calculated over the measurement period.

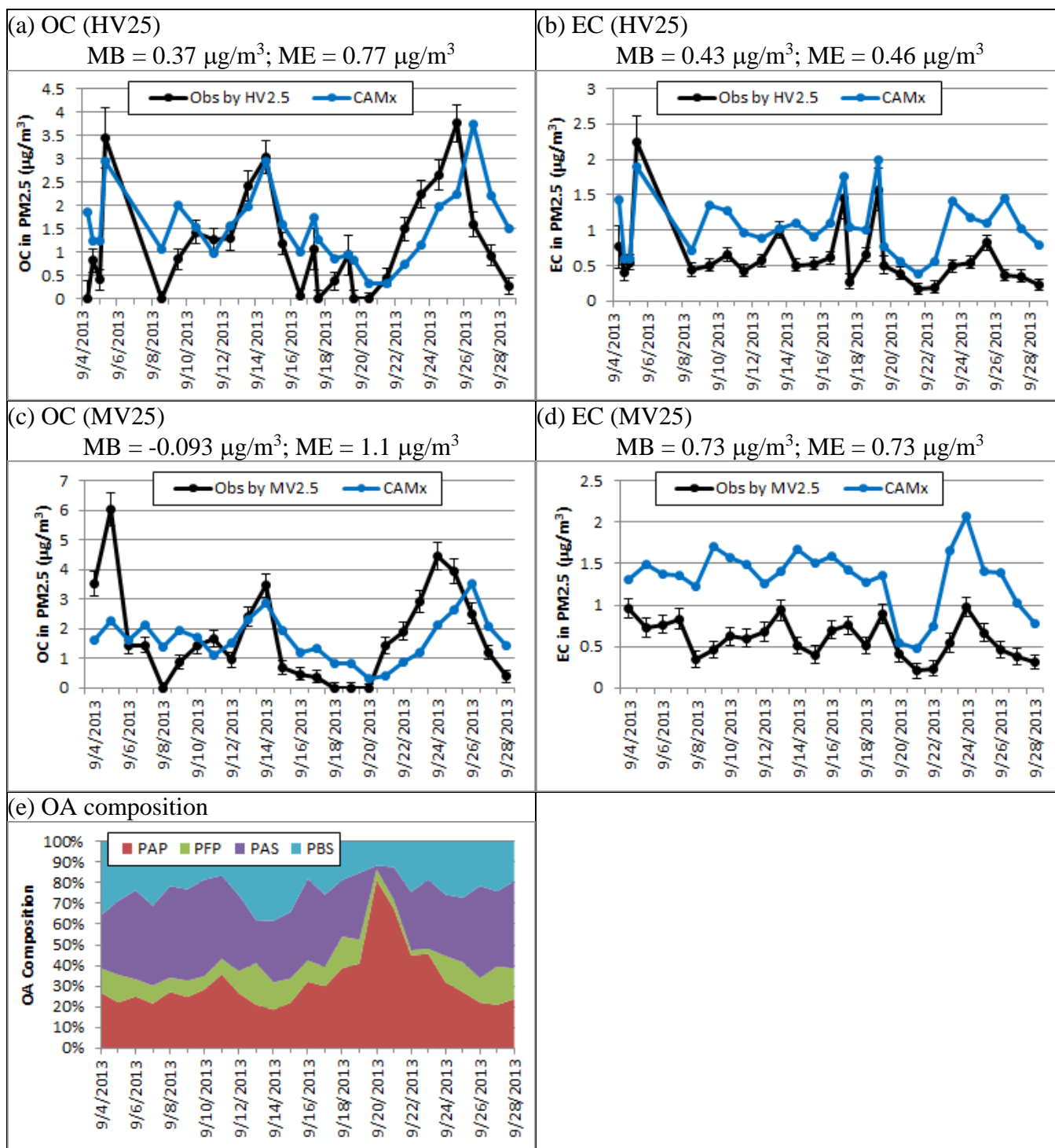


Figure 2. Modeled vs. observed OC (a – HV2.5; c – MV2.5) and EC (b – HV2.5; d – MV2.5) concentrations and modeled OA compositions (e) at Moody Tower during September 2013. Mean bias (MB) and mean error (ME) are calculated over the measurement period.

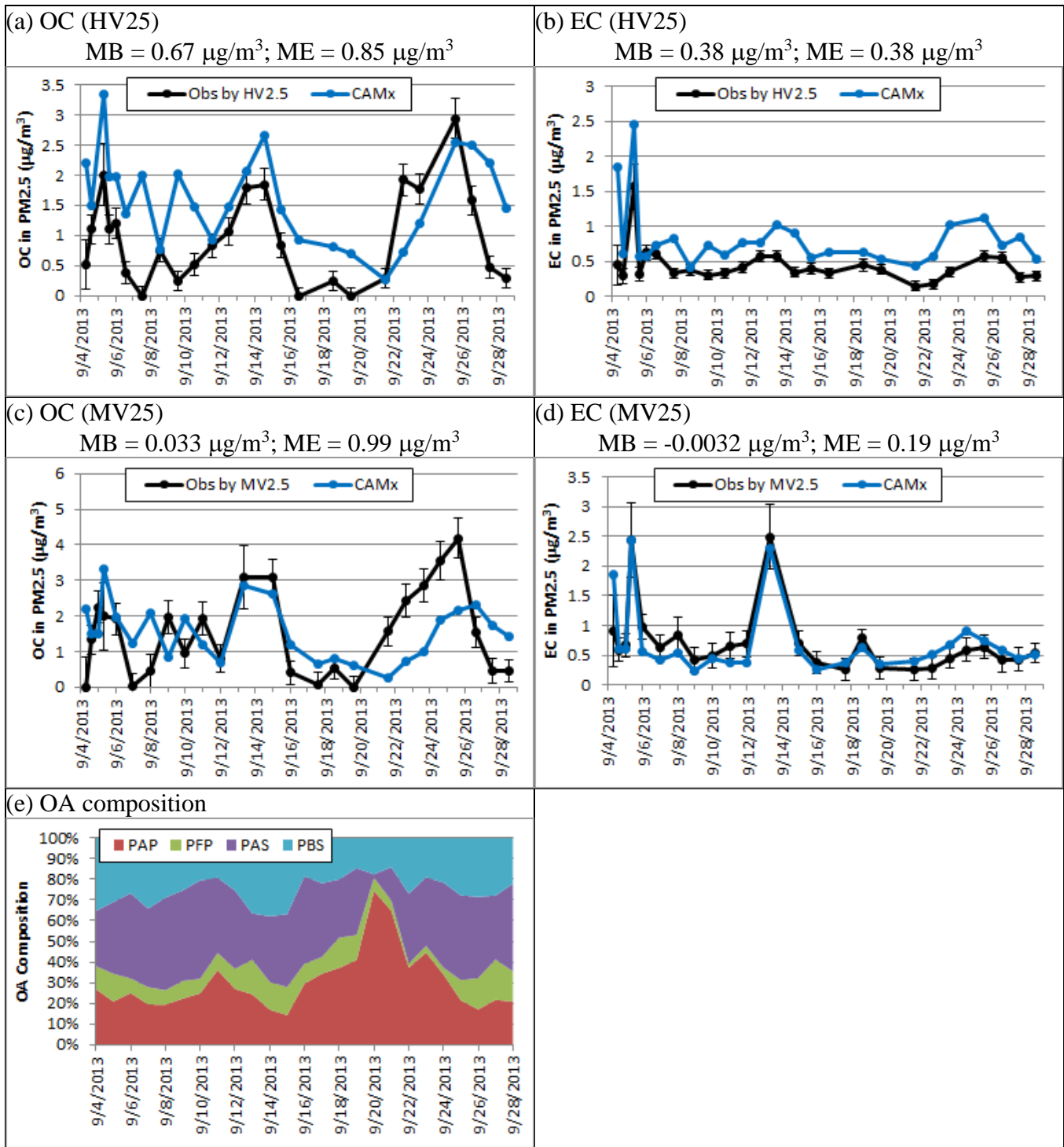


Figure 3. Modeled vs. observed OC (a – HV2.5; c – MV2.5) and EC (b – HV2.5; d – MV2.5) concentrations and modeled OA compositions (e) at Manvel Croix during September 2013. Mean bias (MB) and mean error (ME) are calculated over the measurement period.

Task 5. Discover-AQ Data Analysis

Quality assurance of the bulk composition and concentrations of PM_{10} measured by the ACSM was completed. For bulk composition analysis (organics, sulfate, ammonium, nitrate), every 10

data points were averaged, resulting in a time resolution of approximately 25 minutes (including 12.5 minutes of averaged sample and 12.5 minutes of averaged filter data), and 1607 data points throughout the campaign. (ACSM measurements were taken August 24 – September 30, 2013.) The following detection limits were then calculated according to Ng et al. (2011) and considering the 12.5 minutes sample averaging time: $0.440 \mu\text{g m}^{-3}$ (ammonium), $0.229 \mu\text{g m}^{-3}$ (organics), $0.037 \mu\text{g m}^{-3}$ (sulfate), $0.017 \mu\text{g m}^{-3}$ (nitrate). Application of the detection limits resulted in removal of 82% of the ammonium data, no removal of sulfate data, and removal of 1.2 and 0.6% of the data on organics and nitrate, respectively. Based on mass spectral data the “nitrate” measured by the ACSM was due to organic nitrate species. When ammonium data were available, the mass ratio of ammonium to sulfate was 0.2807 on average, suggestive of acidic aerosol. Since ammonium data were not available for most of the campaign due to low concentrations (and a relatively high level of detection), we estimate that the mass ratio of ammonium to sulfate is the same throughout the campaign to calculate concentrations of ammonium reflected in Figure 4 below.

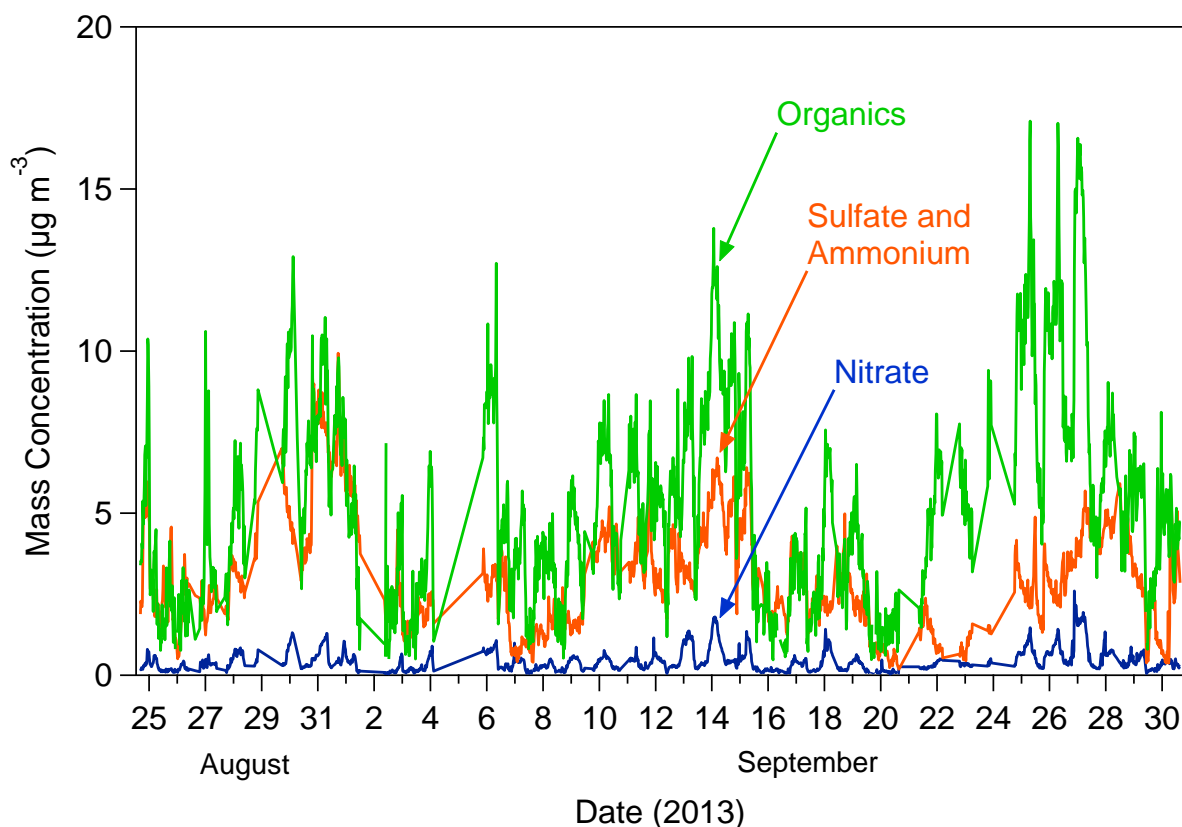


Figure 4. Time series of organics, nitrates, sulfate and ammonium measured throughout the campaign. Measured nitrates were due to organic nitrates.

Figure 5 shows the average diurnal variation of organics, nitrate and sulfate. Analysis of variance (ANOVA) revealed statistically significant variation by time of day for organic and nitrate concentrations ($p < 10^{-16}$), but no statistically significant variation by time of day for sulfate concentrations ($p = 0.77$). This is consistent with a more regional source of sulfate and a more local source of organics and organic nitrates, potentially night-time formation of organic aerosol

from reactions of the nitrate radical with biogenic volatile organic compounds emitted in and near Conroe.

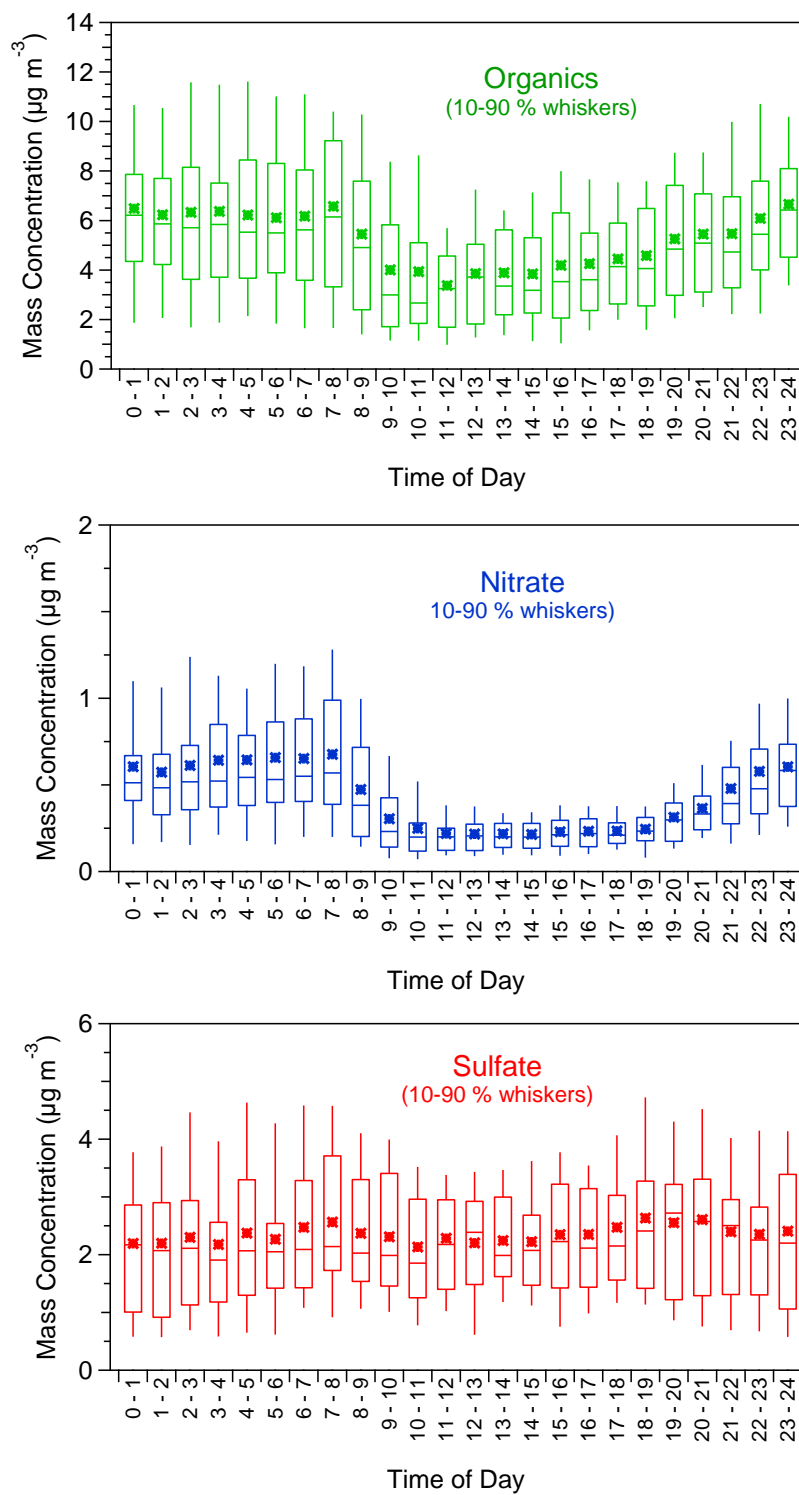


Figure 5. Diurnal cycle of organic, sulfate and nitrate mass concentrations.

Task 6. PMF Analysis

UT Austin conducted positive matrix factorization (PMF) analysis on the aerosol mass spectrometer data collected by the ACSM and identified three factors: hydrocarbon-like organic aerosol (HOA, representative of fresh organic aerosol), less oxidized oxygenated organic aerosol (LO-OOA, representative of moderately processed organic aerosol) and more oxidized oxygenated organic aerosol (MO-OOA, representative of highly processed organic aerosol). These PMF results qualitatively agree with the results of PMF analysis on mass spectrometer data collected at Conroe as part of AQRP project 14-009, which also identified these three factors.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

The GC instrument will not be available for this project until the end of August. Instead of using the GC instrument to quantify the amount of IVOC consumed in the chamber experiments, UT Austin is now conducting all experiments in an excess of propene so that the propene decay or the box model can be used to estimate concentrations of OH. The known reaction constants between IVOCs and OH can then be used to calculate the IVOC decay after correcting for measured IVOC wall losses.

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 mass yields and the volatility (vapor pressure) of secondary organic aerosol formed from the photo-oxidation of the IVOCs.

Task 6. Positive Matrix factorization

PMF analysis on organic aerosol mass spectra measured by the ACSM will be finalized and diurnal variation of the factors will be evaluated.

References

Malm, W.C., Schichtel, B.A., Pitchford, M.L., 2011, Uncertainties in PM_{2.5} Gravimetric and Speciation Measurements and What We Can Learn from Them. *J. Air & Waste Manage. Assoc.*, 61, 1131-1149.

Ng, N. L., Herndon, S. C., Trimborn, a., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L. and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, *Aerosol Sci. Technol.*, 45(7), 780–794, doi:10.1080/02786826.2011.560211, 2011.

Detailed Analysis of the Progress of the Task Order to Date

The project end date has been extended to August 31, 2015. While UT Austin needed to change experimental techniques as explained above, we expect to complete all project tasks and spend all funds by the end of the project period (August 31, 2015).



Lea Hildebrandt Ruiz

Submitted to AQRP by: Lea Hildebrandt Ruiz

Principal Investigator: Lea Hildebrandt Ruiz