AQRP Project 14-024

Sources of Organic Particulate Matter in Houston: Evidence from DISCOVER-AQ data, Modeling and Experiments

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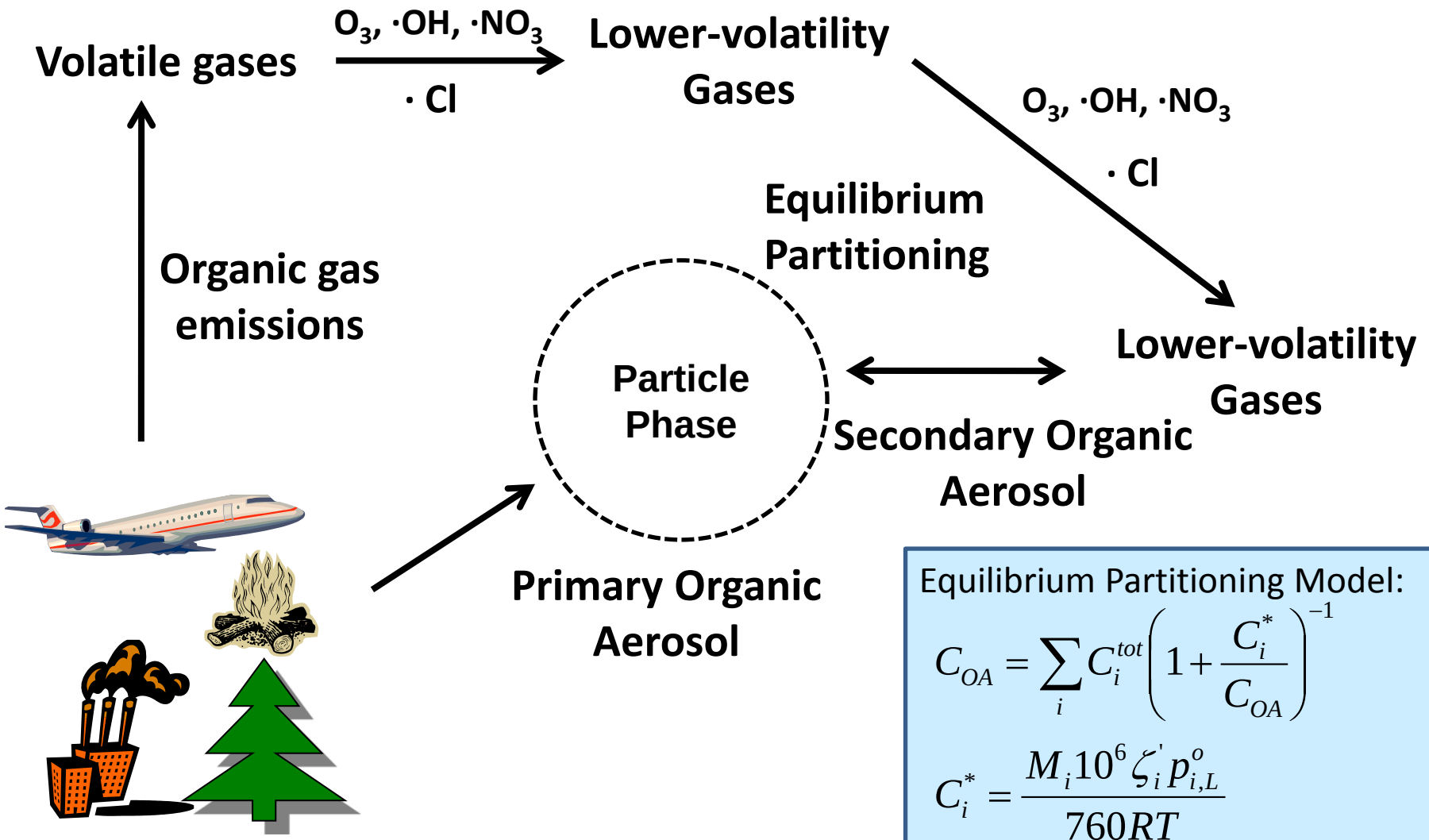
June 18, 2015

Organic Aerosol (OA) in the Atmosphere



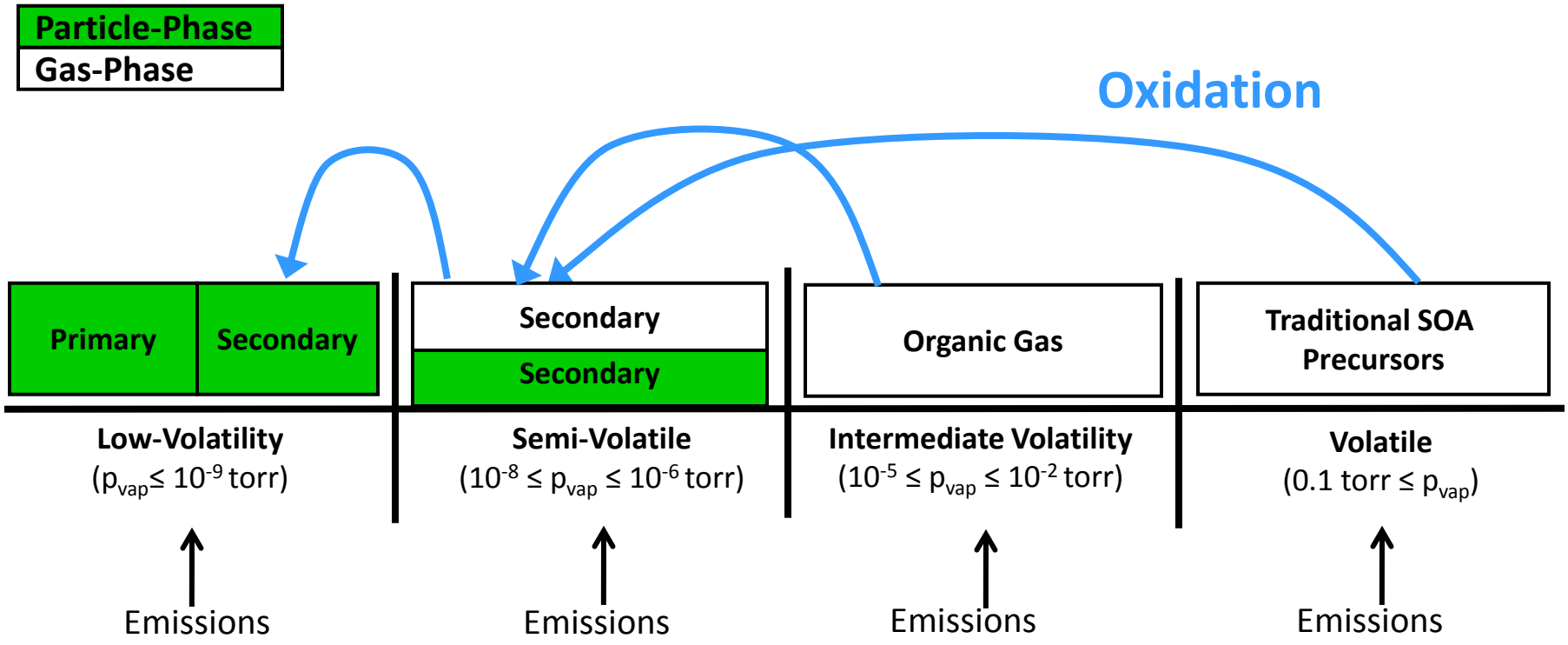
Equilibrium Partitioning Model:

$$C_{OA} = \sum_i C_i^{tot}\left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

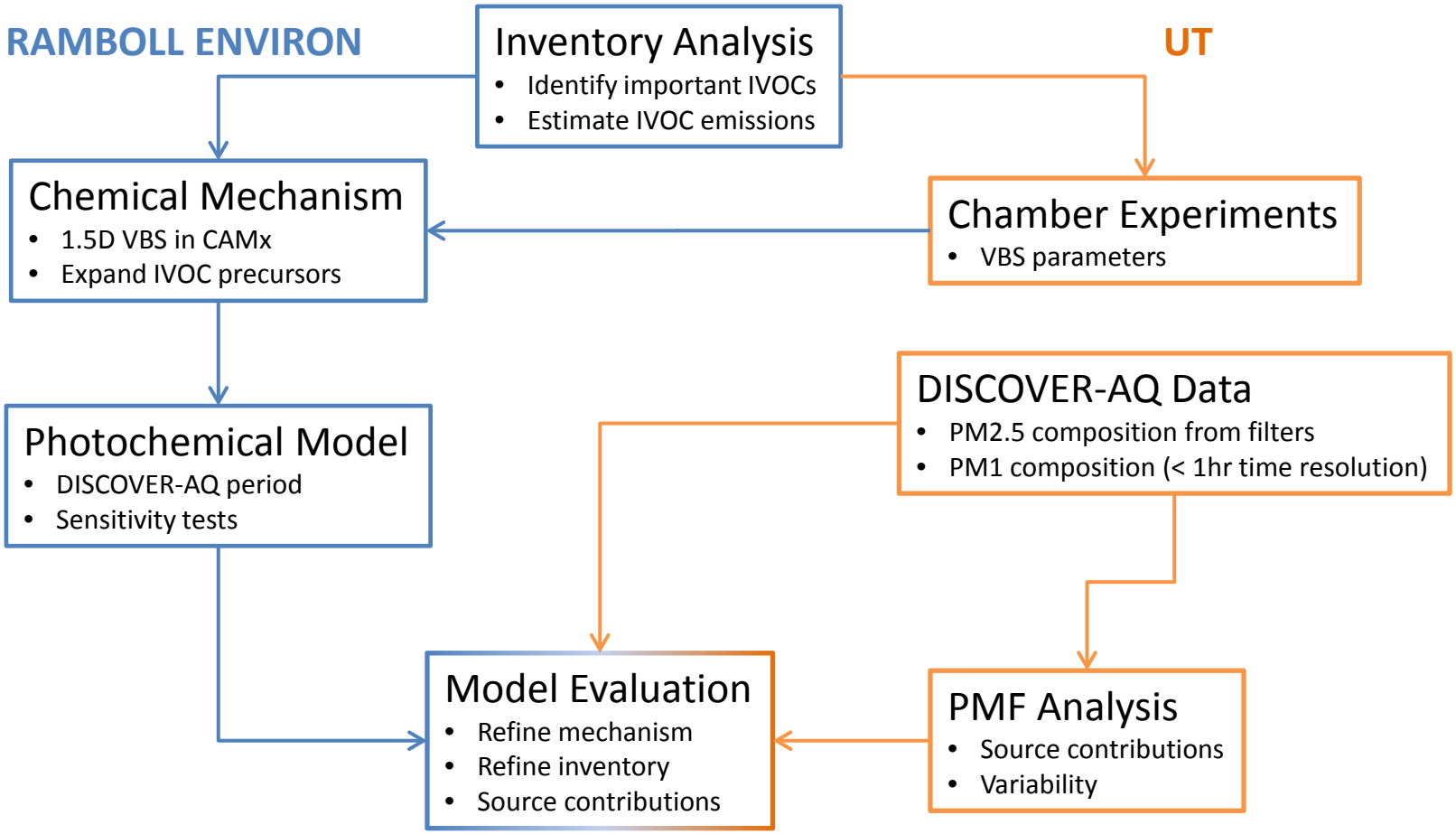
$$C_i^* = \frac{M_i 10^6 \zeta_i' p_{i,L}^o}{760RT}$$

$i \equiv$ organic species

OA in Chemical Transport Models



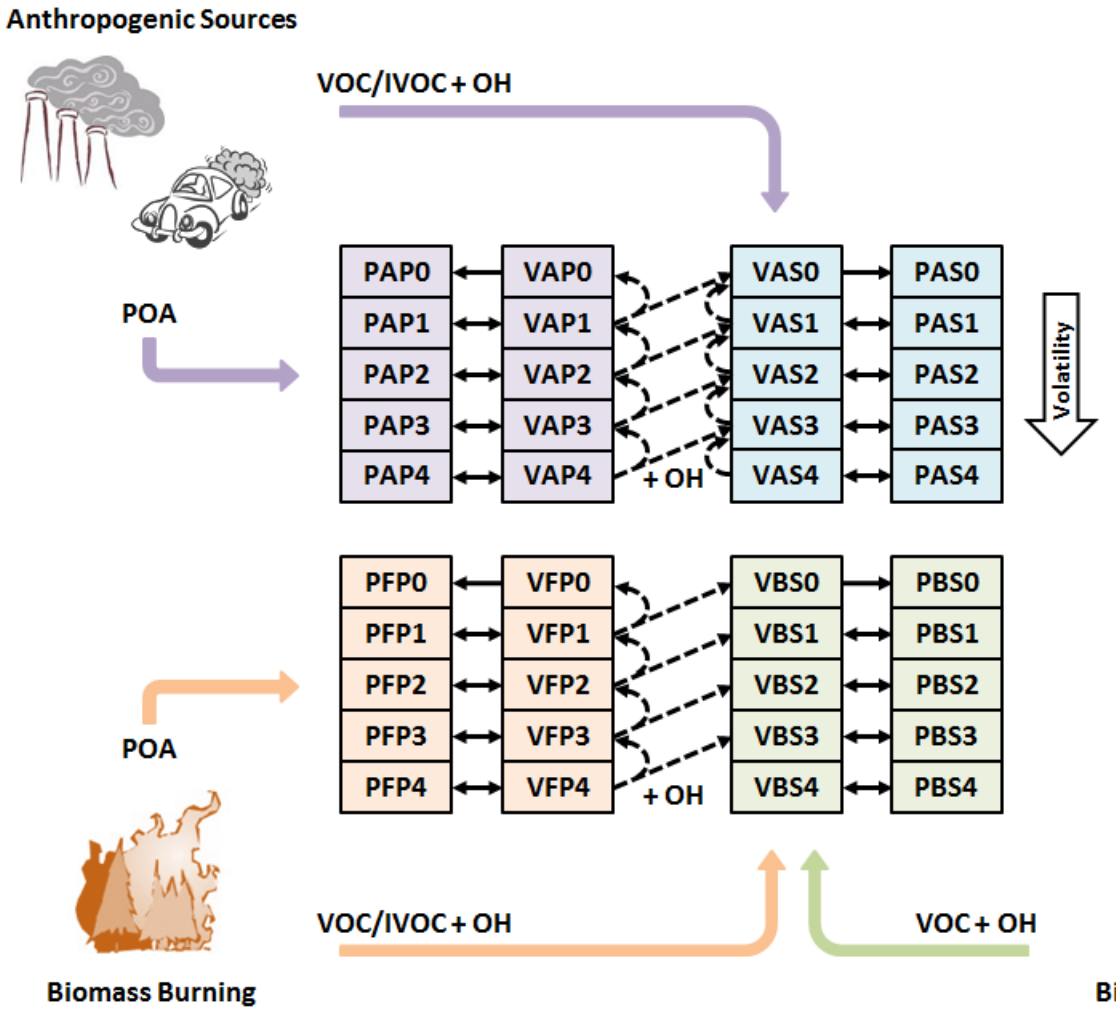
Overview of Study



3-D Grid Model Simulation

- DISCOVER-AQ period (September 2013) with 10-day spinup
- Modeling grids
  - 36-km continental US
  - 12-km entire Texas
  - 4-km Houston region
- CAMx V6.20 with CB6r2 & 1.5-D VBS
- Met inputs modeled by WRF
- Latest TCEQ 2013 emission inventory with estimated IVOC emissions

1.5-D Volatility Basis Set Model



4 basis sets to describe varying degrees of oxidation in ambient OA:

- Hydrocarbon-like OA (HOA) → PAP
- Biomass Burning OA (BBOA) → PFP
- Oxygenated OA (OOA) → PAS & PBS

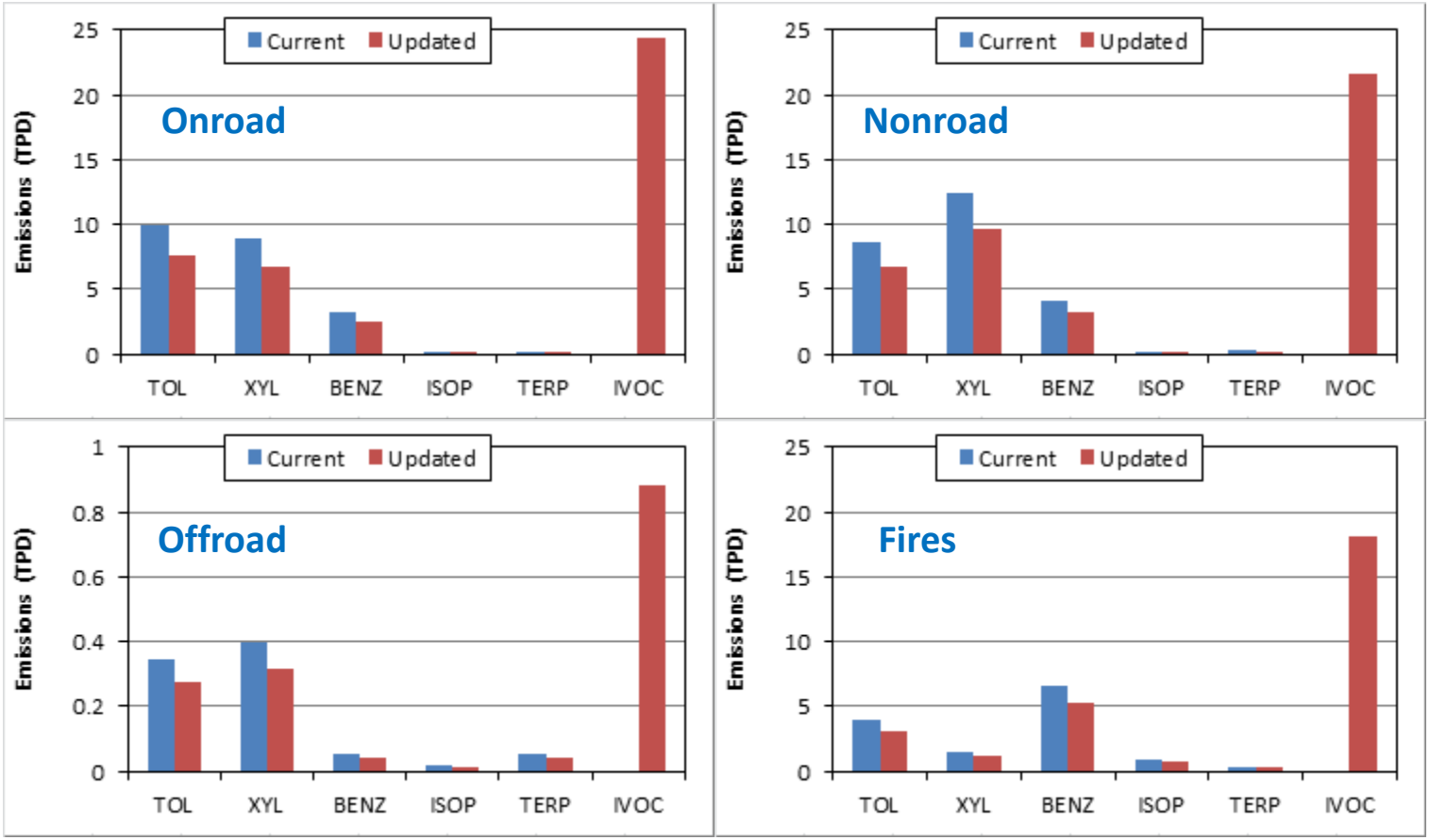
Estimation of IVOC Emissions

- IVOC emissions estimated based on unspeciated fractions of total NMOG emissions
  - Recent chamber study[1] estimated unspeciated NMOG fractions for 3 major combustion sources:
    - Gasoline engines (25%)
    - Diesel engines (20%)
    - Biomass burning (20%)
  - Speciated organics in the current inventory need to be renormalized to account for the unspeciated fractions
- Initial base case simulation did not include IVOC emissions from other sources (e.g., fugitive emissions)

[1] Jathar et al., Proc. Natl. Acad. Sci., 111, 10473-10478, 2014

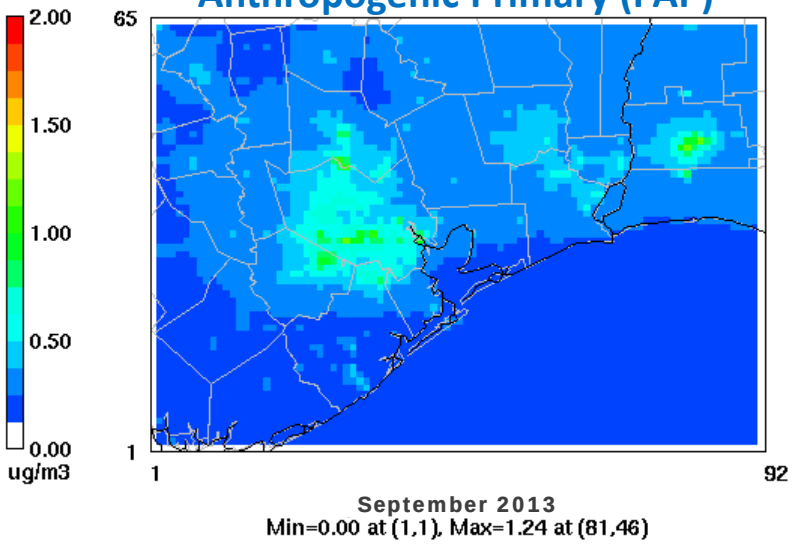
Updated Emissions

4-km domain total emissions

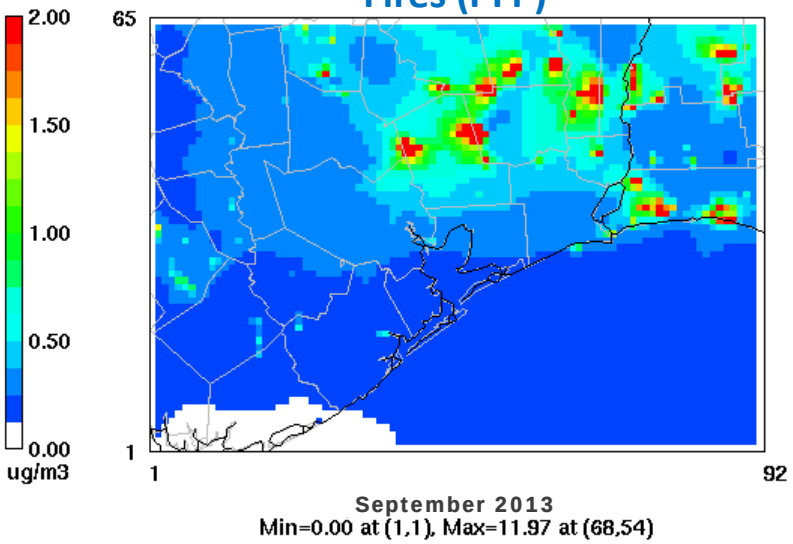


Model Results – Episode Average OA

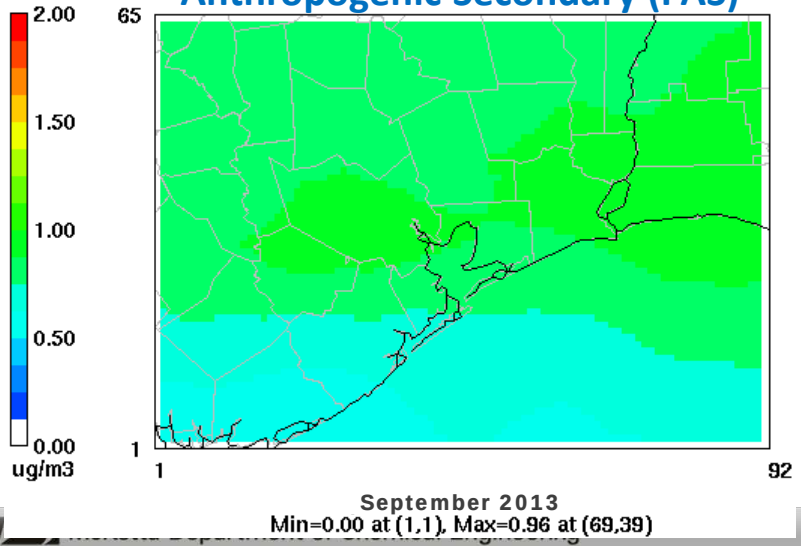
Anthropogenic Primary (PAP)



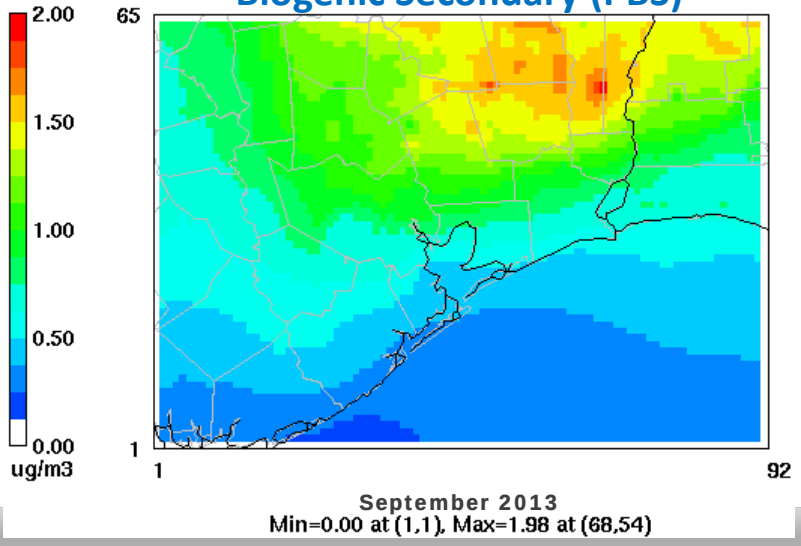
Fires (PFP)



Anthropogenic Secondary (PAS)

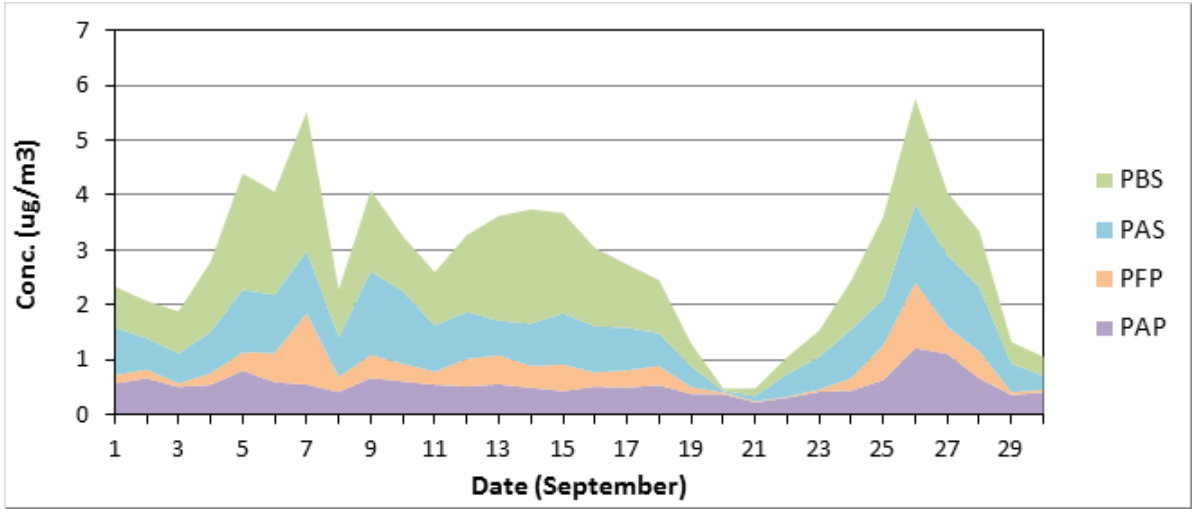


Biogenic Secondary (PBS)

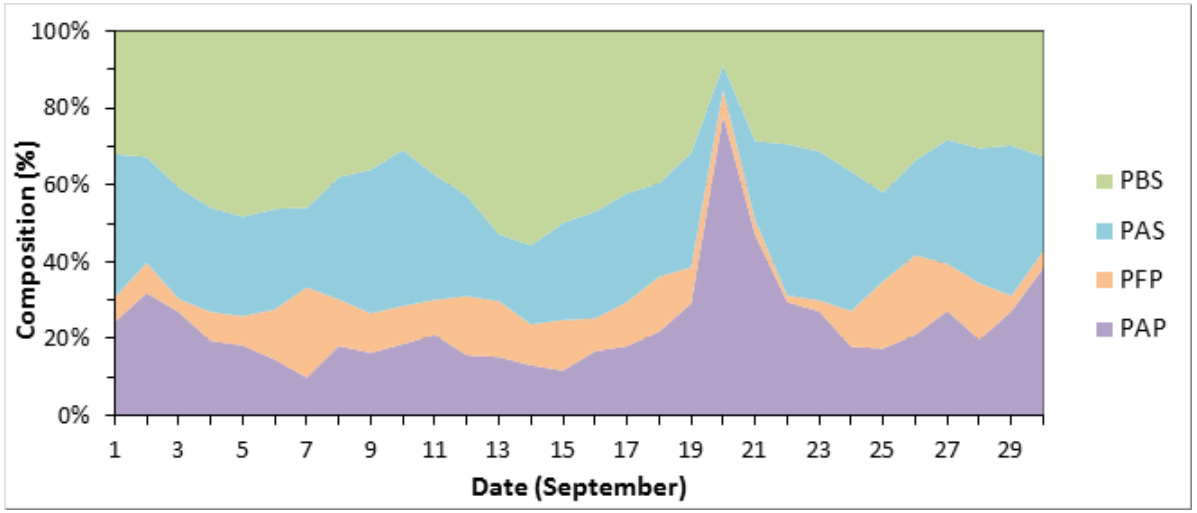


Model Results – Conroe

Daily Average Concentration

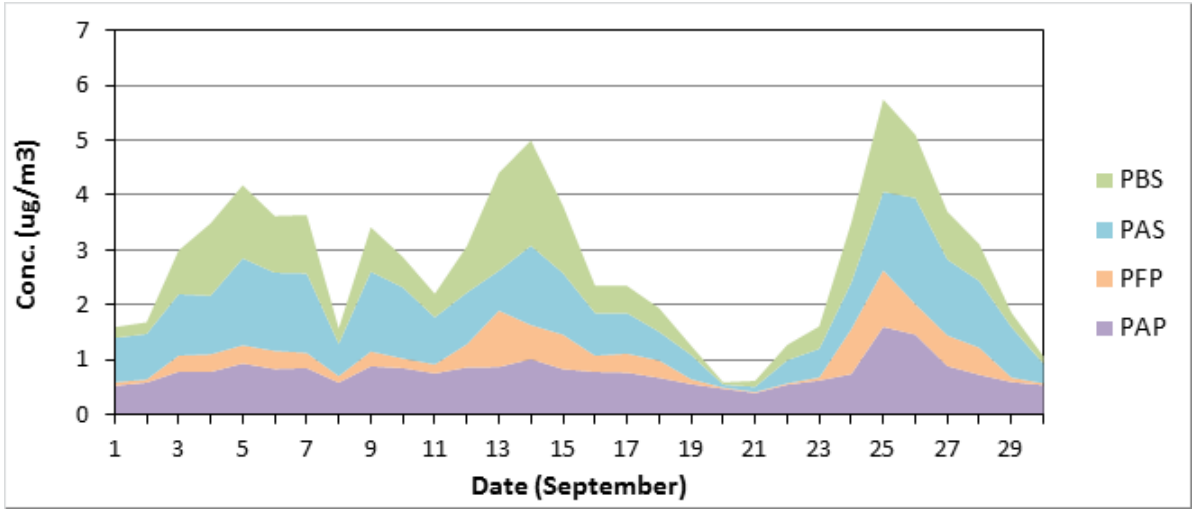


Composition

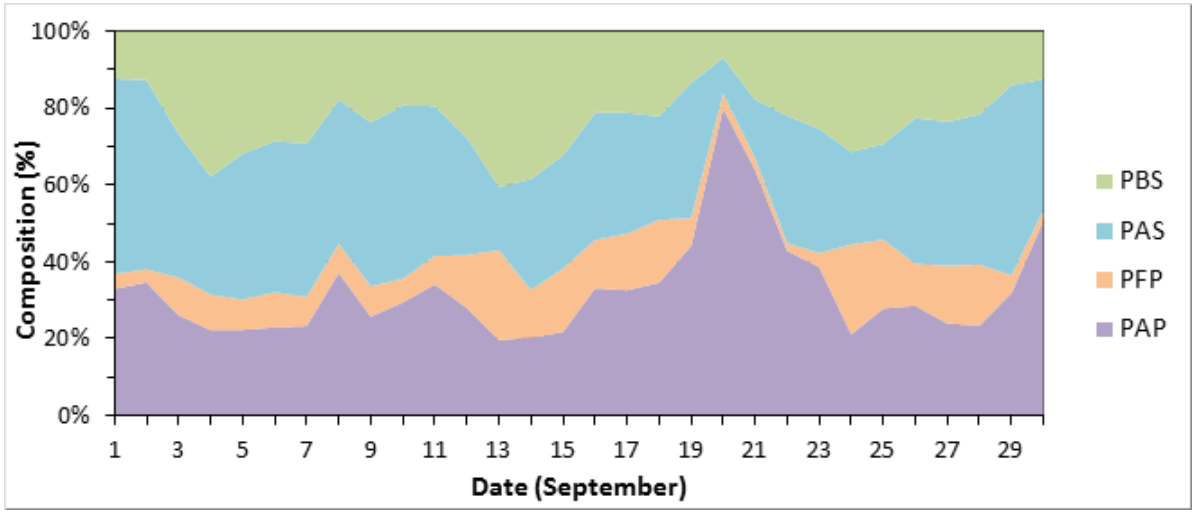


Model Results – Clinton Dr.

Daily Average Concentration

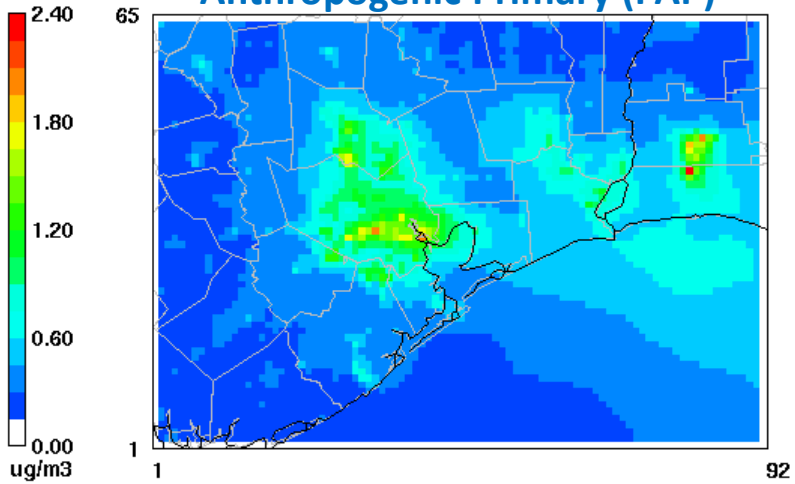


Composition



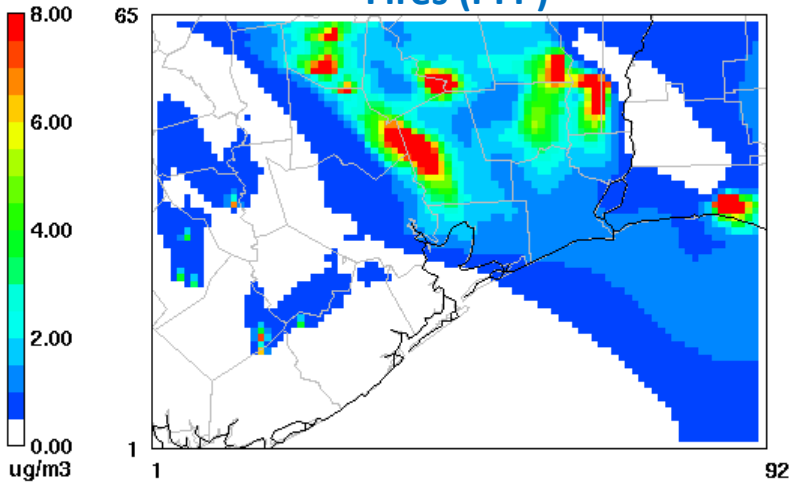
Model Results – September 26

Anthropogenic Primary (PAP)



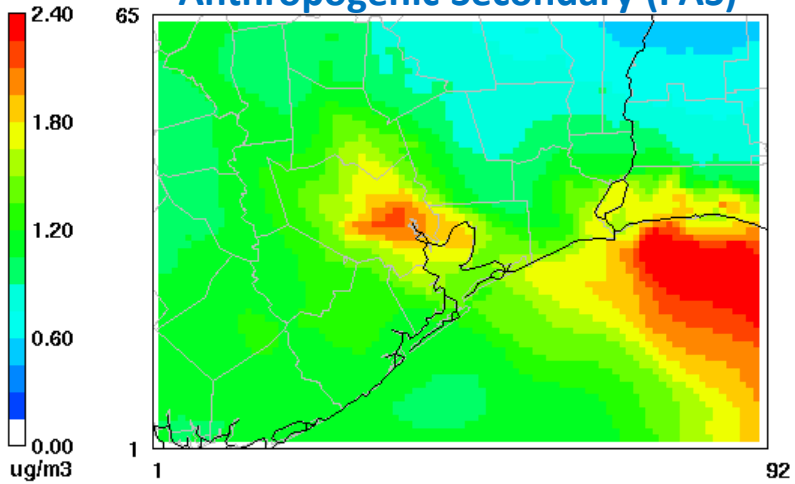
September 26, 2013
Min=0.00 at (1,1), Max=2.38 at (81,42)

Fires (PFP)



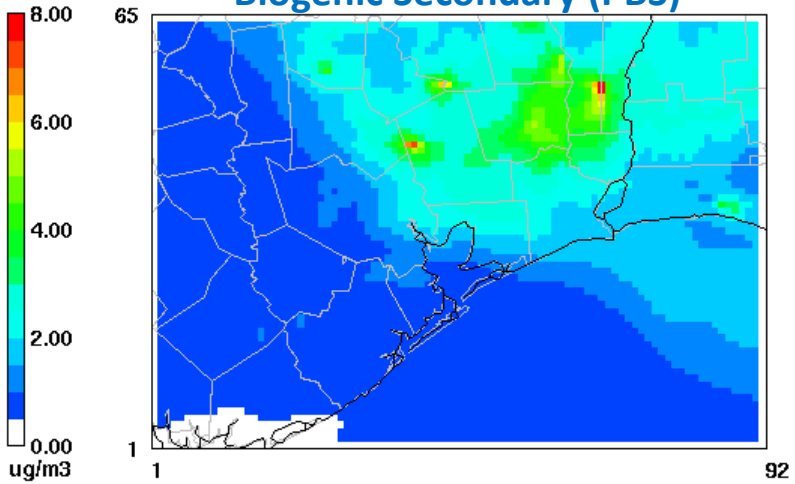
September 26, 2013
Min=0.00 at (1,1), Max=139.95 at (40,46)

Anthropogenic Secondary (PAS)



September 26, 2013
Min=0.00 at (1,1), Max=2.48 at (77,29)

Biogenic Secondary (PBS)



September 26, 2013
Min=0.00 at (1,1), Max=8.97 at (68,55)

DISCOVER-AQ measurements in Conroe - Overview

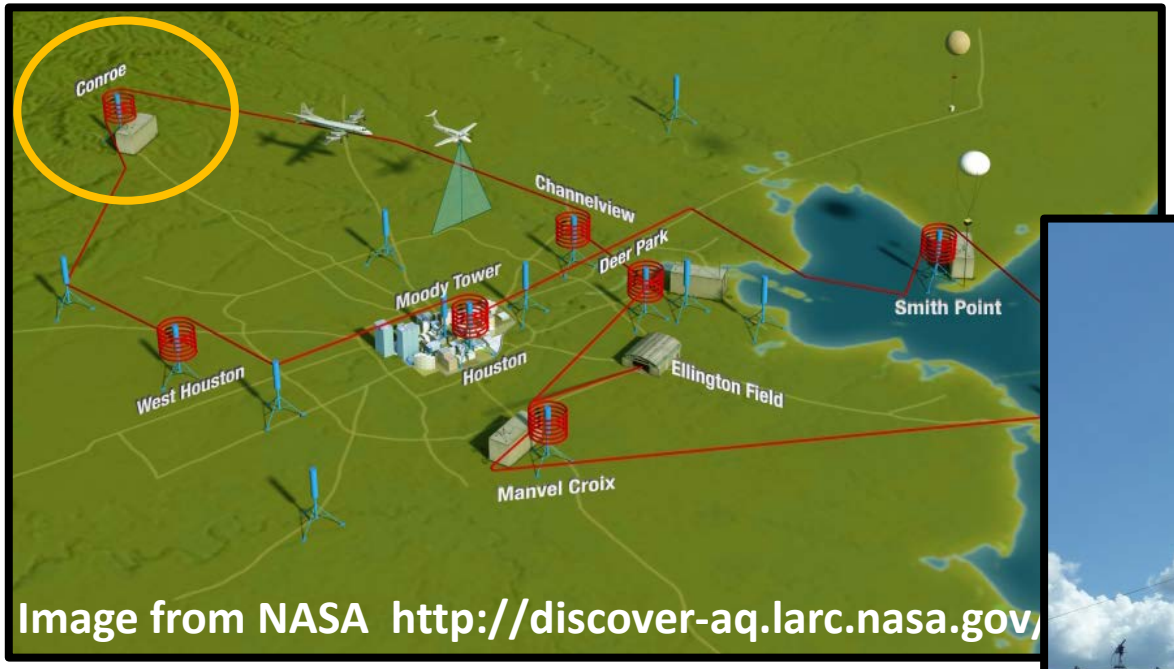
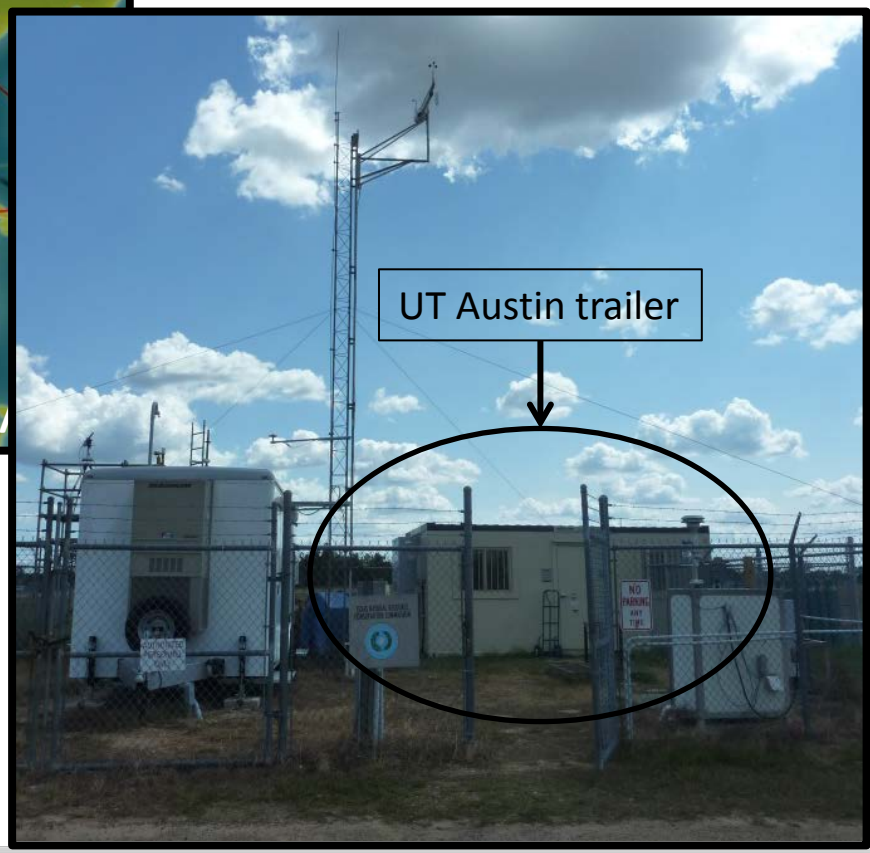
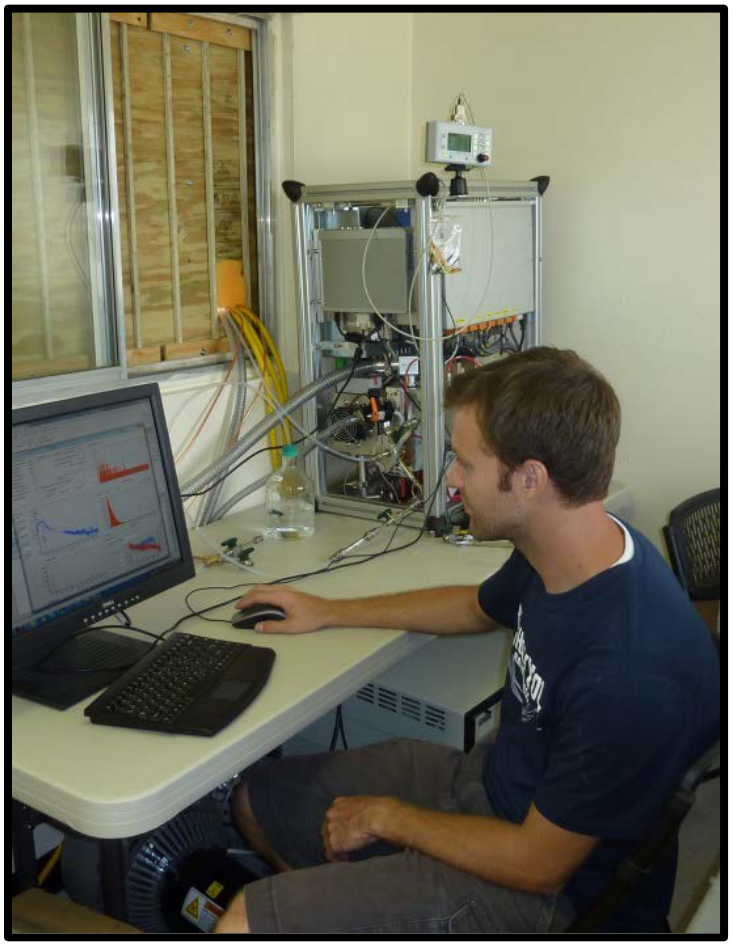


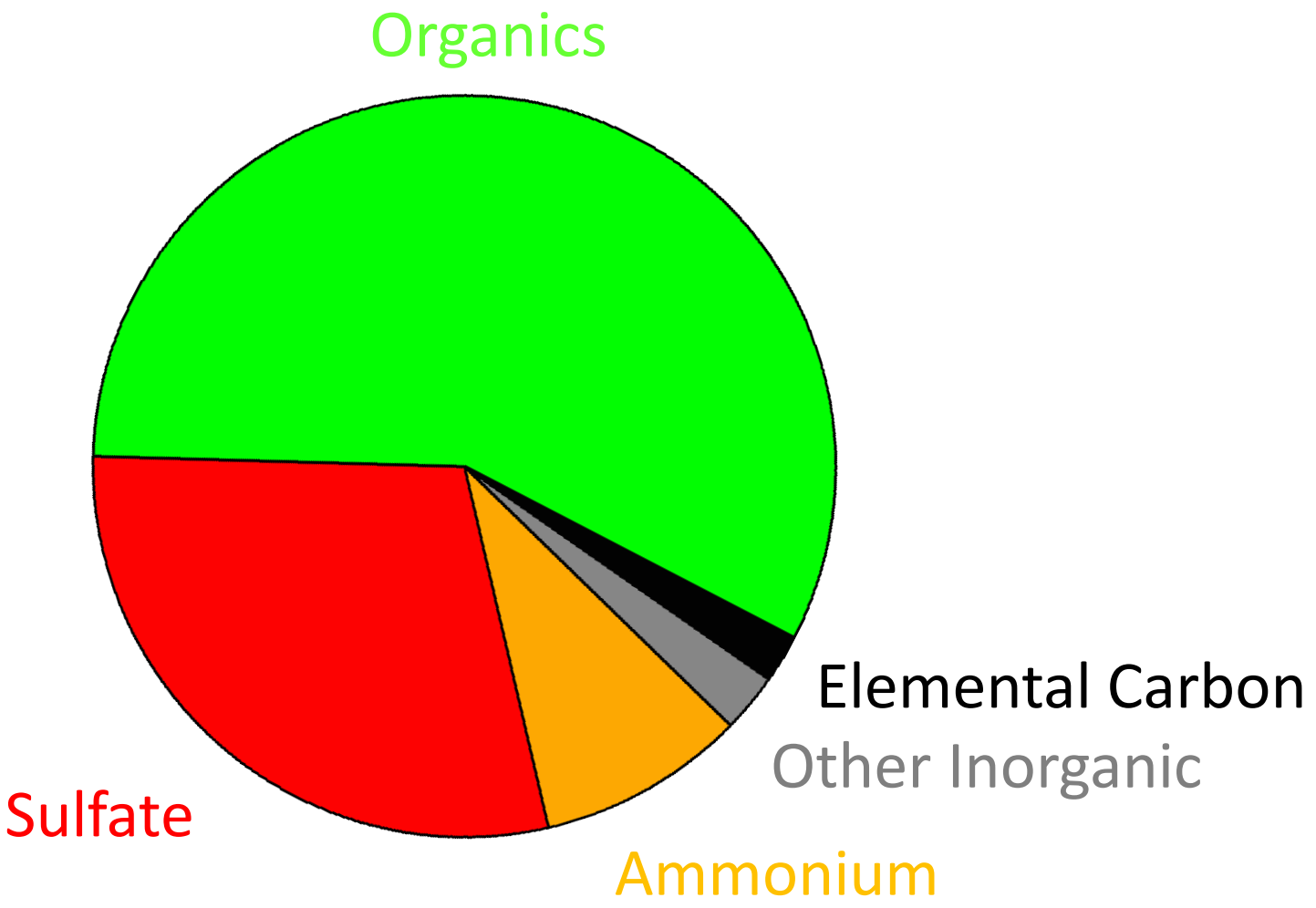
Image from NASA http://discover-aq.larc.nasa.gov/



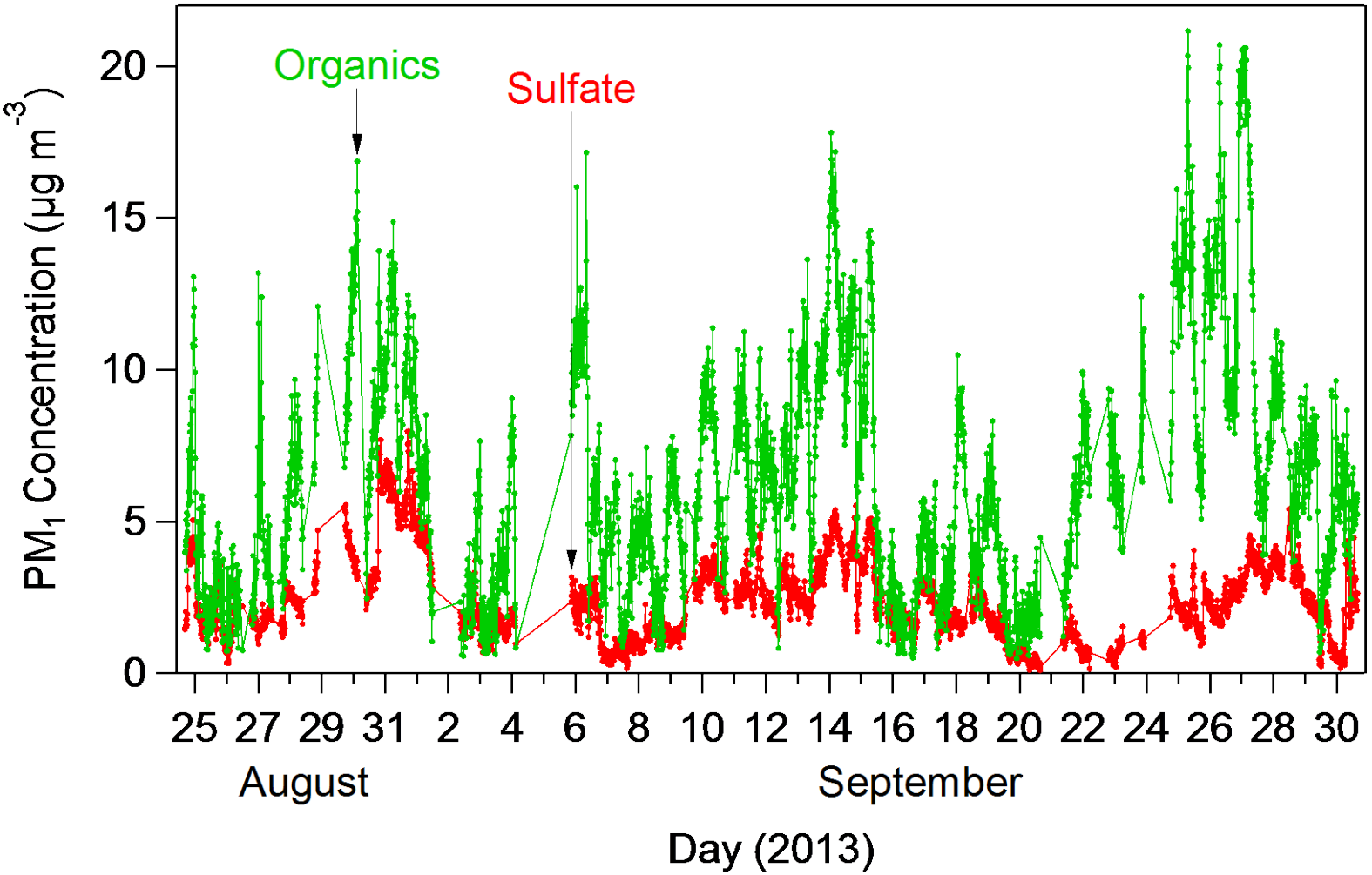
DISCOVER-AQ measurements in Conroe – Instrument set-up



$PM_{2.5}$ Composition
1- month average

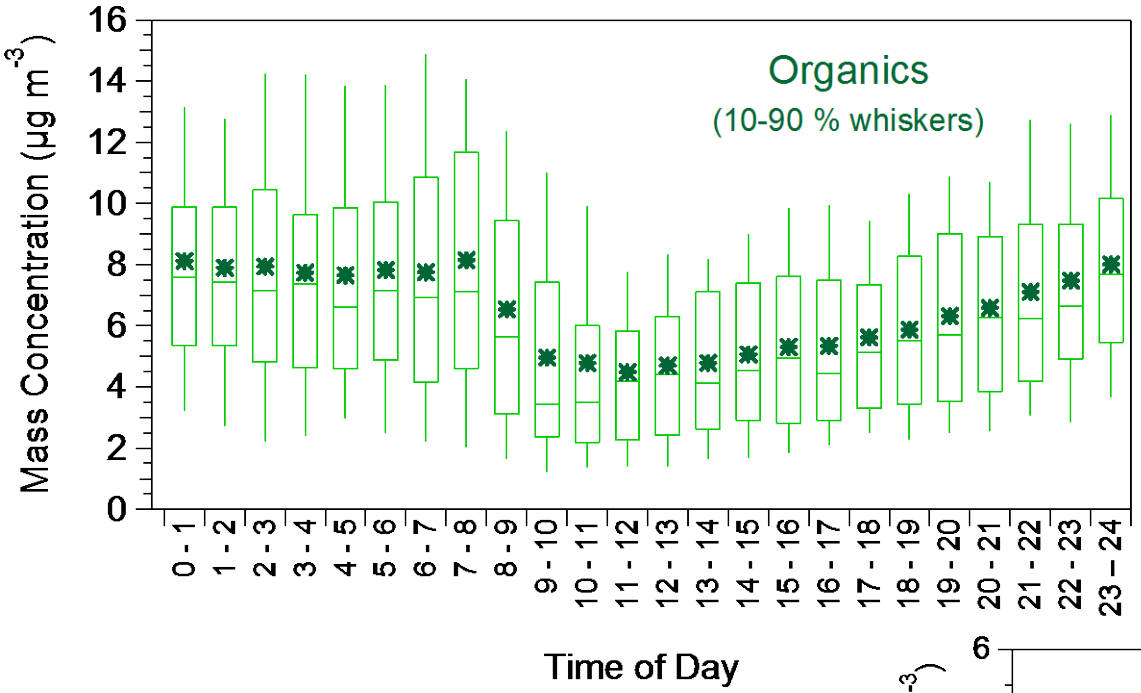


PM_1 Composition - Overview



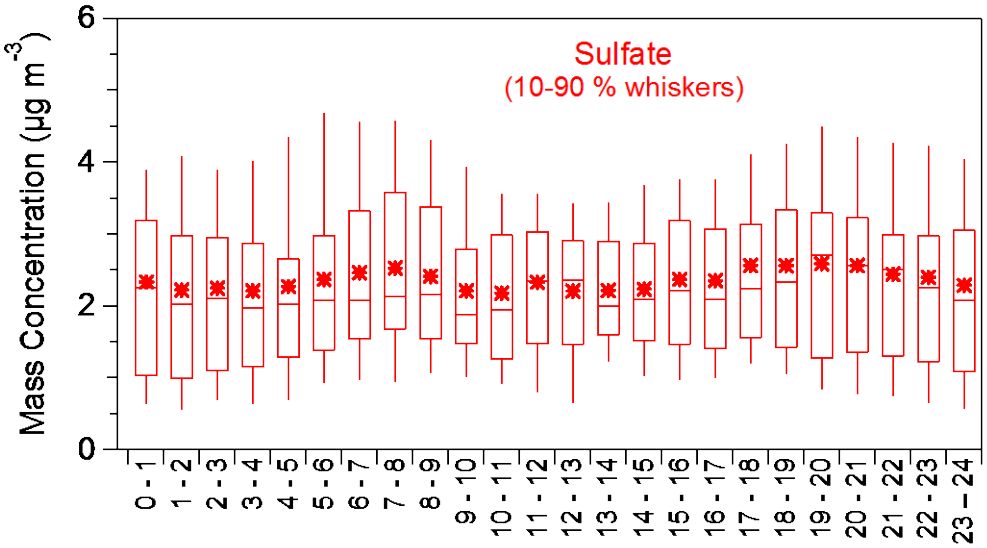
Variability in PM concentrations and composition

Diurnal cycles



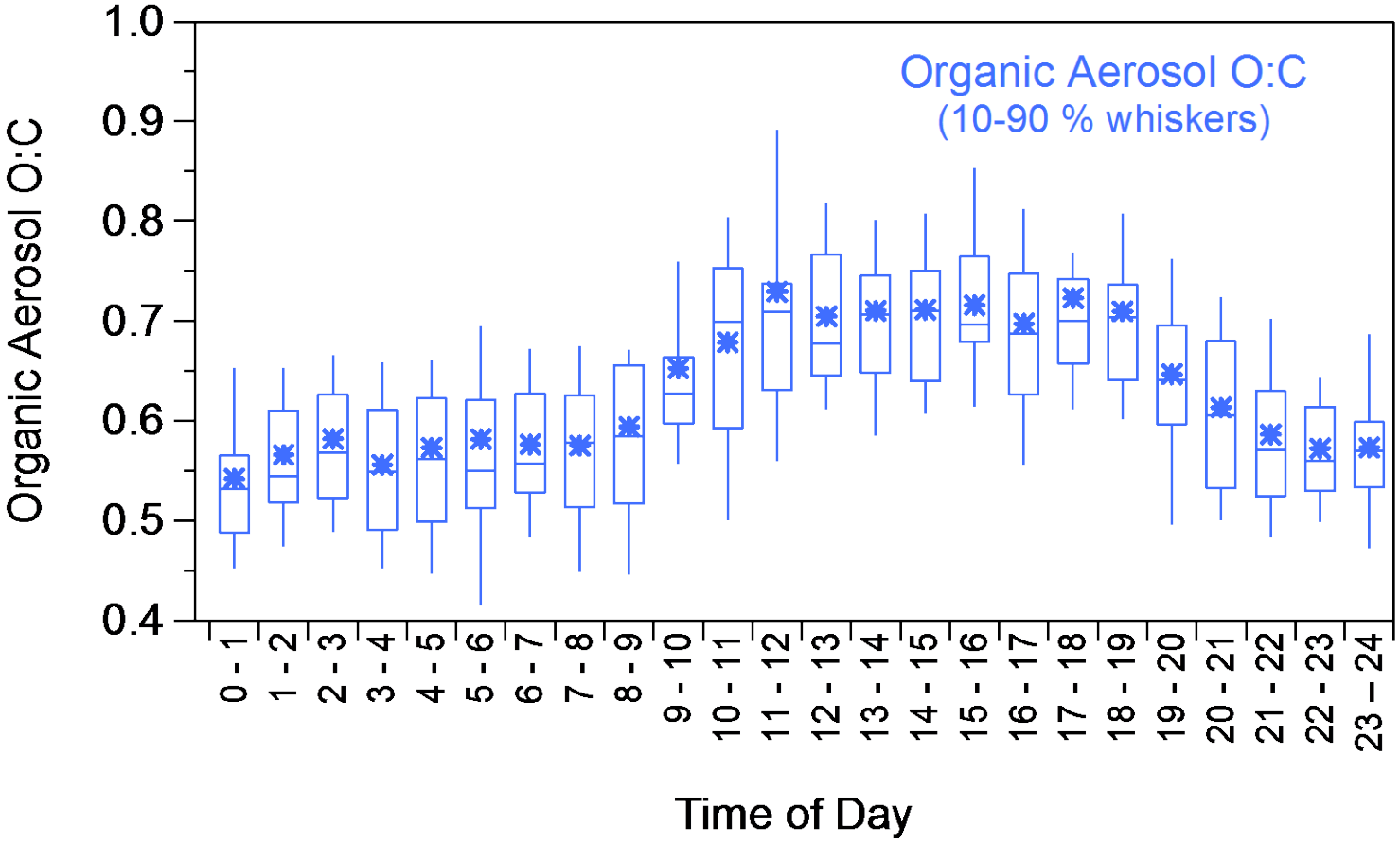
Higher conc. at night:

- partitioning
- day/night time chemistry
- BL height



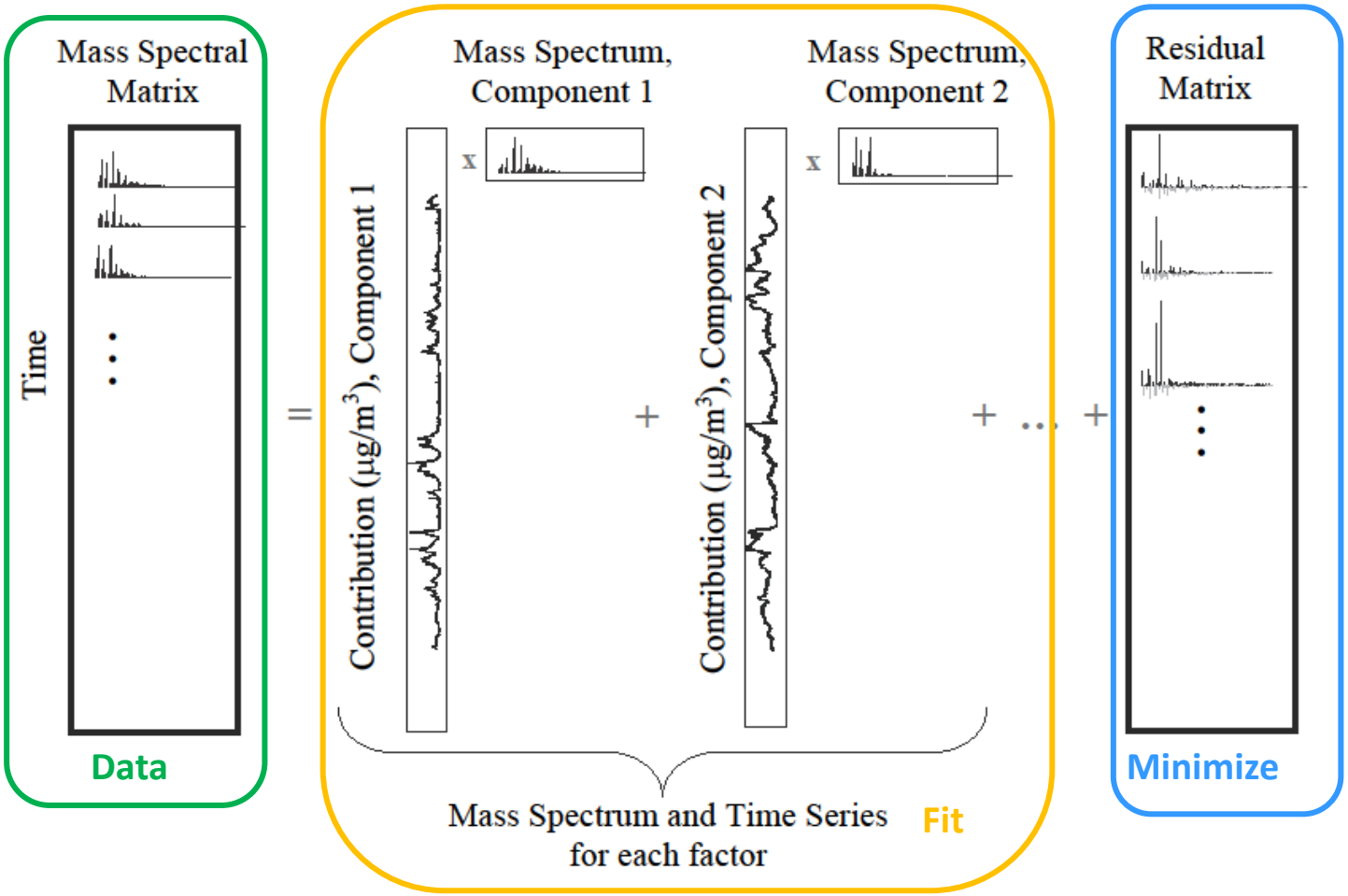
Organic Aerosol Composition

Oxygen to Carbon Ratio (O:C)

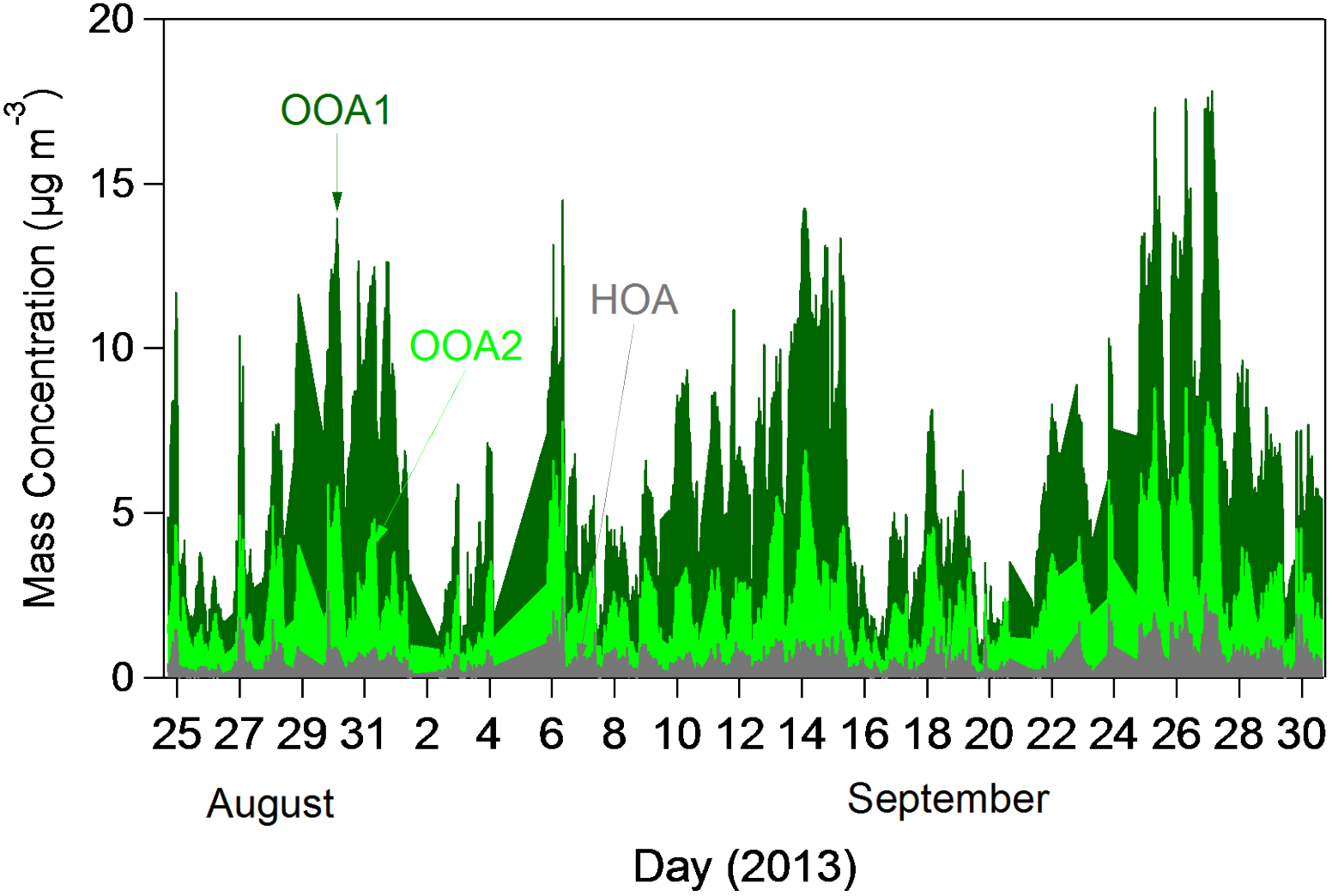


Afternoon increase in O:C indicative of photochemical activity

Positive Matrix Factorization (PMF)



PMF Results – Time Series



most (~ 90%) of PM_1 organics are oxygenated (secondary)

Environmental Chamber Experiments

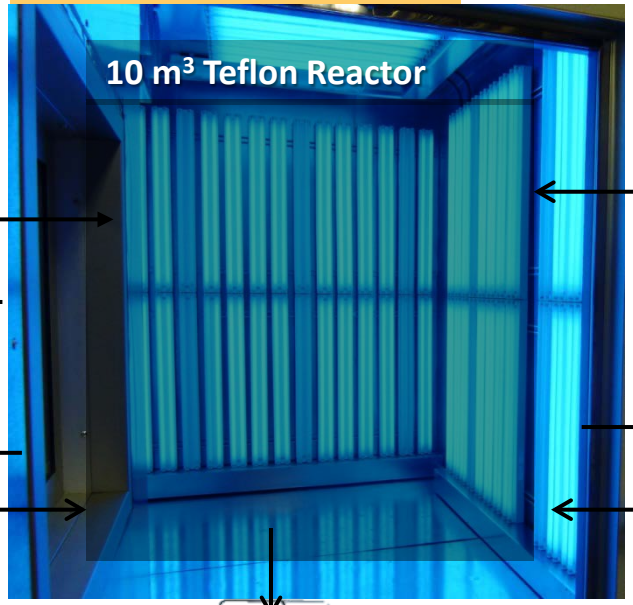
HR-ToF-CIMS

Clean air

Compressed air

Clean air generator

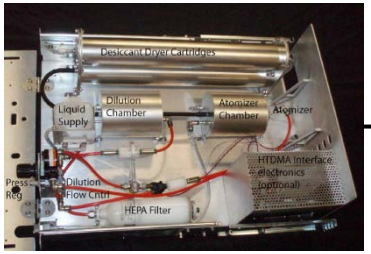
Temperature control



oxidant precursor

NO_2, NO_x. O_3 monitors

Aerosol Chemical Speciation Monitor



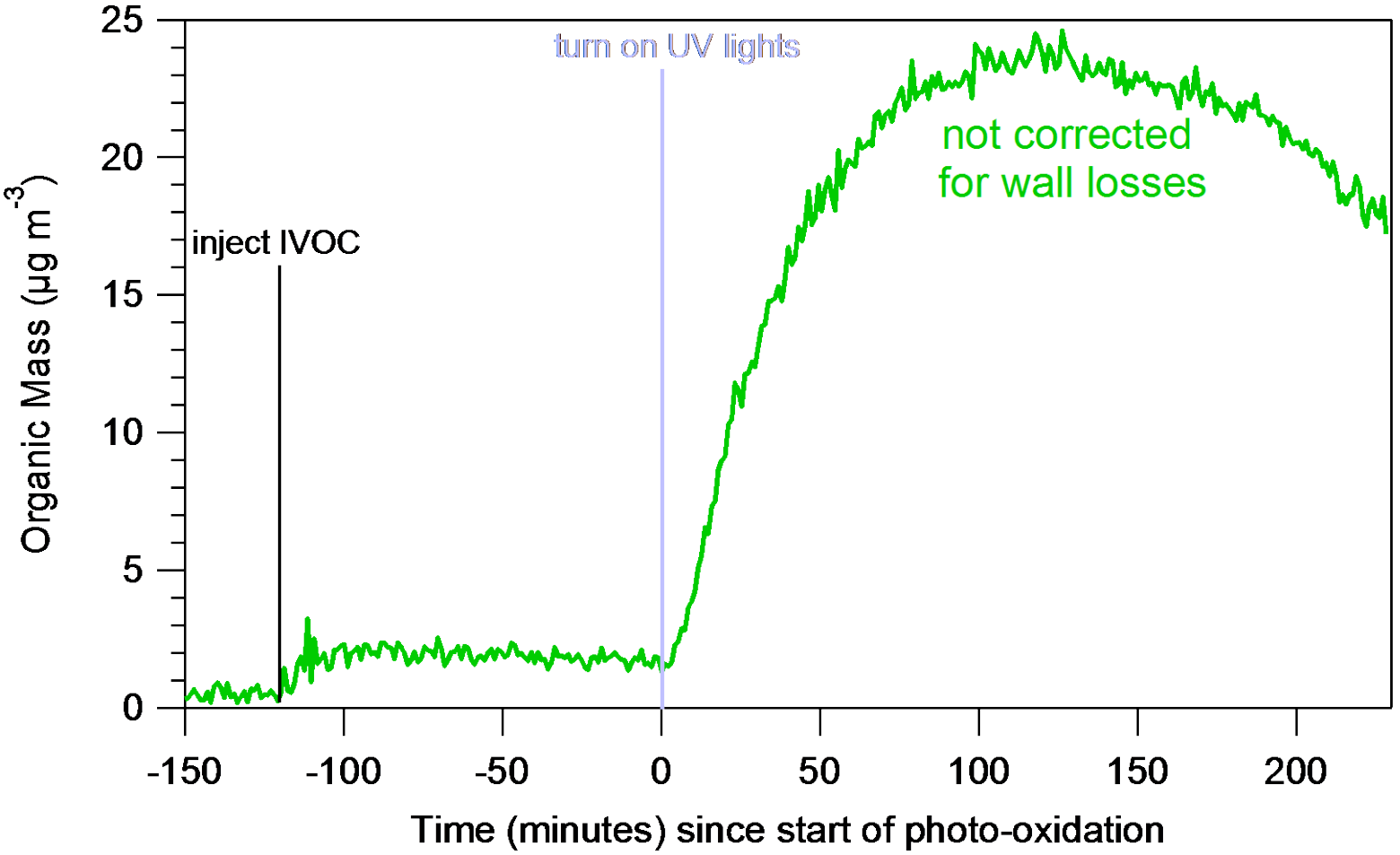
Aerosol generator

Scanning Electrical Mobility System

Cl_2, NO

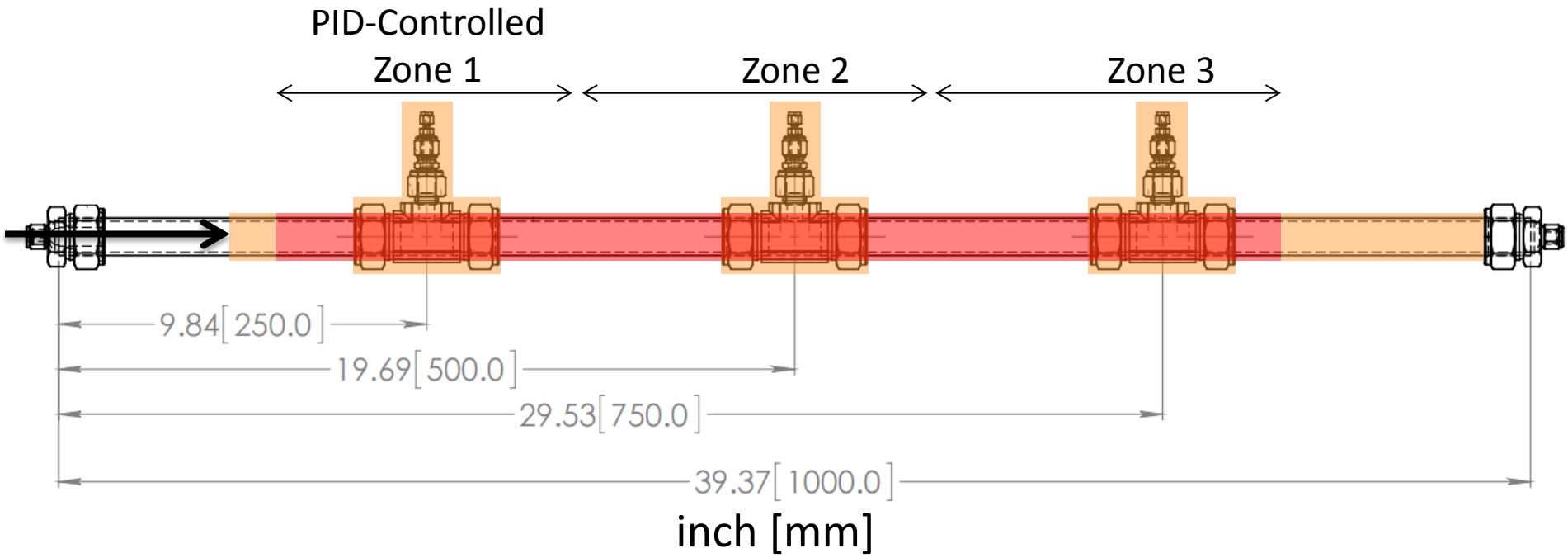
Experiment Time Series

IVOC: pentadecane



calculate aerosol mass yields using gas phase data

Thermodenuder (TD) Design



Heated Region

Insulation

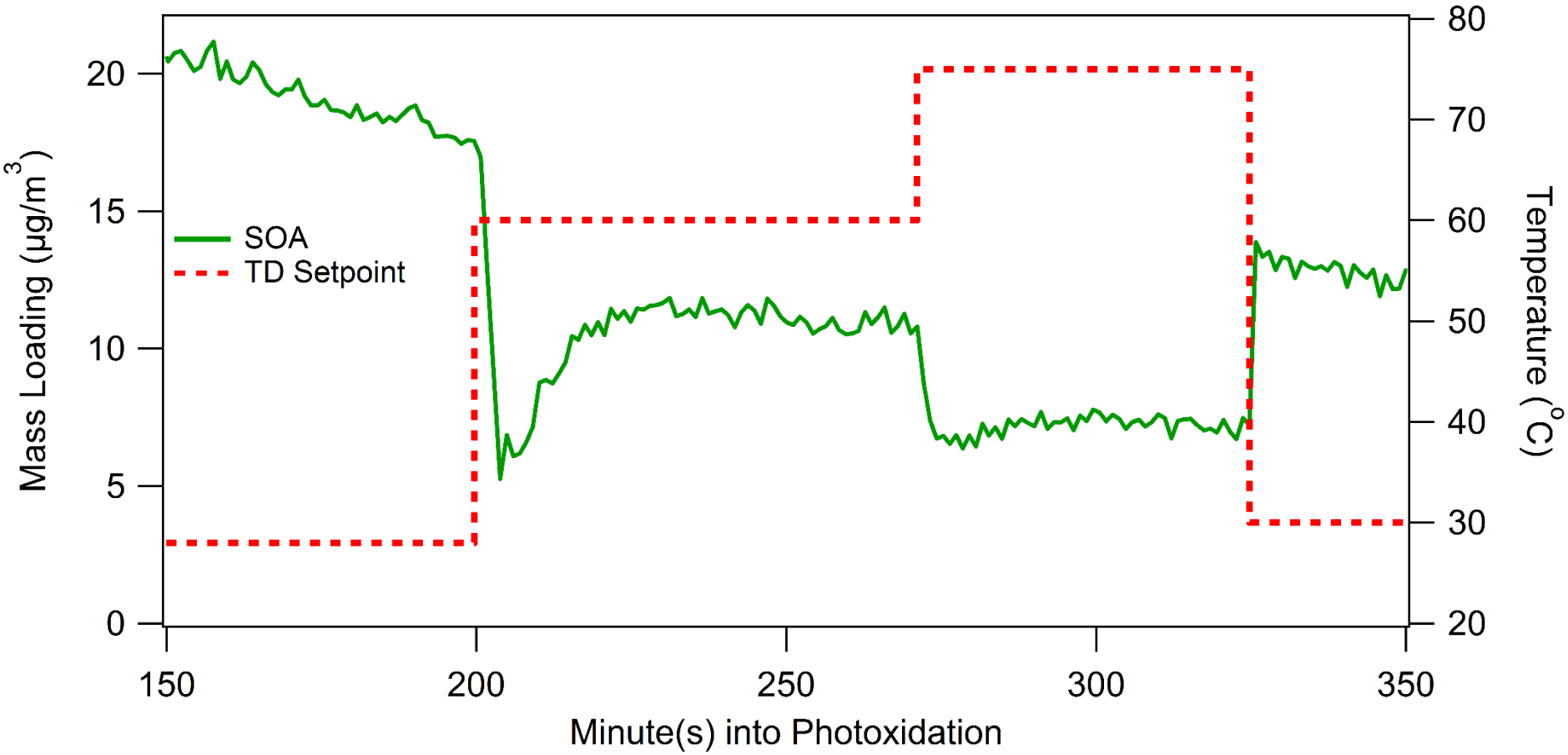
Gas sample flow rate: 1 LPM (1000 cm^3 per minute)

Cross section: 5.067 cm^2

Effective residence time: 17.33 seconds

Maximum operating temperature: ~300 ^oC

TD Test Experiment



Quantify mass fraction remaining (MFR) after heating and evaporation in the thermodenuder.

Use evaporation model to obtain volatility basis set parameters

Summary

DISCOVER-AQ data highlights

- ~ 70% of PM_1 is organic, ~60 % of $PM_{2.5}$ is organic
- More organic PM at night than during the day

Environmental Chamber Experiments

- Built heated injector and thermodenuder
- Conducted SOA formation experiments

Modeling

- Conducted 3-D CAMx base case simulation for the 2013 DISCOVER-AQ period

  IVOC emissions estimated based on unspeciated fractions of NMOG emissions from major combustion sources

Most organic particulate matter is oxygenated /secondary

Next Steps

Evaluate model performance using DISCOVER-AQ measurement data

- Compare total organic PM mass and O:C
- Compare HOA vs OOA (PMF apportionment results)
- Compare modeled and measured diurnal profiles
- Assess missing and/or under-estimated sources of organic PM in the model

Complete laboratory chamber experiments to obtain volatility basis set parameters for model

Assess sensitivity of model results to updated VBS parameterization

Recommendations

- Ambient observations of organic aerosol concentrations, volatility and oxidation state in Texas
- Chamber experiments to obtain VBS parameters for additional precursors and to evaluate aging rate
- Quantify local and transported PM contributions using CAMx PM source apportionment
- Follow up on missing and/or under-estimated sources of organic PM in the model

Acknowledgment

- Thanks to Shantha Daniel (TCEQ), Elena McDonald-Buller (AQRP)
- This research was supported by the State of Texas through the Air Quality Research Program (AQRP) administered by The University of Texas at Austin by means of a grant from the Texas Commission on Environmental Quality (TCEQ), AQRP Project 14-024. TCEQ has not yet reviewed the final project report and has not fully reviewed the findings presented here.