How Physical and Chemical Properties Data Reflects Aerosol Formation Processes and their Evolution

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Outline:

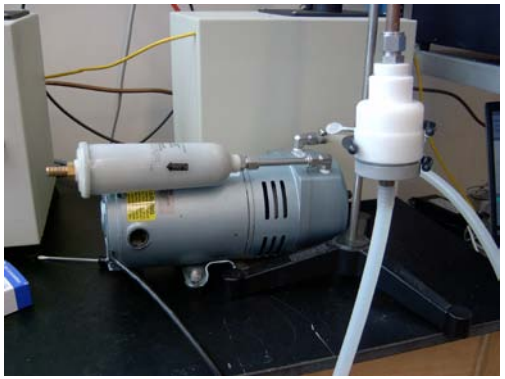
1. Instrumentation based on analysis of water-soluble gas/particle components.
1. Example application: Secondary organic aerosol (SOA) formation in LA vs Atlanta.

Funded by NSF and EPA

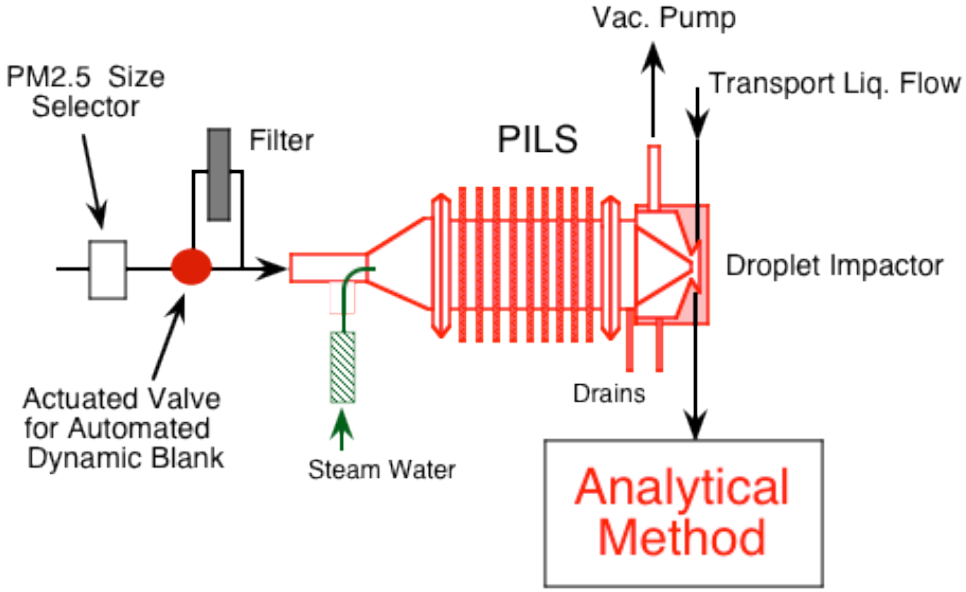
Instruments to Quantify Particle/Gas Components

Particle Phase Species

Filter Collection with Off-line Water-Extraction and Analysis

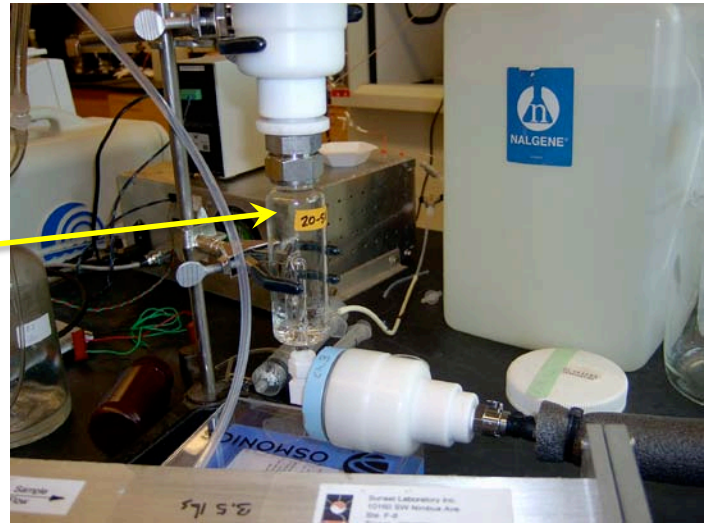


Automated On-line Analysis



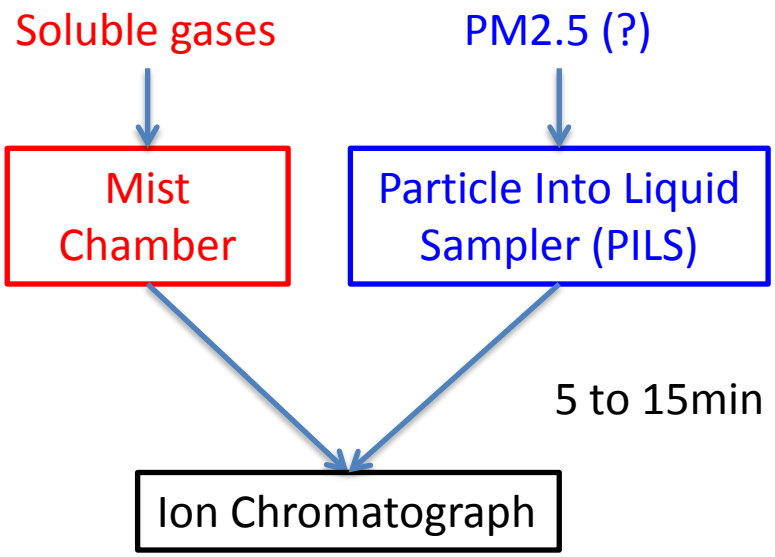
Gas Phase Species

Mist Chamber: gas scrubber (or use; continuous flow wet denuders)



ANALTYICAL METHOD: Approaches to Measure a Range of Gas and Aerosol Phase Properties

Inorganic and Organic Ions

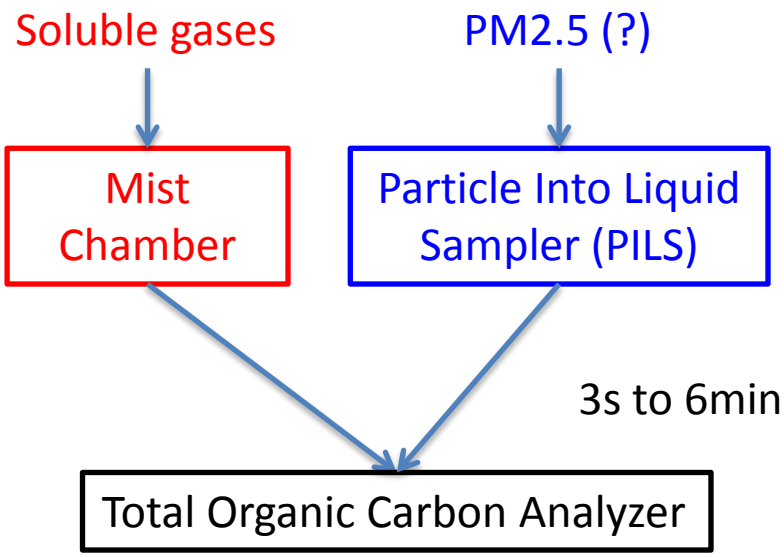


Cations: Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Amines…
Anions: Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Organic Acids…

Cations: NH_3
Anions: Cl, HONO, HNO_3, SO_2, Organic Acids…

(Weber et al AS&T 2001; Orsini et al, Atm Env. 2003)

$WSOC_g$ and $WSOC_p$



$WSOC_g$, $WSOC_p$

(Sullivan et al; GRL 2004, JGR 2006)

ANALTYICAL METHOD: Approaches to Measure a Range of Gas and Aerosol Phase Properties

WSOCp & Hydrophilic/phobic fractions

(Sullivan et al JGR 2006)

PM2.5 (?)

Particle Into Liquid Sampler (PILS)

Actuated Valve

XAD-8 Column

Hydrophobic WSOC Retained (high MW, aromatics, HULIS, less soluble …)

Total Organic Carbon Analyzer

Penetrates Hydrophilic WSOC (lower MW…, highly soluble)

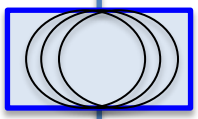
WSOCp & Soluble Light Absorption Spectra

(Hecobian et al, ACP 2010)

PM2.5 (?)

Particle Into Liquid Sampler (PILS)

Compact UV-VIS Spectrophotometer (200 to 800nm)



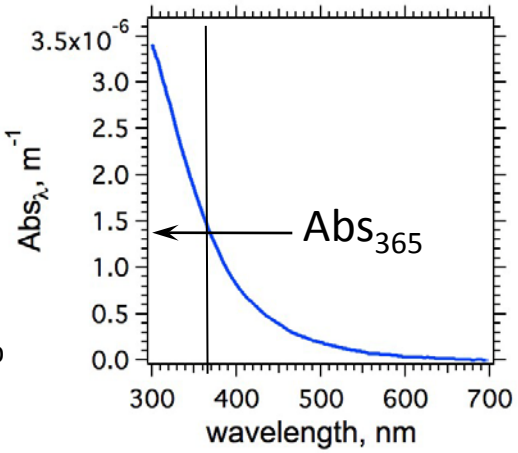
1-m path length LWCC (0.25 mL)

Total Organic Carbon Analyzer

"**Brown Carbon**"

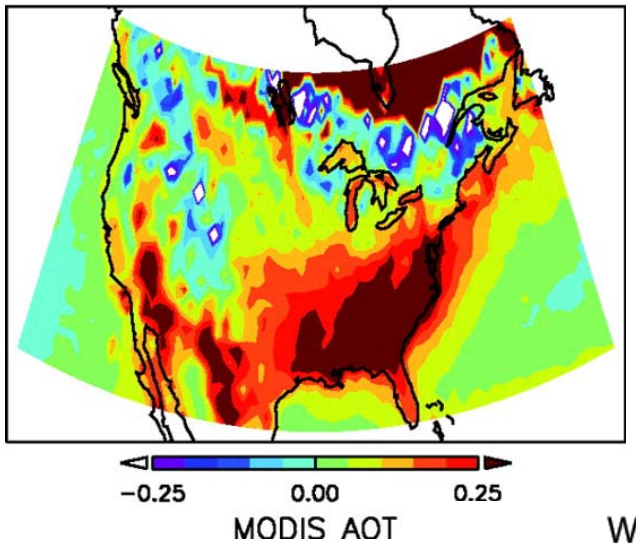
Abs'n Å ~ 2 to 7 ($\lambda^{-Å}$)

Mass Abs'n Eff: Abs/$WSOC_p$



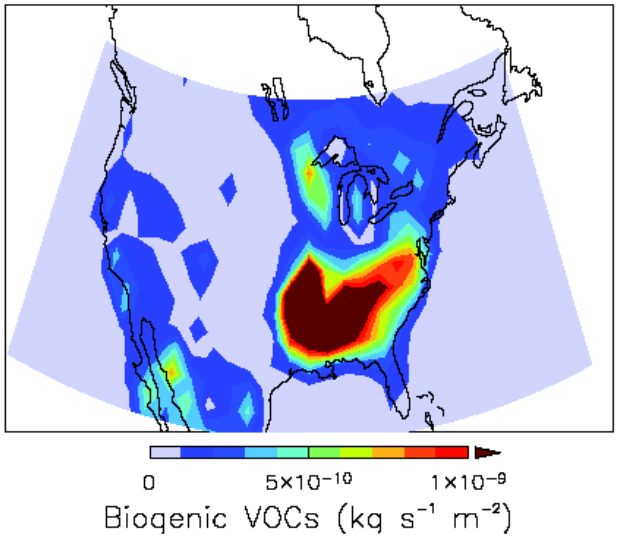
South and Southeastern US are Interesting Aerosol Regions

Aerosol Optical Thickness(AOT): JJA - DJF

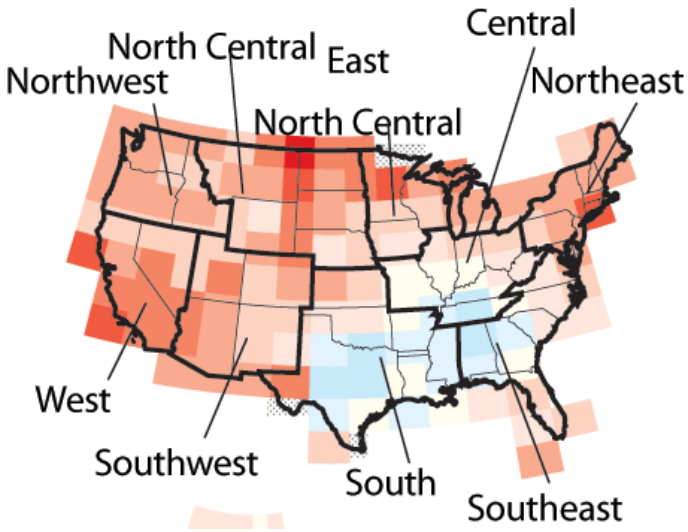


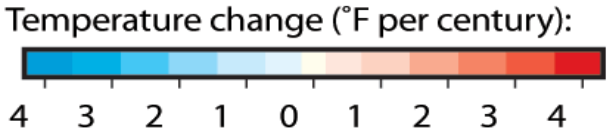
(Goldstein et al., PNAS, 2009)

Predicted Biogenic-VOC Emissions



Annual Temperature anomalies 1901-2005

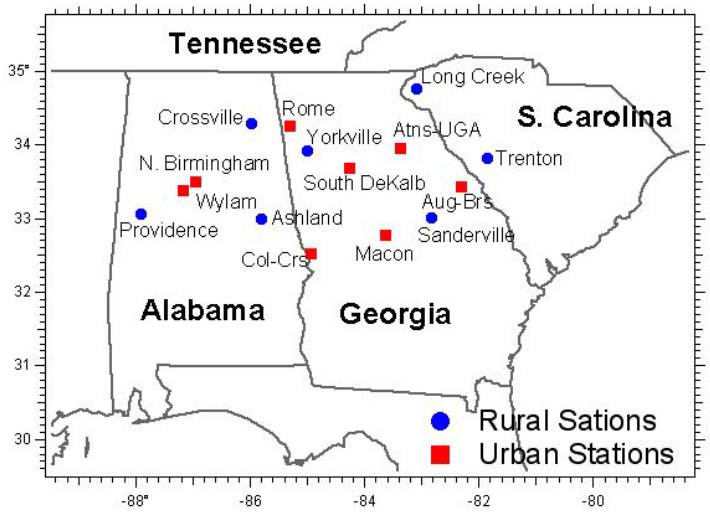




http://www.epa.gov/climatechange/science/recenttc_tempanom.html

Large role played by BVOCs in Eastern US

2007 FRM Filter Data: WSOC High In Summer When Hot

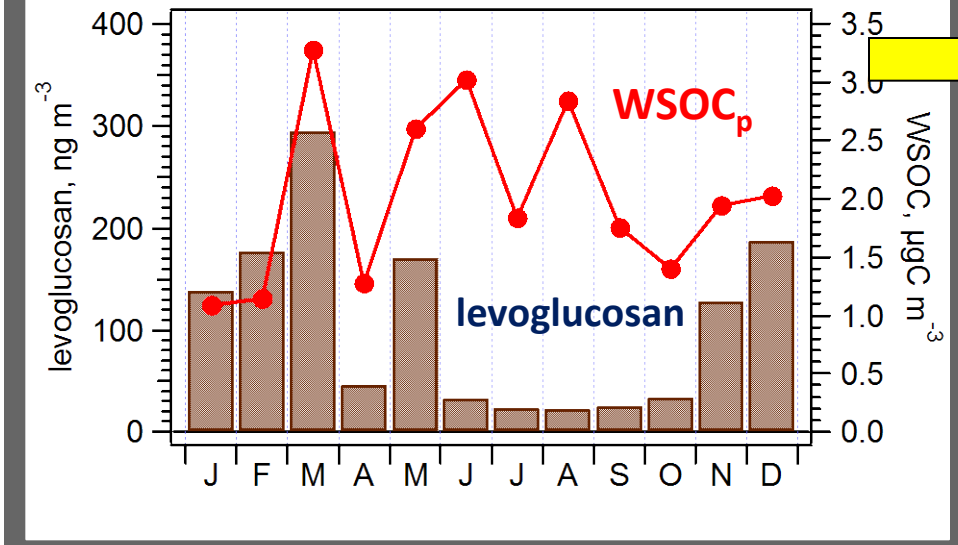


24h-filters from 15 FRM sites throughout SE, 60 filters/site, 900 filters:

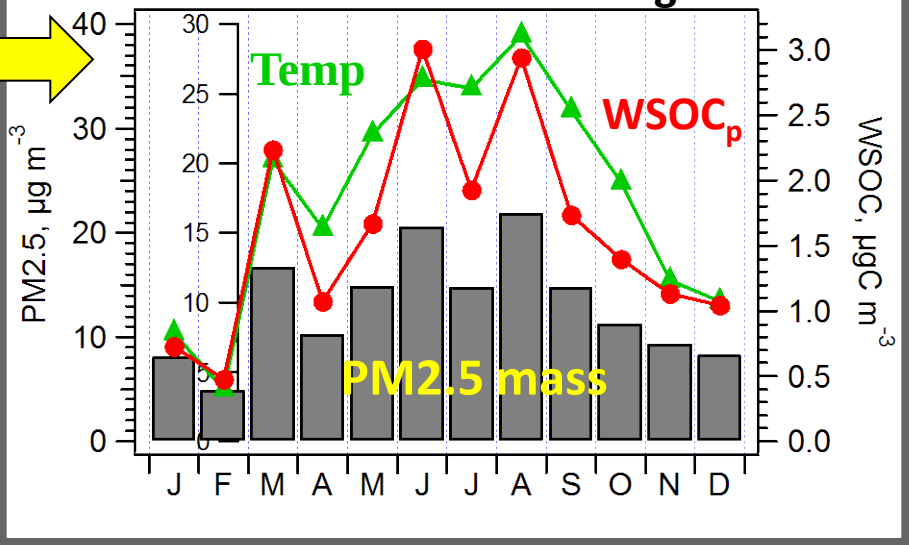
Measured: non-volatile $WSOC_p$, Light Abs, Carbohydrates, sulfate…

$WSOC_p$ Highest in Summer: highly correlated with $PM_{2.5}$ mass (r^2= 0.70) and highly correlated with T (biogenic VOCs?)

Lev < 50 ng/m³



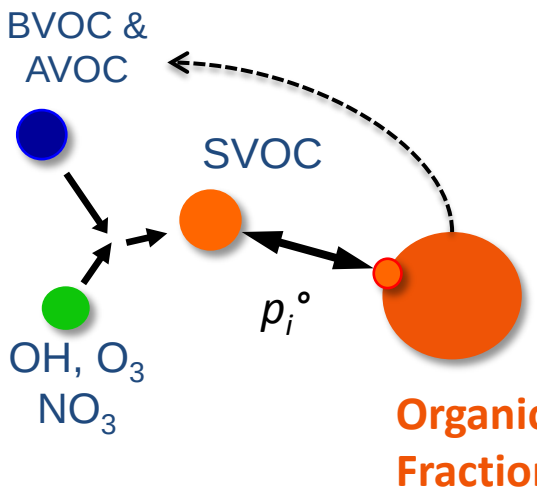
Non-biomass burning



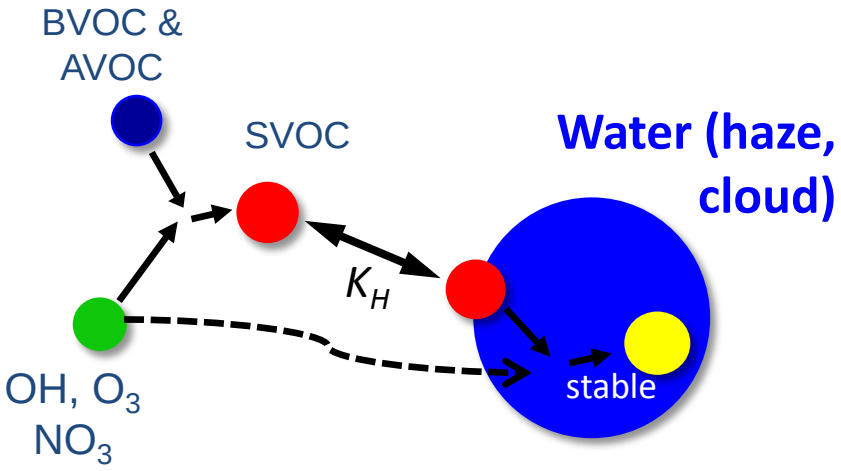
(Zhang et al, ACP 2010)

How Secondary Organic Aerosol Mass is Created
- Conceptual Ideas -

"Classic" (Pankow) Partitioning



Possible aqSOA Route(important?)



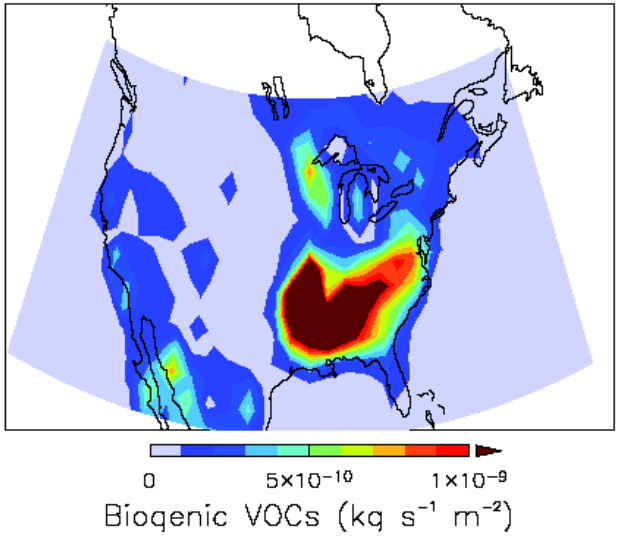
$$K_P = \frac{C_P / M_O}{C_g} = \frac{760\ R\ T\ f_{OM}}{10^6\ MW_{OM}\ \xi\ p_i^o}$$

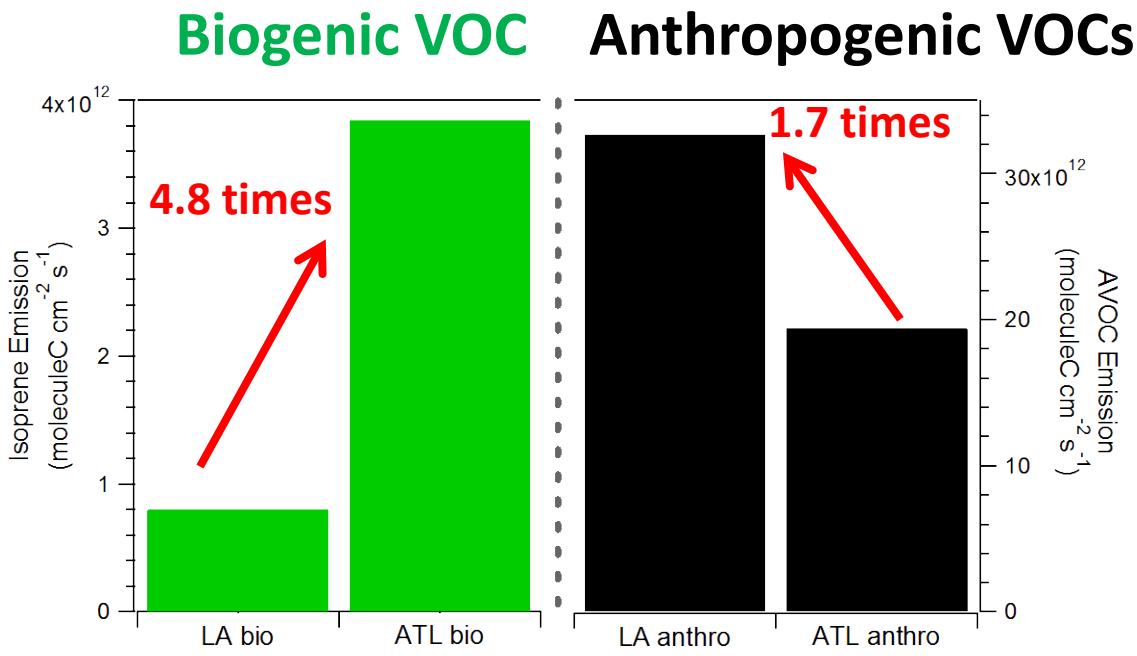
Partitions to aerosol organic mass (M_o) and depends on SVOC vapor pressure

Partitions to liquid water (LWC) and depends on SVOC solubility (Henry's Law Constant, K_H), then undergoes heterogeneous oxidation to lower $p_i°$

Estimated VOC Emissions in LA and Atlanta

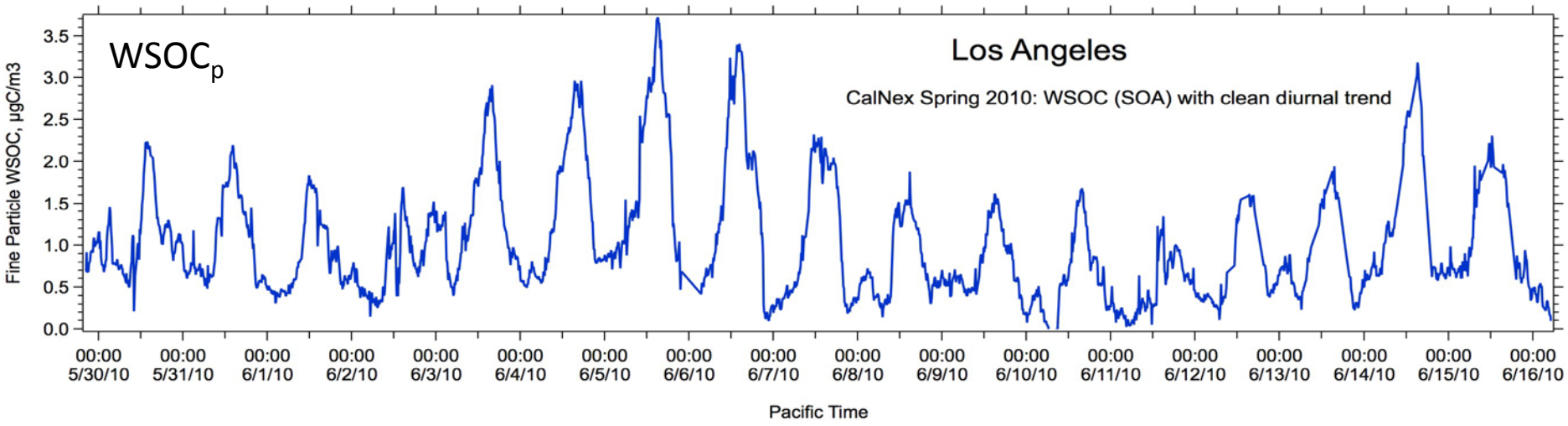
Predicted Biogenic-VOC Emissions

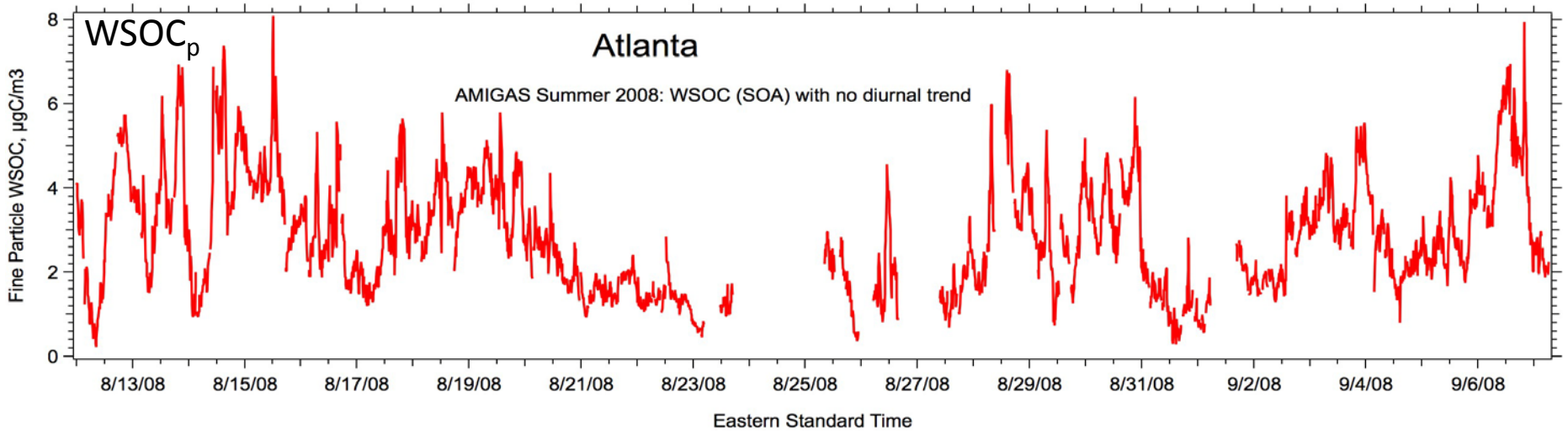




- BVOCs are much higher in the SE and within Atlanta, does that impact SOA formation within Atlanta ? Compare Atlanta to LA

SOA Formation in the SE is Subtle

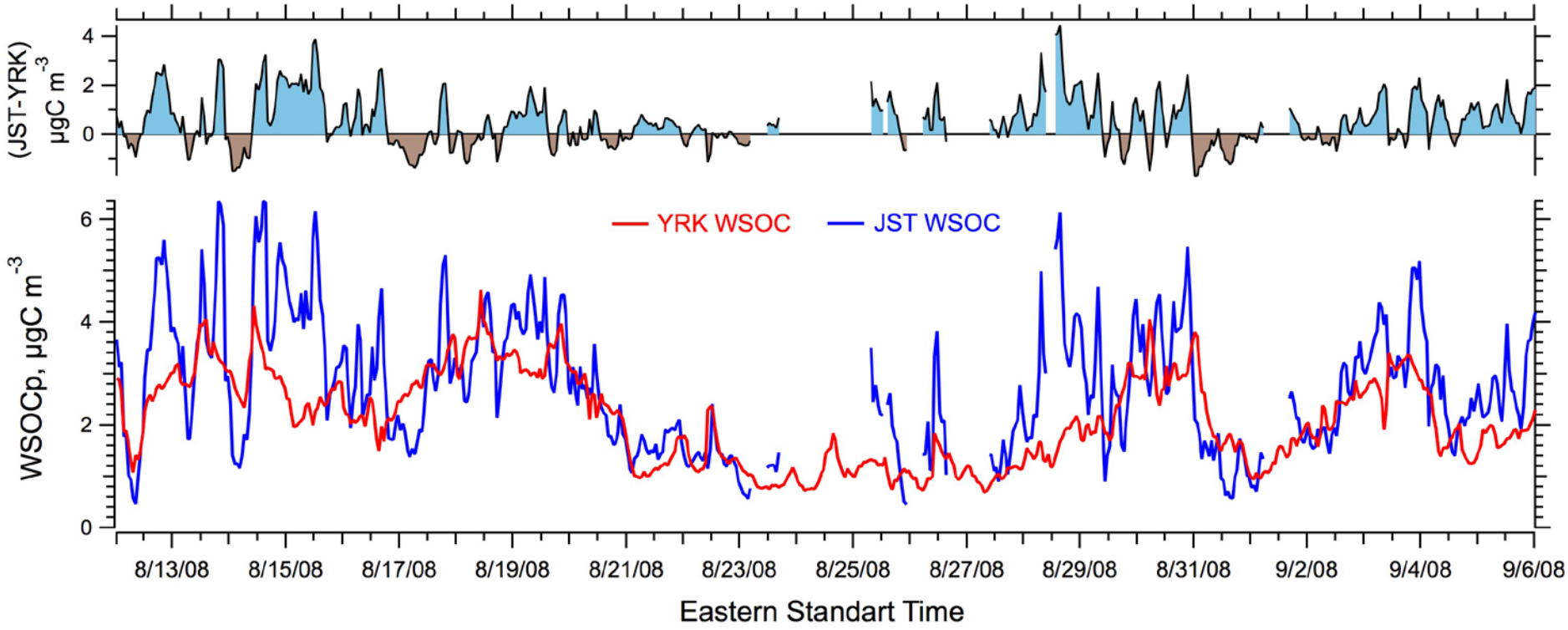




In Atlanta (and other sites in eastern US) no clear diurnal trend to SOA

Atlanta: Urban vs Rural

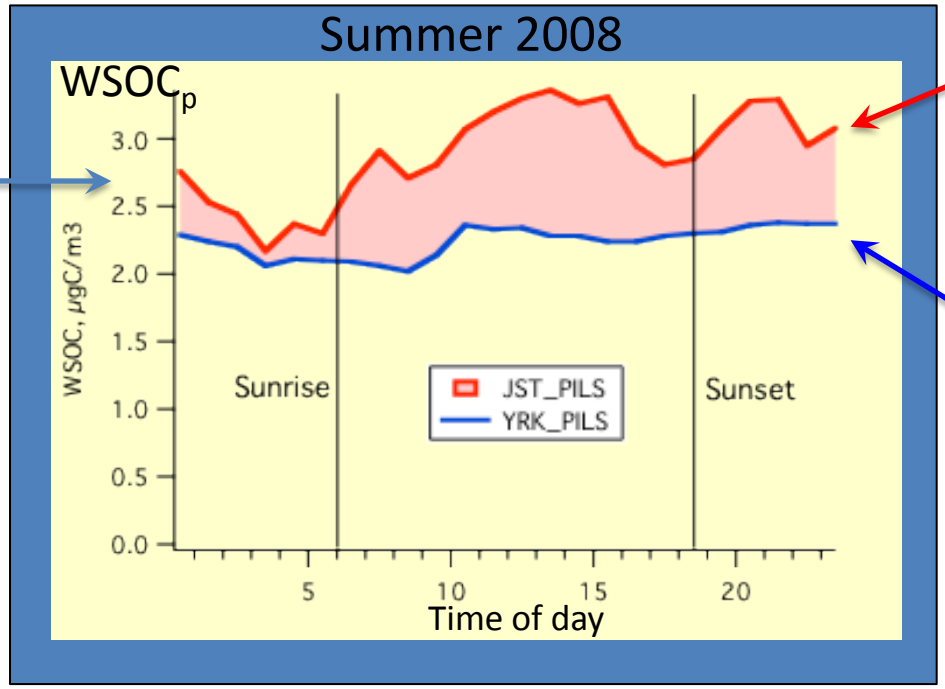
(Atlanta vs Yorkville)



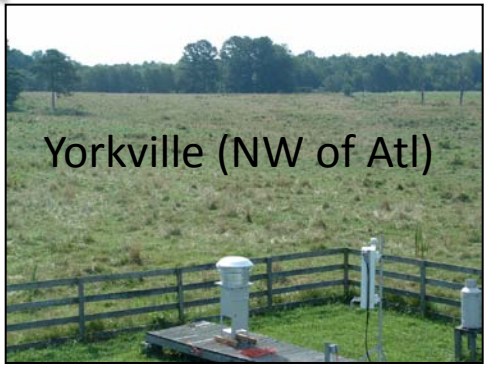
Jst and Yrk generally track on times scales of synoptic meteorological processes

Jst consistently higher on a higher frequency scale due to anthrop. Influence.

Urban/Rural $WSOC_p$ Diurnal Tends



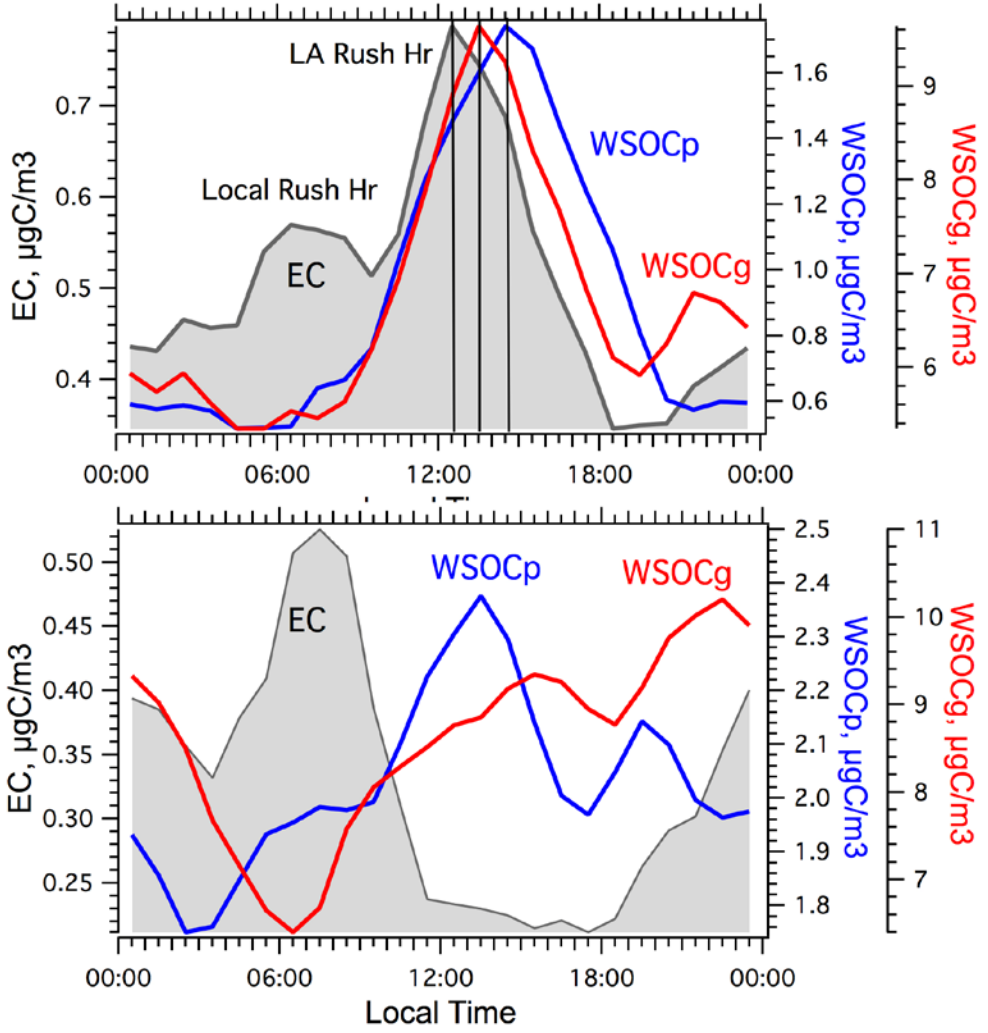
~ 70 km apart



Atlanta signal riding on large regional background
Some evidence for a daytime increase (photochemical SOA)

Comparison of Diurnal Trends: Daytime Increases

Changes relative to background → Secondary process that day



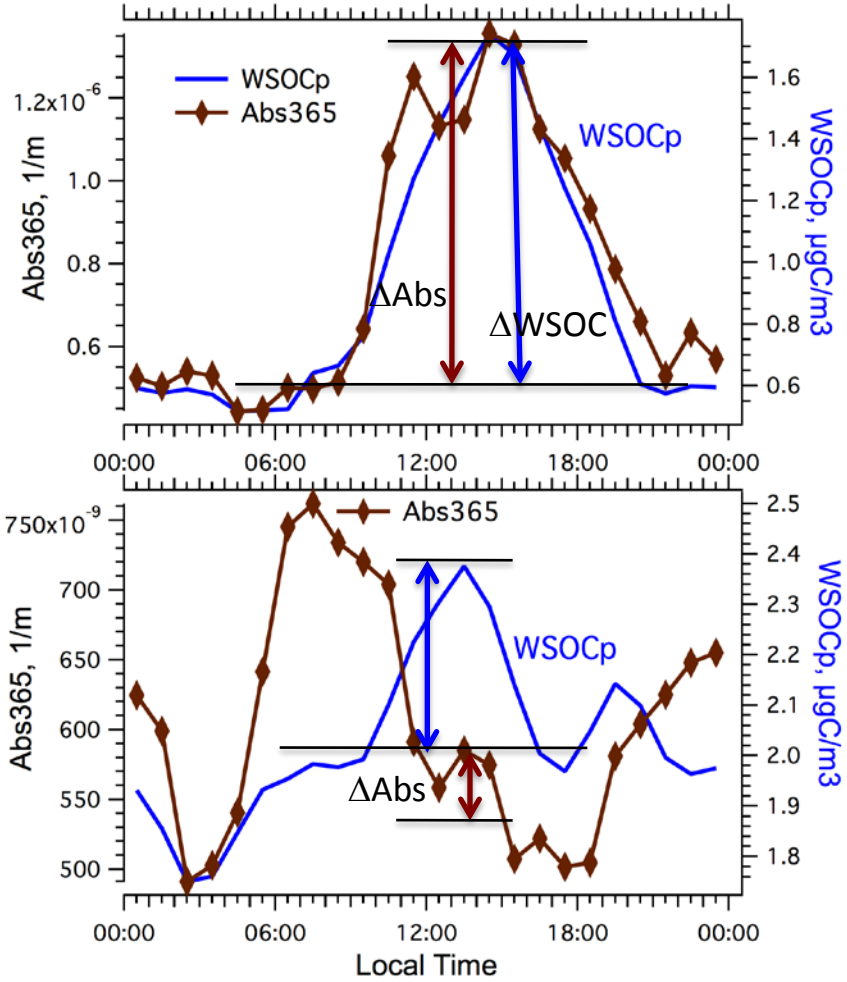
LA: CalTech

ΔWSOCg tracks other Δ(Oxyg-VOCs)
ΔWSOCp tracks other ΔSOA
(eg, gas and particle organic acids)

Atl: GaTech

ΔWSOCg and ΔWSOCp completely different trends wrt each other and LA.

Comparison of Diurnal Trends: Abs_{365}



LA-CalTech

$$\frac{\Delta Abs}{\Delta WSOCp} = 0.77 \times 10^{-6}$$

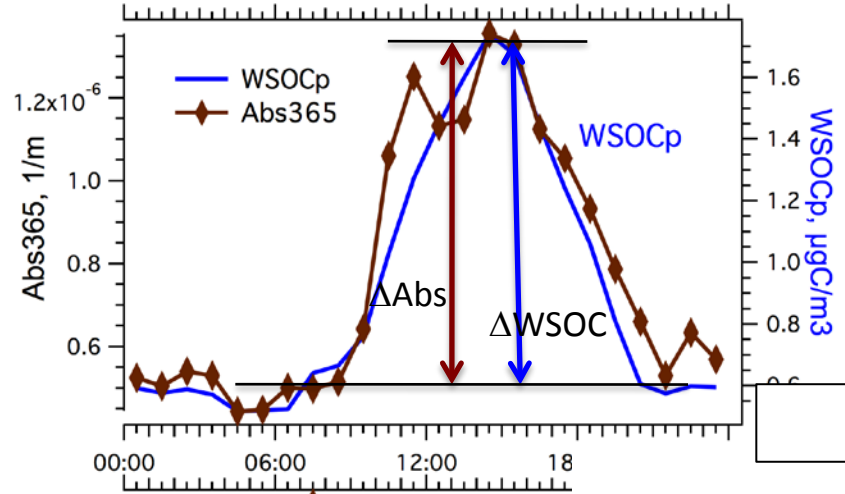
LA 5 to 6x higher

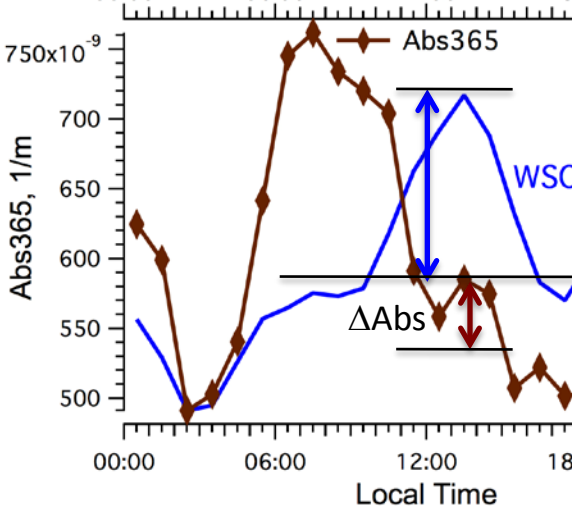
Atl-GaTech

$$\frac{\Delta Abs}{\Delta WSOCp} = 0.14 \times 10^{-6}$$

LA: Colored SOA
Atl (fresh) SOA is not.

Comparison of Diurnal Trends: Abs_{365}



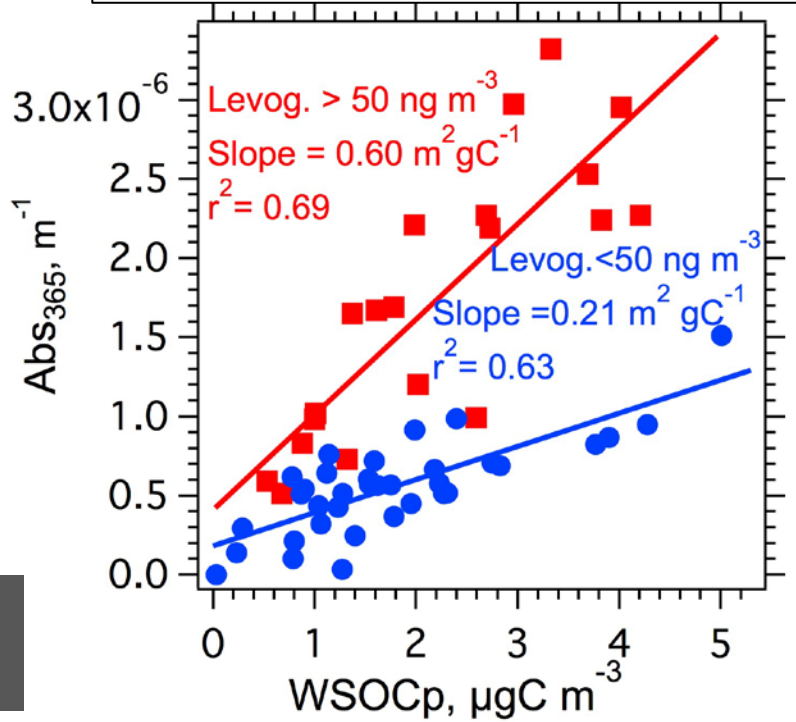


LA-CalTech

$$\frac{\Delta Abs}{\Delta WSOCp} = 0.77 \times 10^{-6}$$

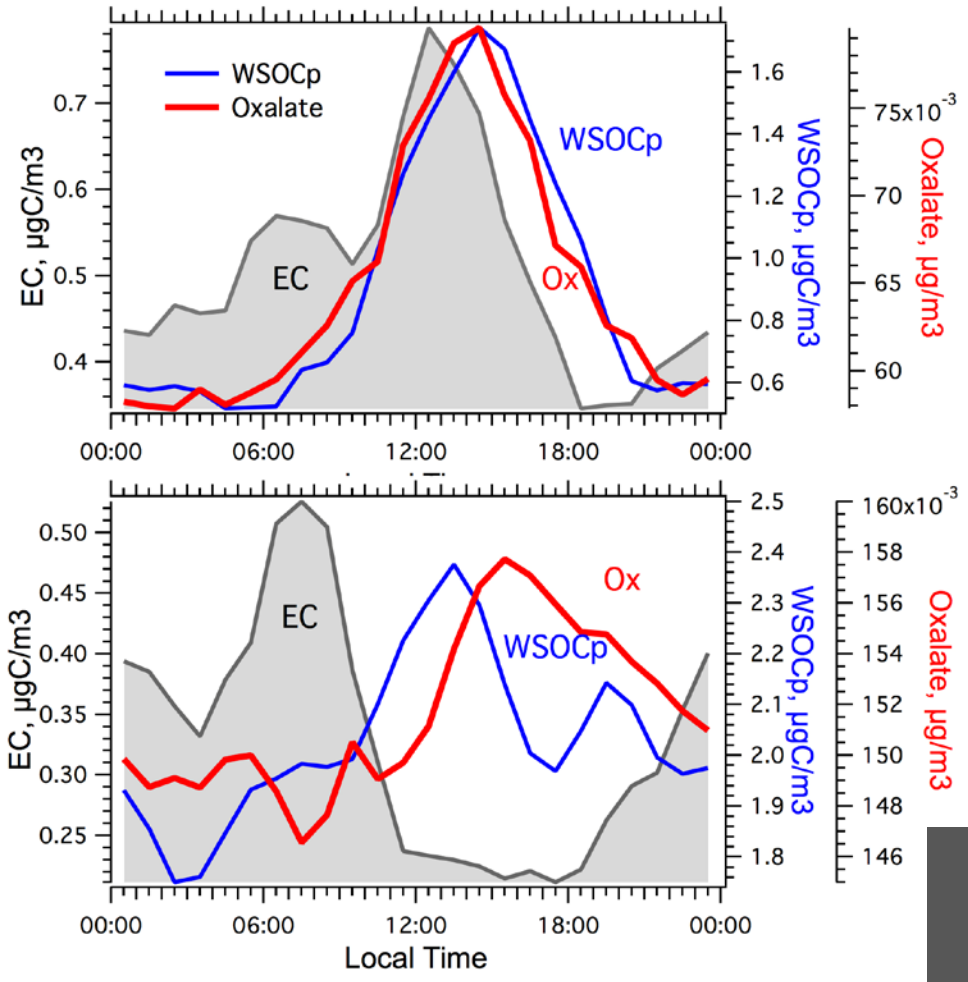
FRM Data From One Site

6x higher



But over time in Southeast, Abs and WSOCp are related

Comparison of Diurnal Trends: Oxalic Acid



LA: CalTech

Oxalic acid and WSOCp (SOA) track

Atl: GaTech

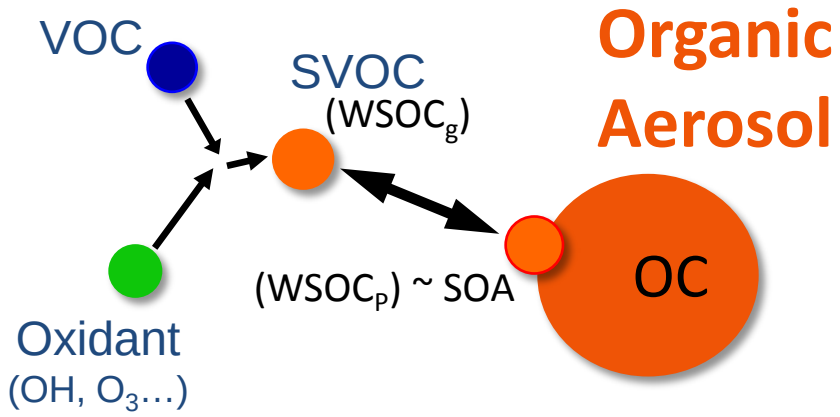
Oxalic acid formed later in day

But over time (FRM Data) WSOCp, Abs365, Oxalate become correlated (PMF analysis)

Many more differences… → differences in the SOA formation process??

Different Process?

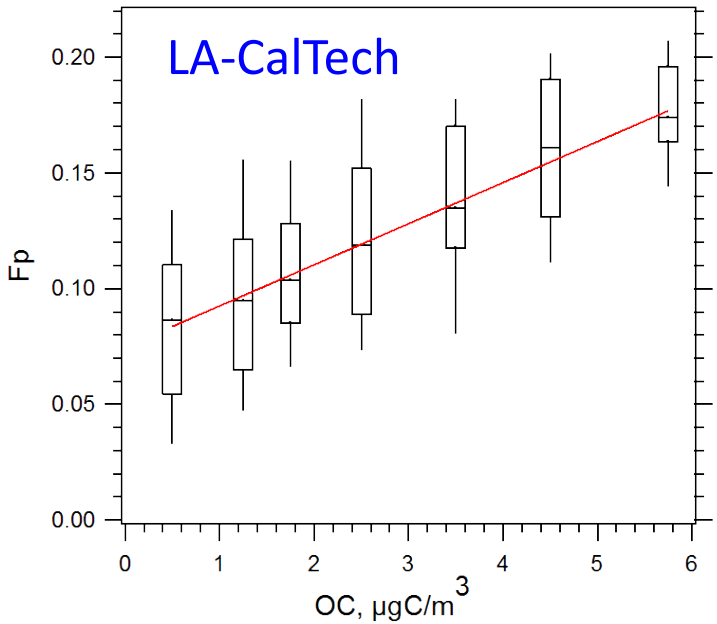
Partitioning to Organic Mass?



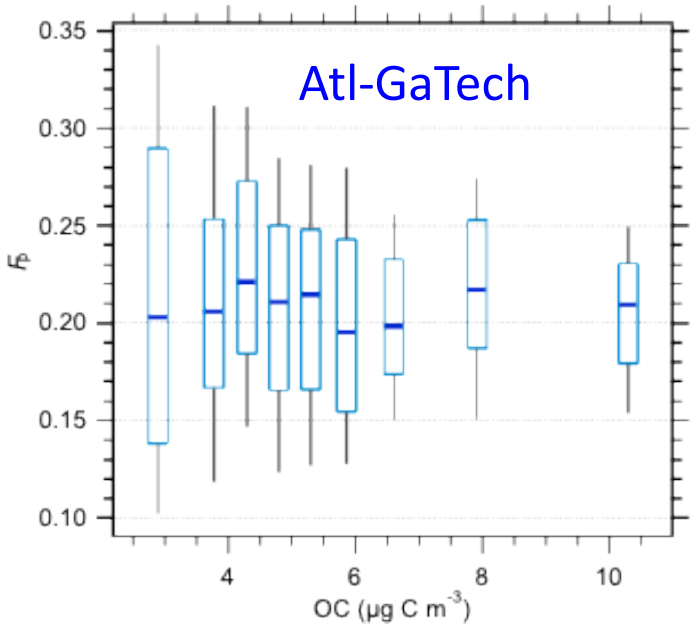
"Classic" (Pankow) Partitioning Theory

$$K_P = \frac{C_P / M_O}{C_g} = \frac{760\ R\ T\ f_{OM}}{10^6\ MW_{OM}\ \xi\ p_i^o}$$

$$F_p = \frac{\mathrm{WSOC_p}}{\mathrm{WSOC_p} + \mathrm{WSOC_g}}$$



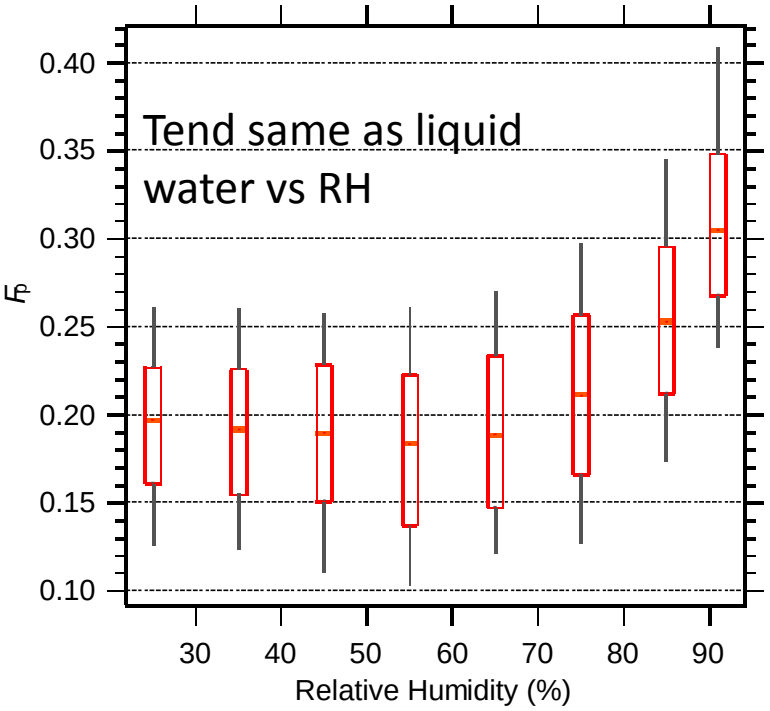
Partitioning related to OC ?



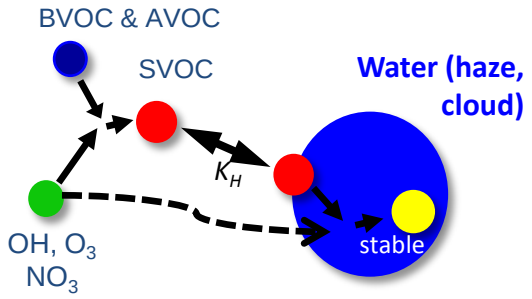
Not Partitioning to OC ?

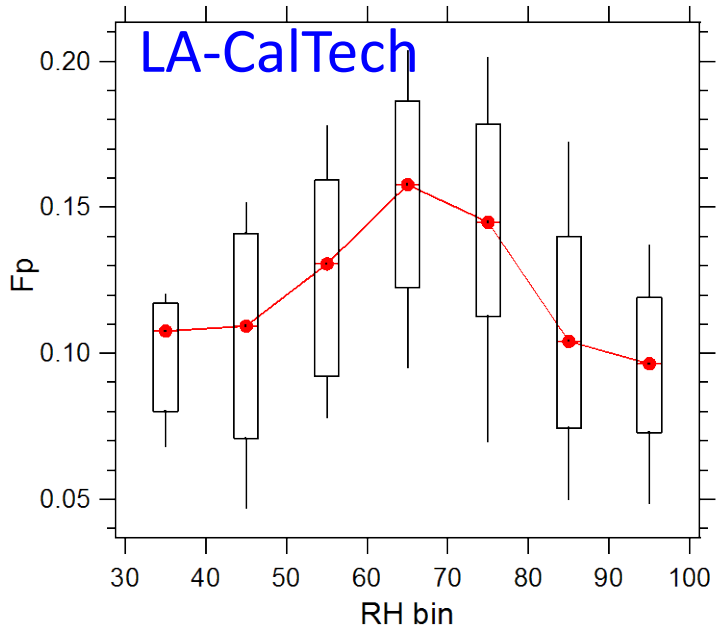
Different Process?

Partitioning to Aerosol Water ?



Fp partitioning to liquid water



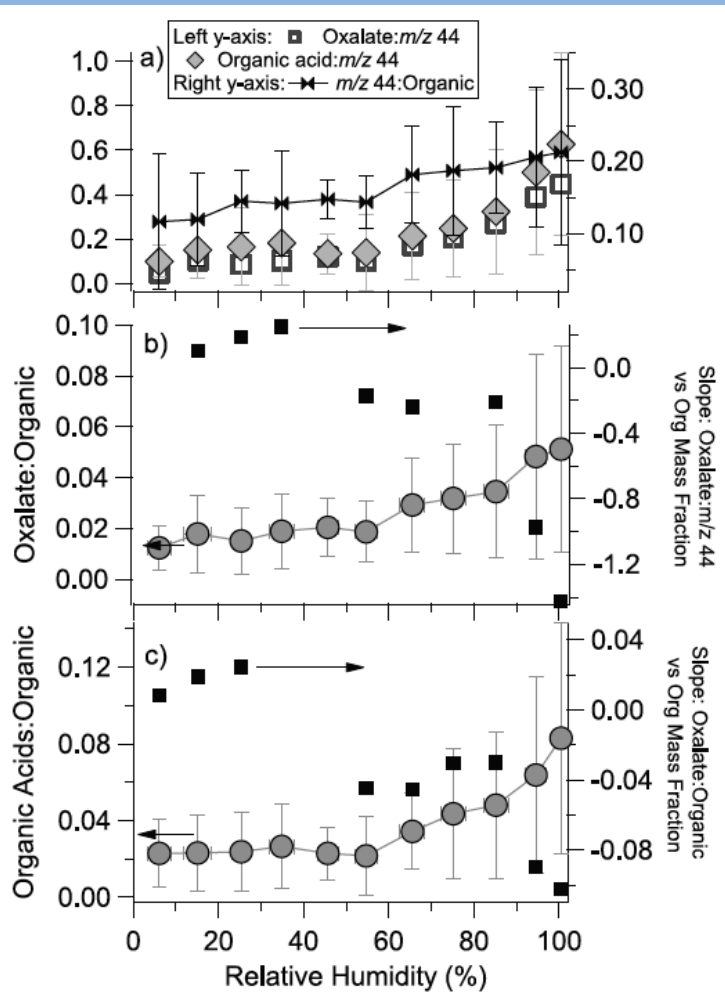


Peak at 60 – 70% RH is due to Fp peak in afternoon, no relationship to RH.

Atlanta SOA formation process very different from LA and generally consistent with aqSOA formation route

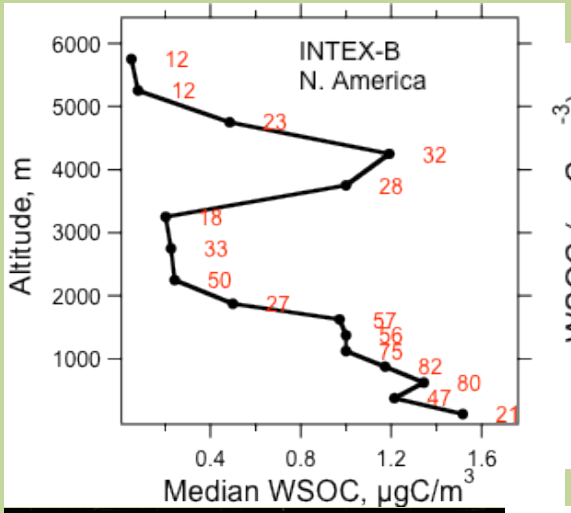
Aircraft Measurements also Indicate AqSOA Occurs Aloft

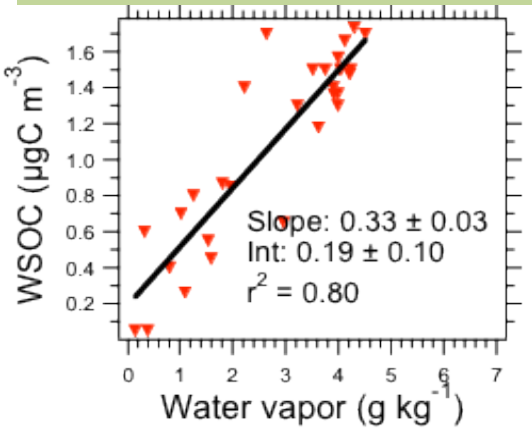
Sorooshian et al, GRL 2010
Ensemble of Caltech aircraft data

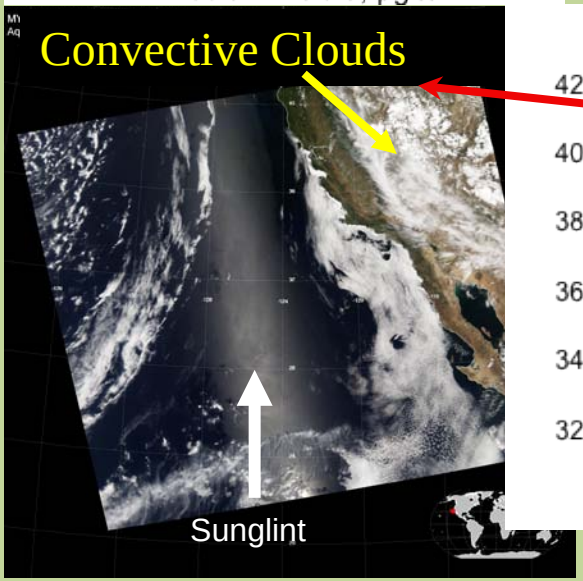


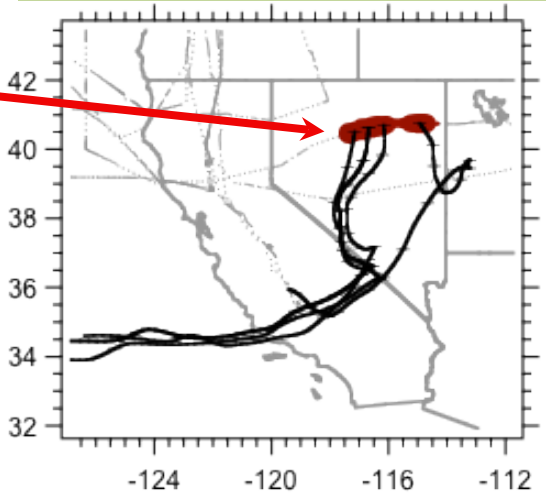
Organic acids produced in haze/clouds

Peltier et al., ACP 2008; NSF C-130 INTEX-B





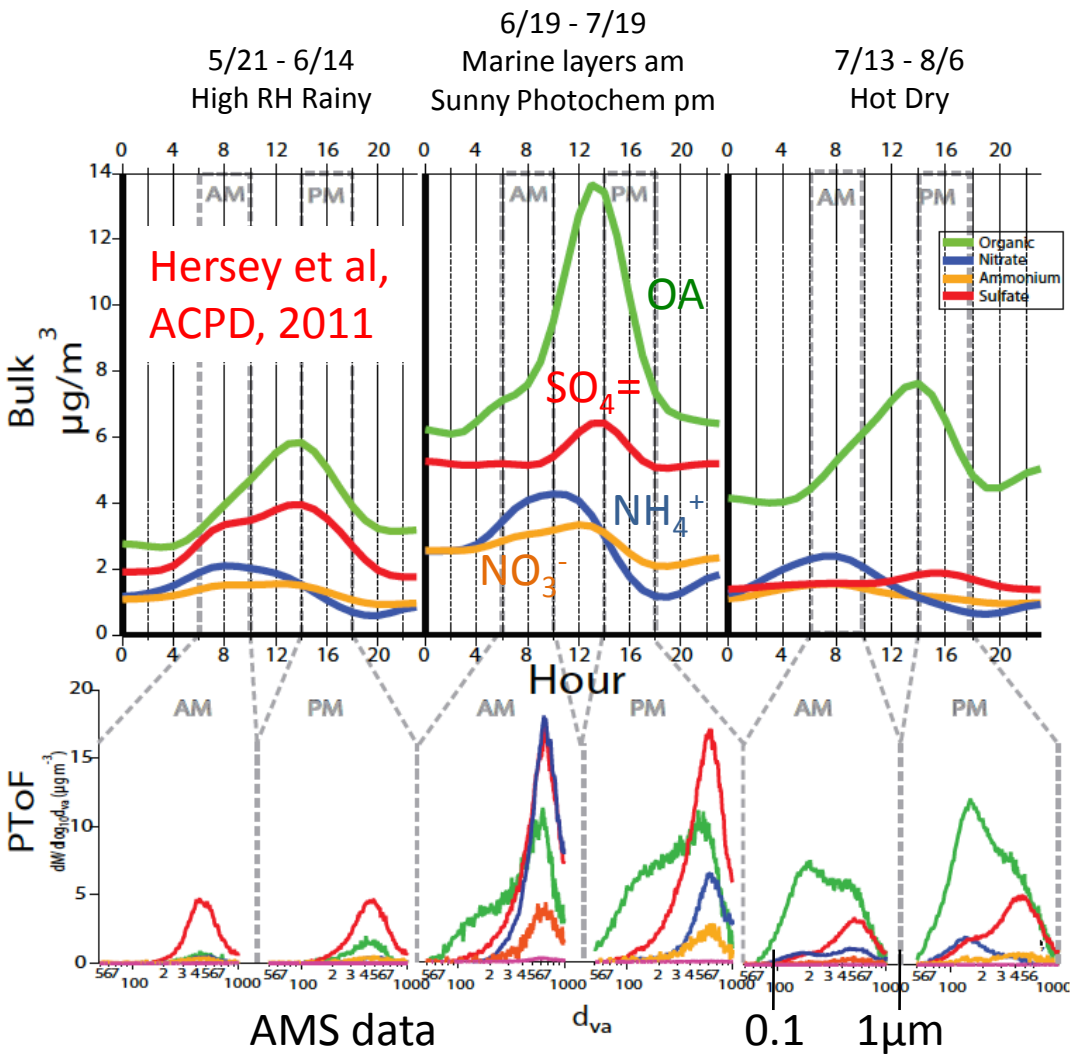




WSOCp formed in (associated w/) clouds

Size Distributions of Organic Aerosol and Correlations with $SO_4^=$ also Provide Evidence For Prevalence of aqSOA

Pasadena Aerosol Characterization Observatory (PACO) 5/21 to 8/6 2009 CalTech



Other studies show organic acids & WSOC correlated with droplet mode and sulfate

- Huang et al, *JGR* 2006 (S. China)
- Lin et al, *JAS* 2010 (Rural S. China)
- Sorooshian et al, *JGR*, 2006 (midwest)
- Yao et al, *Atm Env* 2003 (Beijing)

Summary Thoughts

1. Understand processes to assess responses to changing climate
   - Eg, role of T on BVOCs and their link to SOA: BVOC ≠ "natural" BSOA.
2. Current models predicting SOA ignore aqSOA route, most interested in getting SOA mass, yet process affects size distribution → CCN, Scattering
3. aqSOA has interesting cloud-SOA-cloud interactions
   - WSOCp mass fraction affects water uptake; haze and CCN activation
   - WSOCp, to some extent, is produced in haze and clouds
   - WSOCp aqueous chemical aging affects MW, light abs, surfactant properties …

   (aerosol undergoes many cycles of wet/dry…, day/nite and cloud cycling)

Measurement Opportunities/Needs

1. Utilize existing network sites by developing novel analysis techniques (use FRM-filters for: BC by filter darkness, WSOCp, Absn Spectra, levog … from teflon filters)
2. To understand partitioning process, measure gas and particle.
3. Size-resolved composition informs process: condensation/droplet modes
4. Aerosol phase oxidants critical for aqSOA (interest in health studies)