

# Measurements of light absorption spectra of fine particle aqueous extracts during CalNex at the Pasadena ground site

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CalNex Data Analysis Workshop

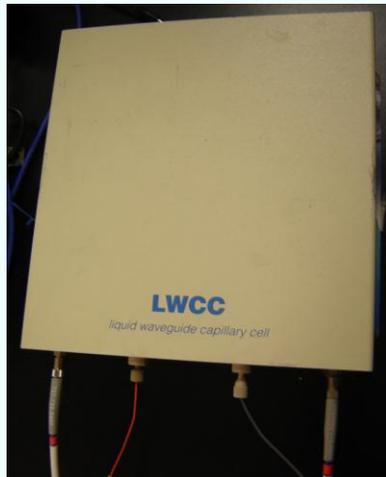
May 16-19, 2011

Sacramento, CA

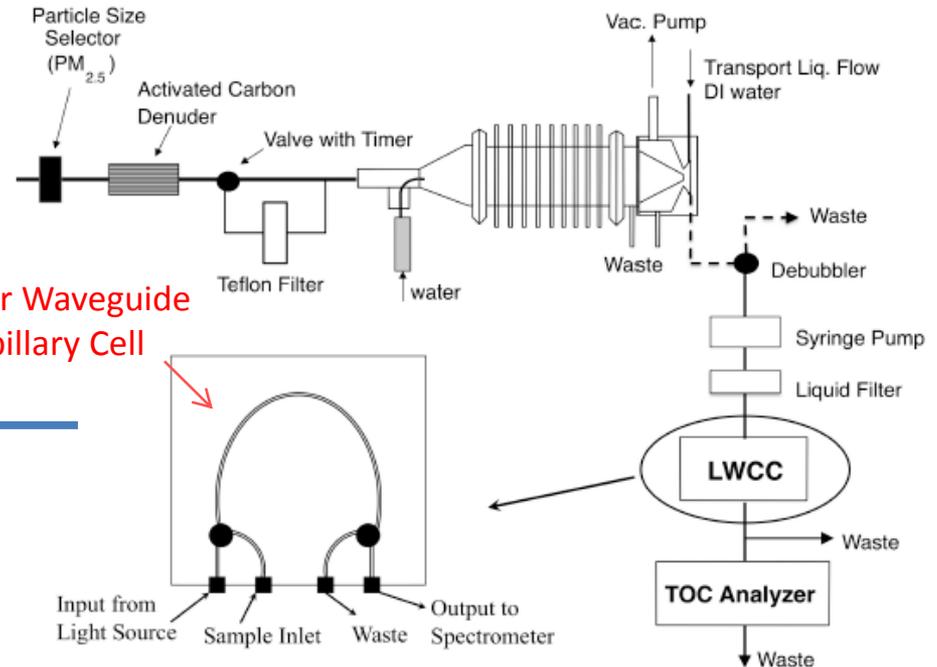
# Real-time light absorption spectral measurement

## Simultaneous measurements of soluble particle absorption spectra and carbon mass

### Long Optical Path Spectrometry With Liquid Wave guides (LWCC)



1 meter Waveguide  
Capillary Cell



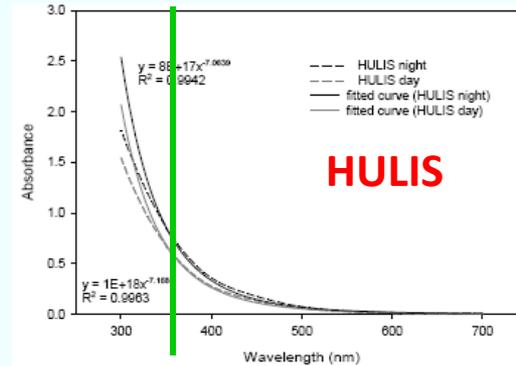
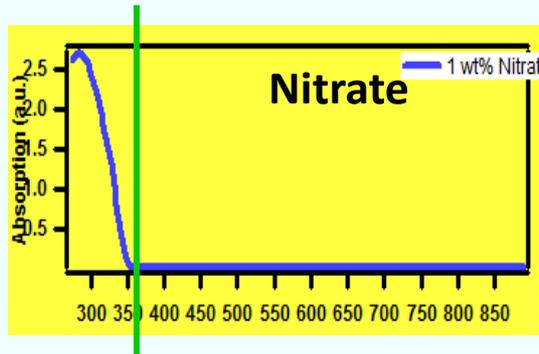
(Hecobian et al., 2010)

- Complete absorption spectra (200 – 800nm) was saved every 15 min
- Absorption coefficients at selected wavelengths (365nm, 700nm) were saved every 60 sec

# Choice of wavelength: $\lambda = 365\text{nm}$

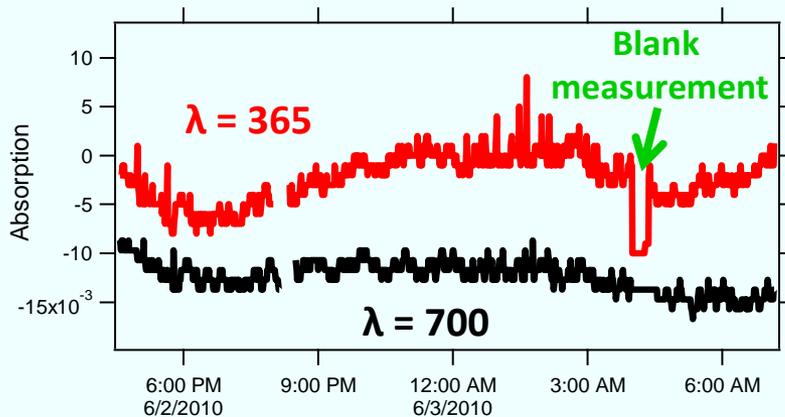
$\lambda = 365\text{nm}$  : Absorption averaged between 360 and 370nm

- Soluble Brown Carbon, specifically associated with HULIS (Lukacs et al., 2007);
- Avoid interferences from other species: e.g. Nitrate;



(Hoffer et al., 2006)

$\lambda = 700\text{nm}$ : Reference wavelength



Absorption coefficient at 365nm ( $Abs_{365}$ )

$$Abs_{\lambda} = (A_{\lambda} - A_{700}) \frac{V_l}{V_a \cdot l} \cdot \ln(10)$$

Unit:  $\text{m}^{-1}$

# Sources of brown carbon: PMF result on FRM filters

PMF analysis on 900 FRM filters collected at 15 sites in SE US

**Biomass Burning**      **Ammonium Sulfate/WSOC**  
**Refractory Material**   **Mobile Sources**  
**WSOC/Oxalate**        **Residual**

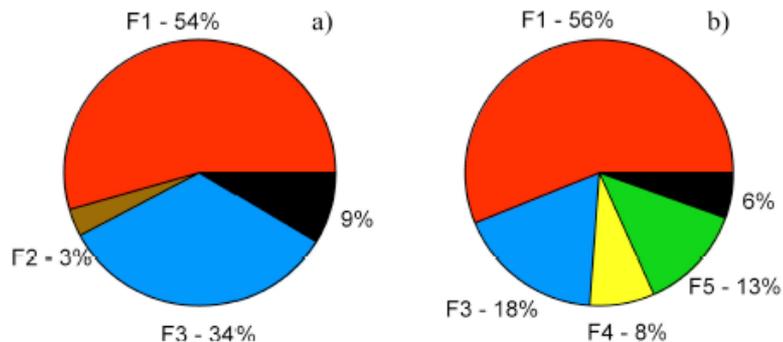


Fig. 7. PMF results on the 2007 average distribution of  $A_{365}$  amongst (a) the four factors resolved for all FRM sites (rural and urban) using a limited suite of species, and (b) the five factors resolved for only urban speciation sites listed in Table 1. The factors were identified (Zhang et al., 2010a) as, F1: Biomass Burning, F2: Refractory Material, F3: WSOC/Oxalate, F4: Ammonium Sulfate/WSOC, F5: Mobile Sources, remaining is the unresolved fraction.

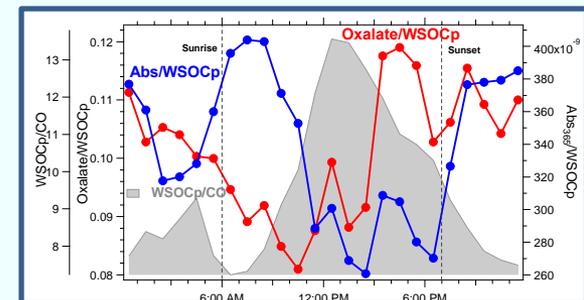
(Hecobian et al., 2010)

## Major sources of Brown Carbon ( $Abs_{365}$ ) in the southeast:

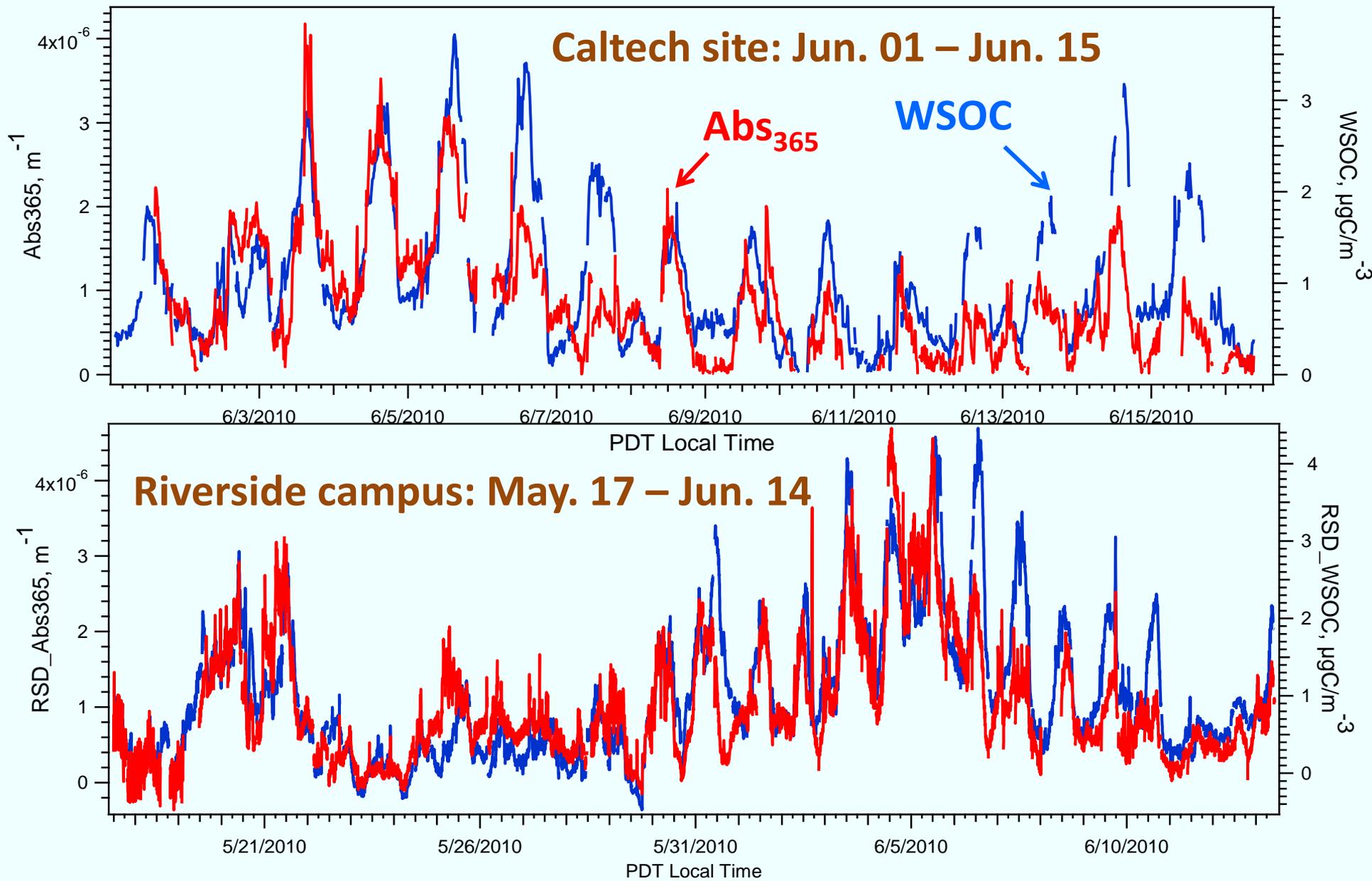
- Biomass burning;
- Primary emissions from vehicle;
- SOA formation (WSOC/Oxalate);



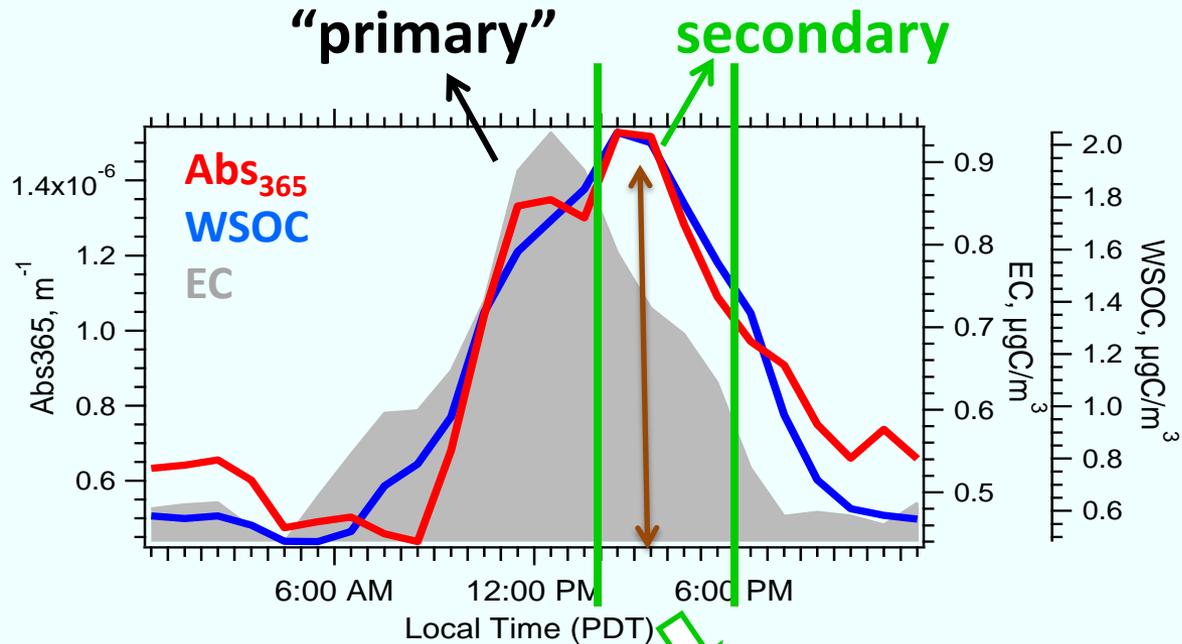
Possibly related to aqueous SOA formation/chemical aging – oxalate and brown carbon peak hours after WSOC peak on diurnal average from online dataset in Atlanta.



# WSOC and brown carbon during CalNex



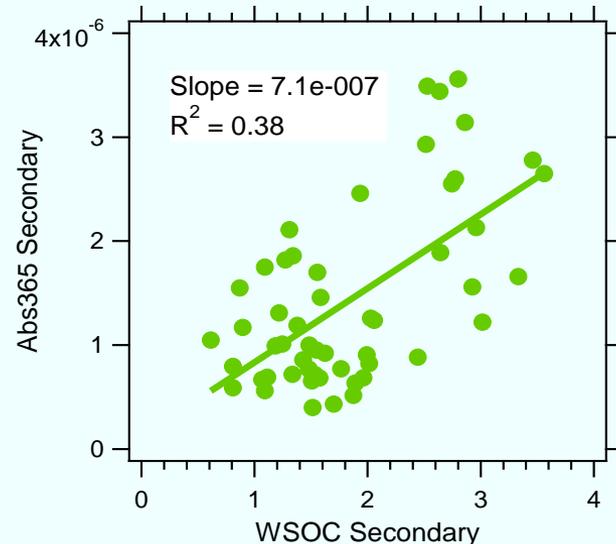
# CalNex: mass absorption efficiency



Mass absorption efficiency ( $\alpha_{abs}$ )  
 $\Delta Abs_{365} / \Delta WSOC$

at 360-370nm  $\alpha_{abs} = 0.71 \text{ m}^2/\text{g}$

Small compared to  $\alpha_{abs}$  for soot  $\sim 7.5 \text{ m}^2/\text{g}$   
*(Bond and Bergstrom, 2006)*



# Mass absorption efficiency: LA compared with Atlanta

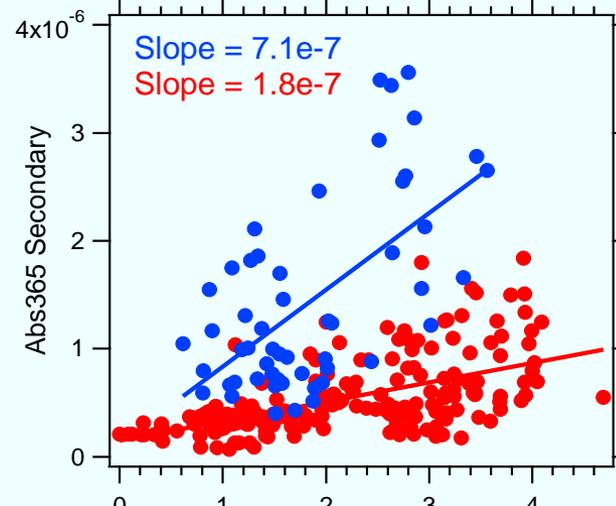
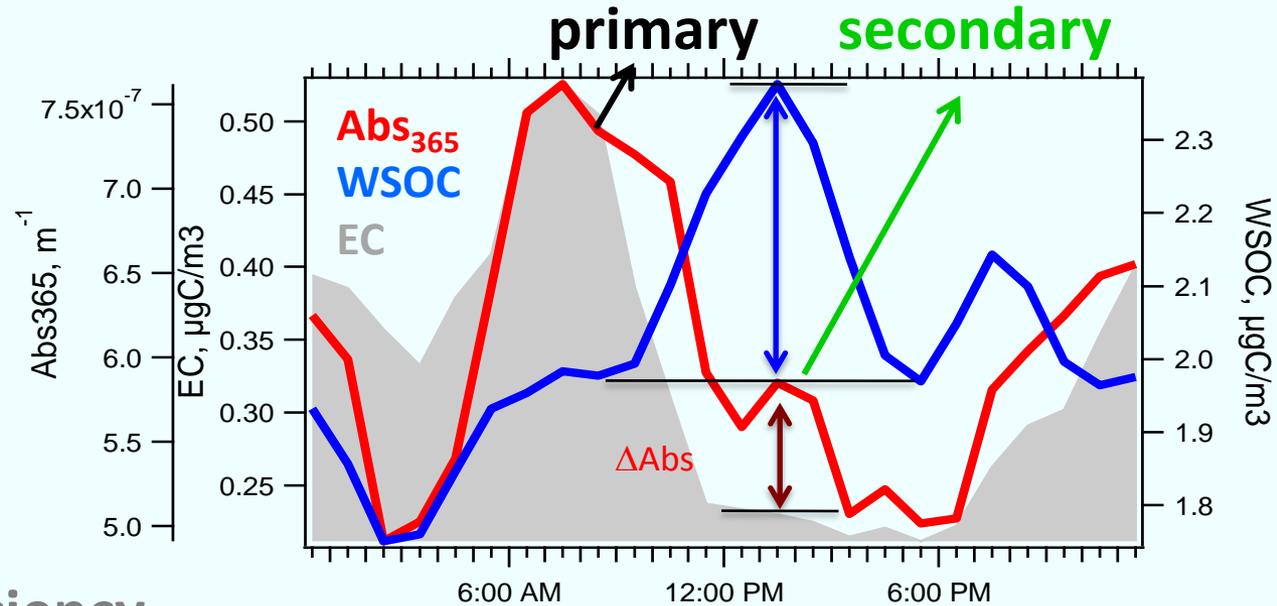
Gatech campus  
in Atlanta, Aug. 2010

Mass absorption efficiency

$$\text{LA: } \alpha_{\text{abs}} = 0.71 \text{ m}^2/\text{g}$$

LA 4 x higher

$$\text{ATL: } \alpha_{\text{abs}} = 0.18 \text{ m}^2/\text{g}$$

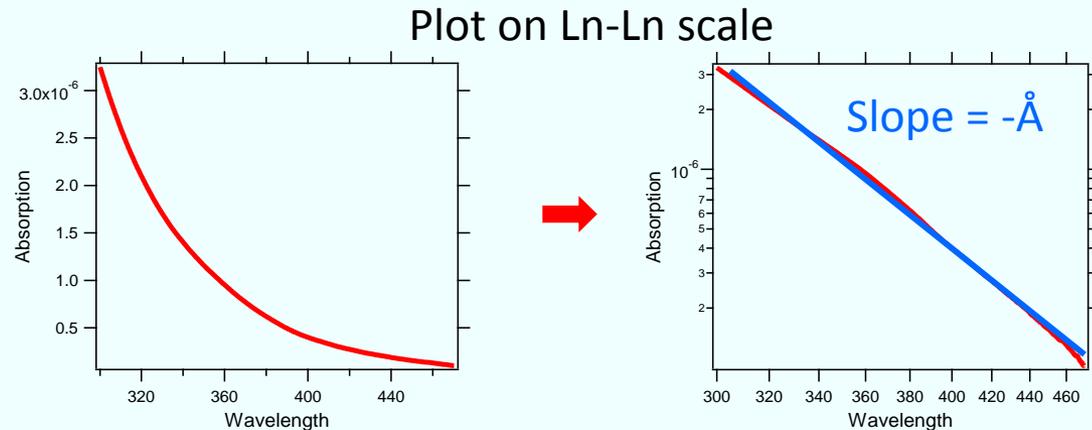


LA fresh secondary WSOC is much more light-absorbing than Atlanta

# Angström exponent

## Wavelength dependence of the absorption coefficient

$$\alpha_{ab} = K \cdot \lambda^{-\text{\AA}}$$



### For ambient aerosol

\AA ~1: black carbon (absorbs at all wavelengths)

\AA ~2: ambient biomass burning aerosol (Kirchstetter et al., 2004)

\AA ~3.5: polluted region in China (Yang et al., 2009)

### For liquid extracts (this study)

\AA ~7: water-soluble HULIS (Hoffer et al., 2006)

\AA ~7-16: smoldering smoke (Chen and Bond, 2010)

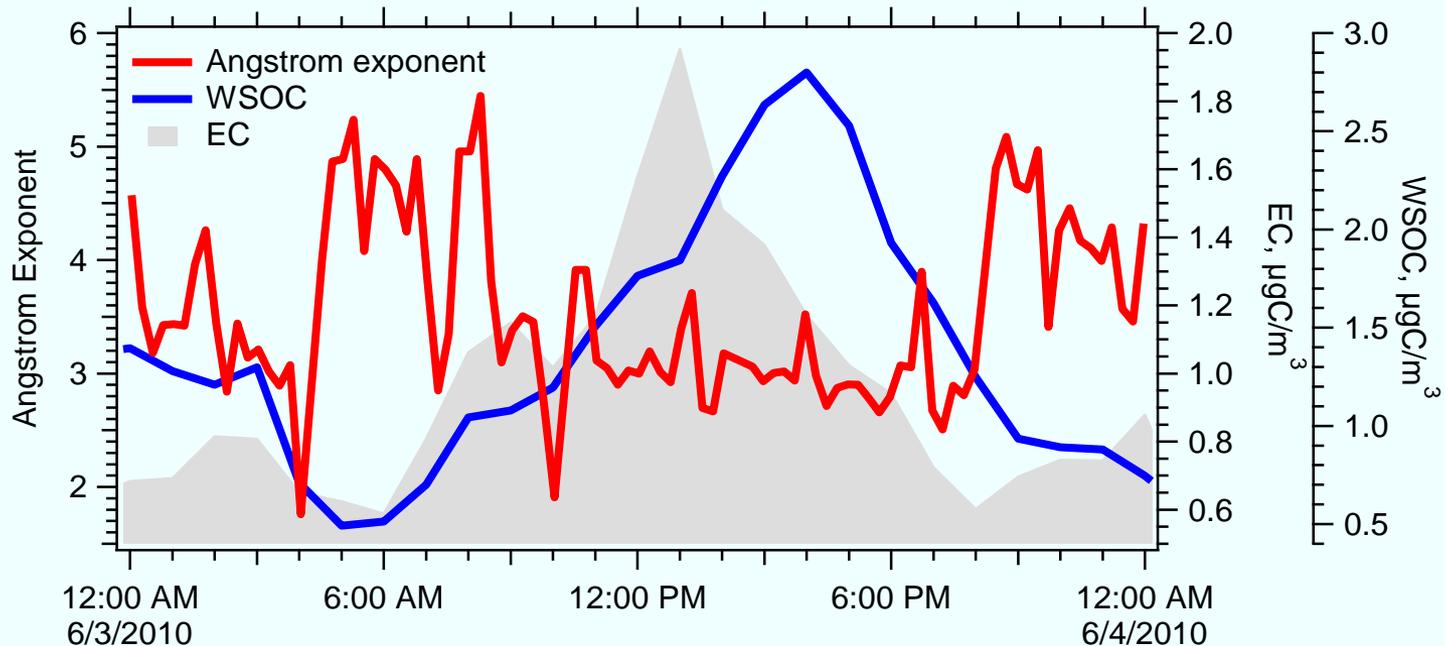
\AA ~7: fresh limonene SOA (Bones et al., 2010)

\AA ~4.7: aged limonene SOA (Bones et al., 2010)

\AA ~6-8: FRM filters in SE US (Hecobian et al., 2010)

# Variation of Angström exponent

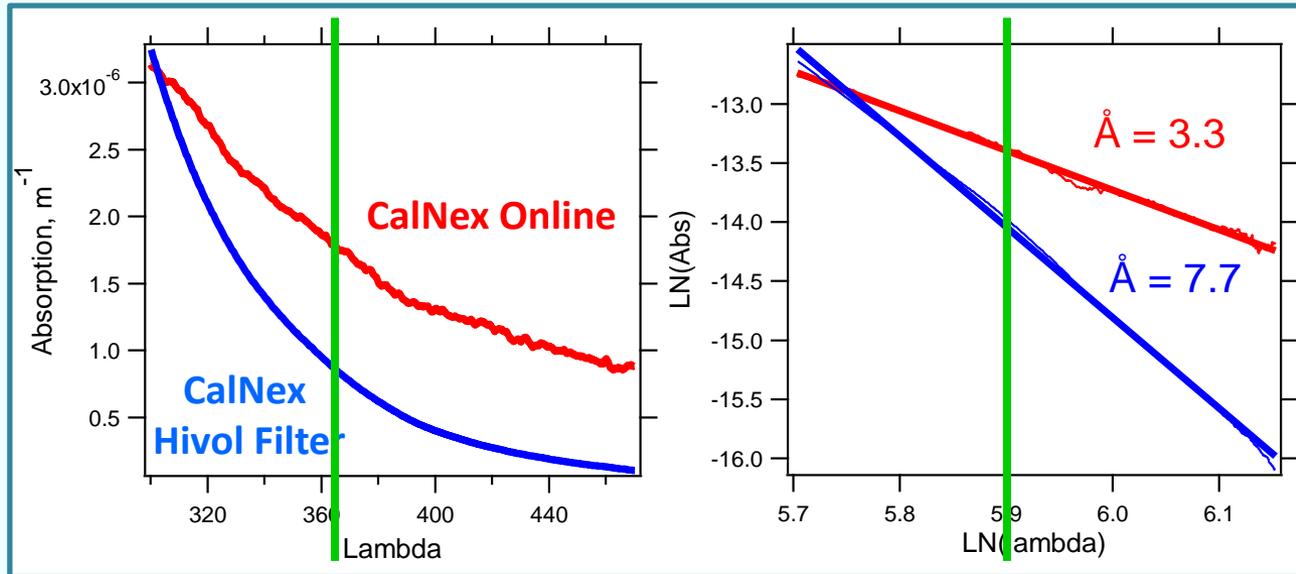
Example: **6.3.2010** – high concentration of Abs<sub>365</sub>



- Å varies between 2 and 5.5, lower during daytime and higher at night; Å increased from “fresh” to “aged” SOA?
- Å derived from online measurement significantly lower than Å from filter-based measurement (discussed in the next slide);

# Filter-based vs. online absorption measurements

## Comparing Absorption coefficient ( $Abs_{365}$ ) and Angström exponent



- Some underestimation of  $Abs_{365}$  by high-vol filter;
- Online and filter  $\text{\AA}$  quite different; For filter less absorption at higher wavelengths;

## Possible artifacts of filter-based brown carbon measurement:

- **Storage:** 1-yr in the freezer leading to changes?
- **Extraction:** extraction/sonication leading to degradation of larger chromophores which absorb light at higher wavelengths? (*Sun et al., 2007*)
- **Time resolution:** filter liquid extracts sit for 1-2 days before analysis

# Summary and Implications

## Summary

- Major sources of brown carbon during CalNex is SOA formation and mobile emission ;
- Fresh LA WSOC is ~4 times more light-absorbing than fresh ATL WSOC, possibly due to a larger fraction of anthropogenic aerosol in LA;
- Angström exponents lower during daytime and higher morning and night (evidence for anthropogenic SOA evolution?);
- Filter-based measurement not consistent with online measurement (*more experiments*)

## Why care about Brown Carbon?

- Generally not thought to have effect on radiative forcing due to small mass absorption efficiency (*Andreae & Gelencser, 2006*), BUT
- *SOA properties, source and evolution:*
  - Component of fresh anthropogenic SOA (related to aromaticity?) (*Sun et al., 2007*), useful for contrasting SOA in different urban settings (e.g. LA vs ATL);
  - Dissolve in liquid droplets, affect cloud absorption (*Mayol-Bracero et al., 2002*) & useful to study heterogeneous processing;

## Future work/collaboration

- Try to find correlation between brown carbon and specific SOA component?