(Some!) Outstanding Questions in Organic Aerosols

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SAS Data Workshop

April 1, 2014

Whither SOA?

- Interaction of biogenic and anthropogenic precursors can synergistically increase OM. (*e.g. de Gouw et al., 2005; Volkamer et al., 2006; Weber et al., 2007;Surratt et al., 2007; Goldstein et al., 2009; Schilling et al., 2012…*) OM >50% of $PM_{2.5}$ in the Southeast

- **When, where, how and by how much?**

- Different campaigns indicate different drivers
- Molecular tracers and bulk composition can inform us

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What Was Learned Recently Elsewhere?

Regional differences in SOA formation drivers

- New York (summer 2009) *(Sun et al., 2012)* many types of OA with different drivers when include inorganics in PMF

- CARES campaign (Sacramento; summer 2010)
  - Anthropogenic NOx enhanced isoprene SOA formation; mechanism unclear *(Schilling et al., 2012)*

- One CalNex assessment (Los Angeles basin; summer 2010) suggests major knowledge gaps *(Ensberg et al., 2013)*
  - Either vehicular emissions not dominant source of anthropogenic fossil SOA or ambient SOA yields substantially higher than those derived in lab chambers
  - Missing IVOC precursors (vehicular, biogenic *(Chan et al., 2013 IAMA; Goldstein et al., 2009)*, other…) and their SOA yields?
  - Other anthropogenic VOC emissions?

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SOA Formation in the Southeast (pre-SAS)

- Link ΔOC to ambient particle acidity was very weak to unmeasurable even with subdaily lags *(Tanner et al., 2009)*

- Isoprene SOA tracer links to acidity *(Surratt et al., various)* could be weak, even when conditionally-sampling time periods when clear ground level power plant plumes with SO4 captured *(Lin et al., 2013)…* perhaps reflecting difficulty of estimating acidity?

- Some link of organosulfate tracer (by single particle MS) to NOx ? *(Hatch et al., 2011)*

- ACSM in Atlanta and Look Rock found IEPOX-OA factors with better correlations to SO4 *(Budisulistiorini et al., 2013 and in prep)*

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SOA Formation in the Southeast (pre-SAS)

- Proposed direct role of SO4 as a nucleophile; importance of LWC particularly appropriate in the Southeast *(Nguyen et al., 2013 ACPD)*

- Other SOAS results suggest non-AMS indicators of biogenic SOA do not correlate with SO4? *(Carlton talk)*

OM fraction from isoprene SOA on order of 20%(?) leaving 80%(?) from other processes (*other biogenic precursors, biomass burning, mobile…*)

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Empirical Estimates of POC and SOC

Daily predicted POC = f(EC, CO, non-soil K)

"combustion OA", fresh and aged

Daily predicted SOC = g(O_3, SO_4)

"non-combustion" secondary OA

Blanchard et al. 2008. Atmos Environ.; Pachon et al. 2010. Atmos Environ.

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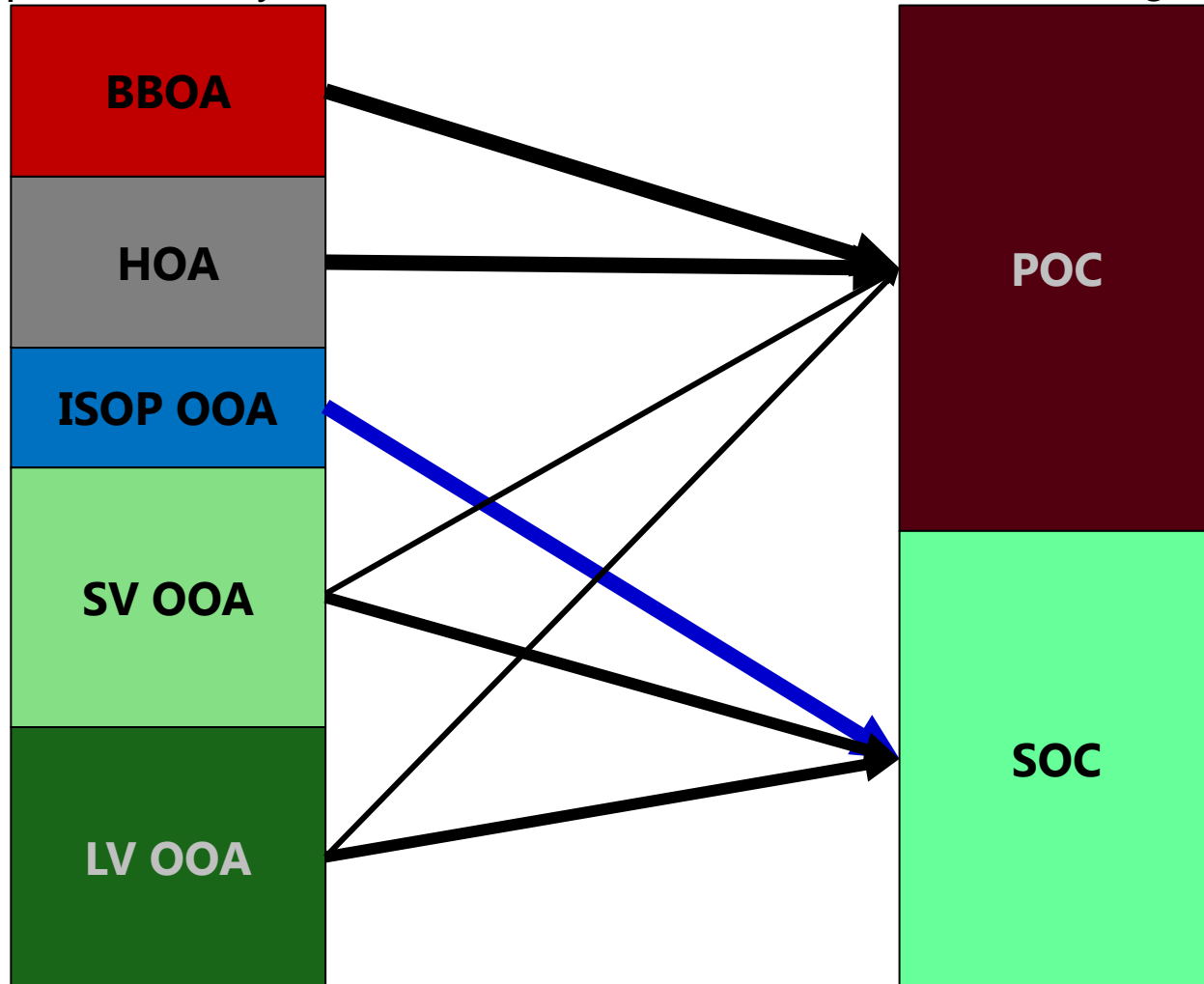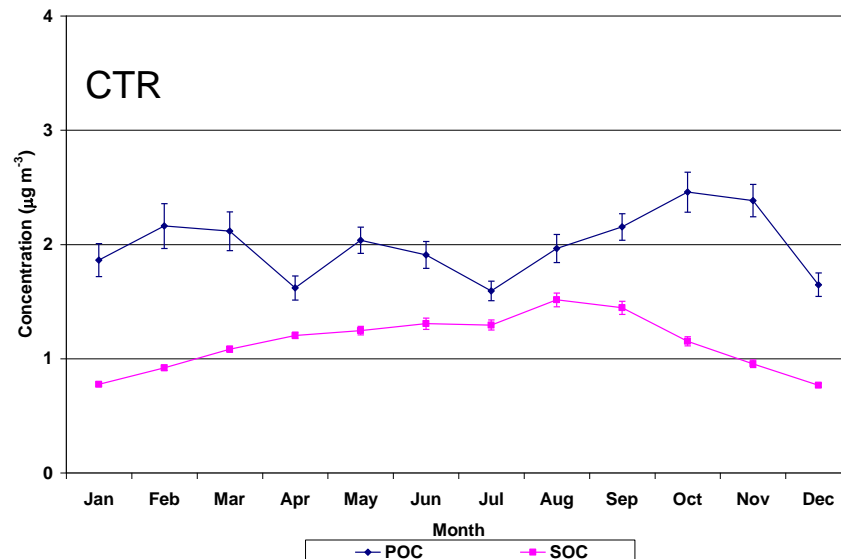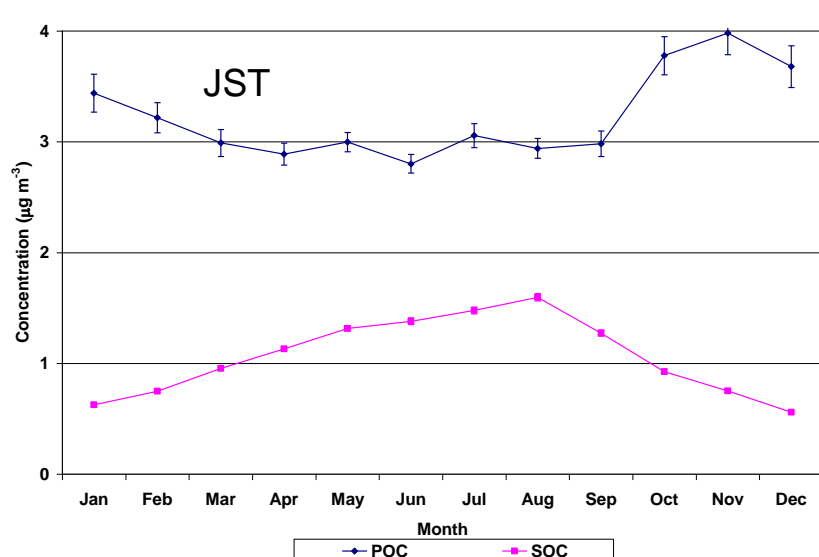
AMS Factors vs. POC & SOC Analysis

Composition & Dynamics
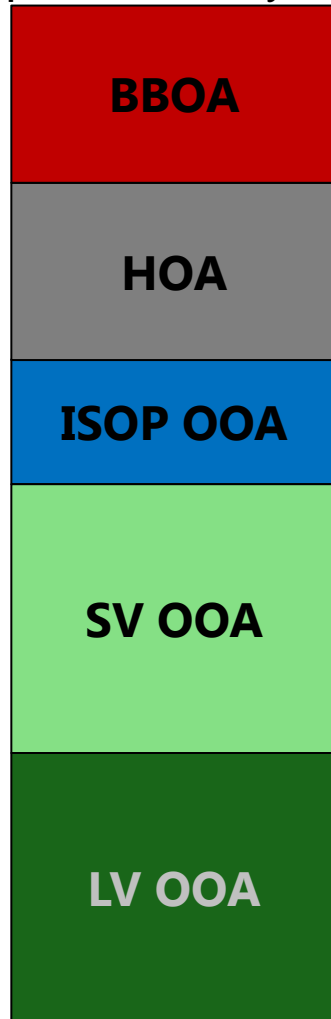
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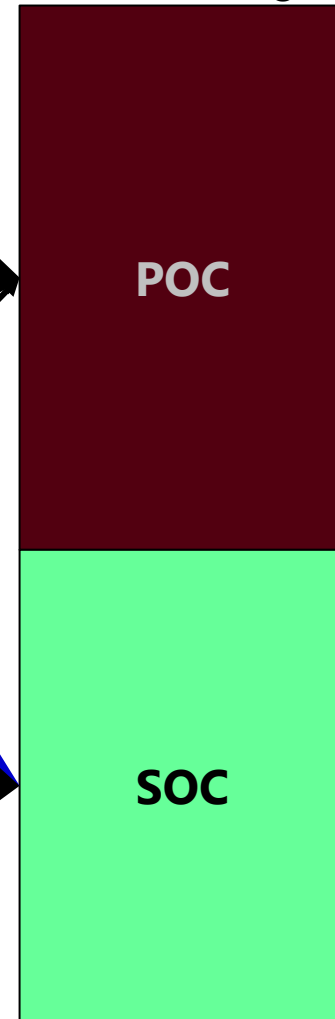
| BBOA |
| HOA |
| ISOP OOA |
| SV OOA |
| LV OOA |

| POC |
| SOC |

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Empirical Estimates of POC and SOC

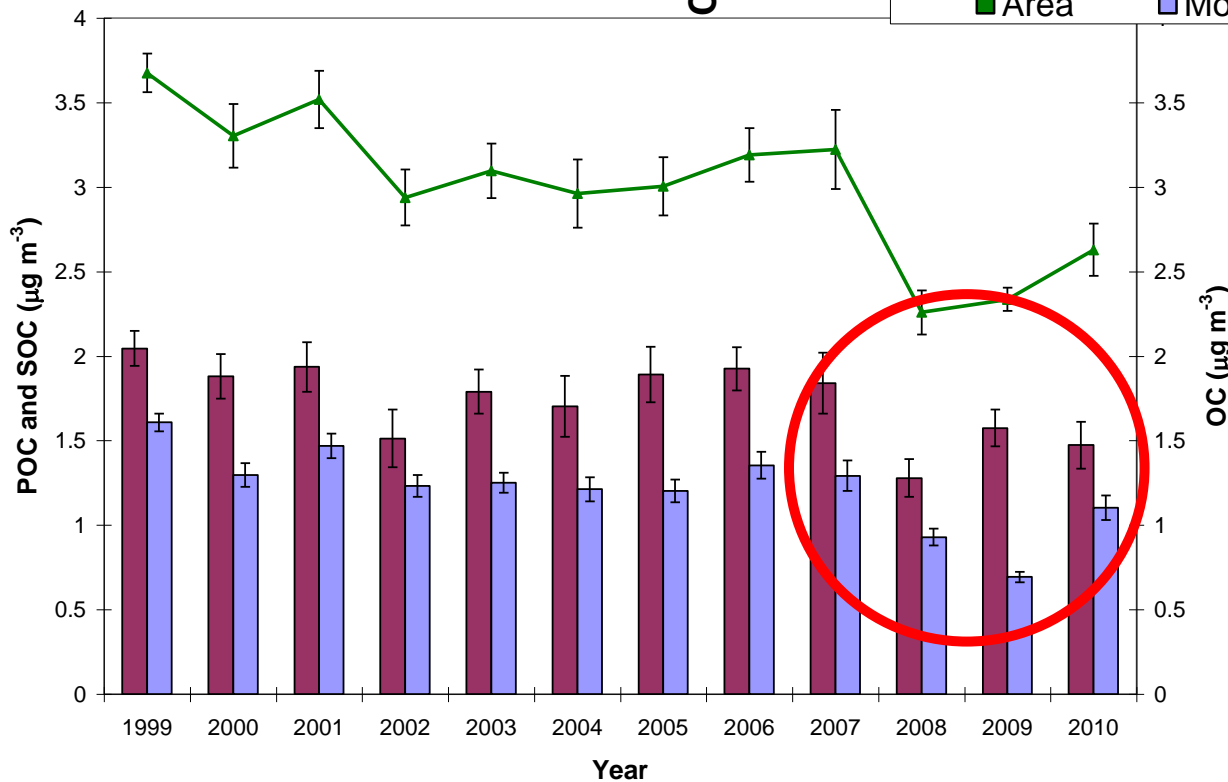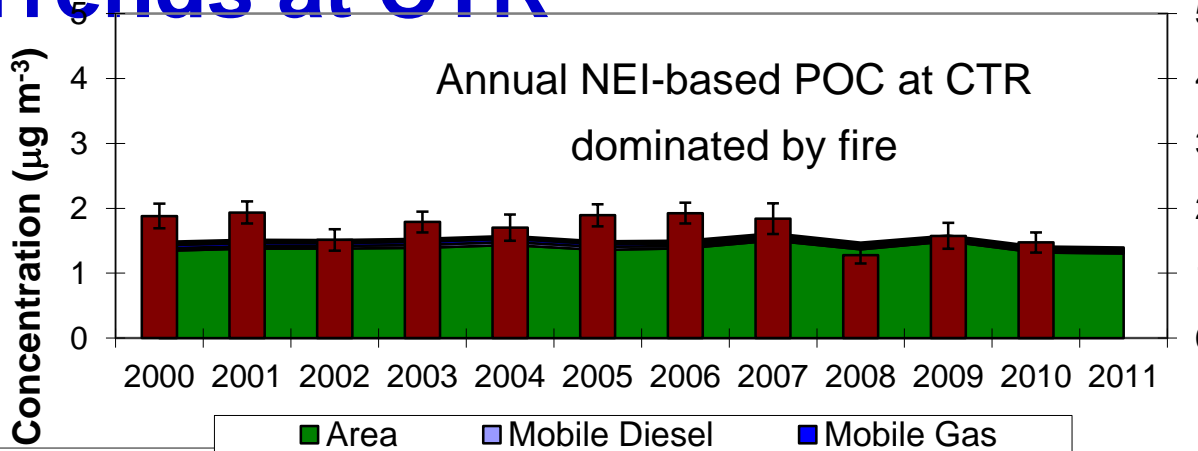Daily predicted POC = f(EC, CO, non-soil K)

"combustion OA", fresh and aged

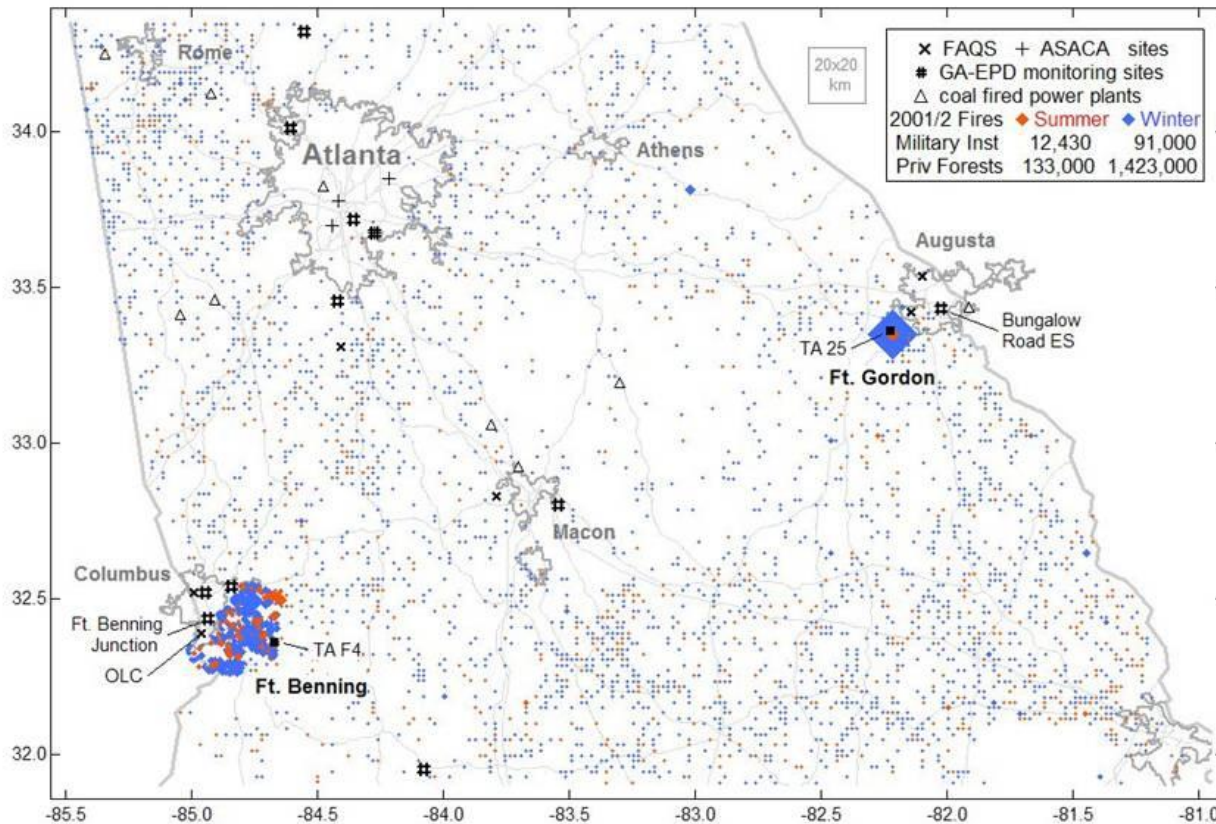Daily predicted SOC = g(O_3, SO_4)

"non-combustion OA"

Site-specific, reasonable SOC seasonality, compares well to seasonal mass fraction method *(Kleindienst 2010)*

POC and SOC Trends at CTR

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Prescribed Burning in the Southeast

- Many small, low intensity fires, can be simultaneous
- Satellites see only 25% of actual fires in SE as they are subcanopy *(Raffuse, pers. comm.)*

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Biomass Burning: Not Just Winter Only?

Various indicators suggest some fire influence year-round

1.

Southeast region burned area, 2008
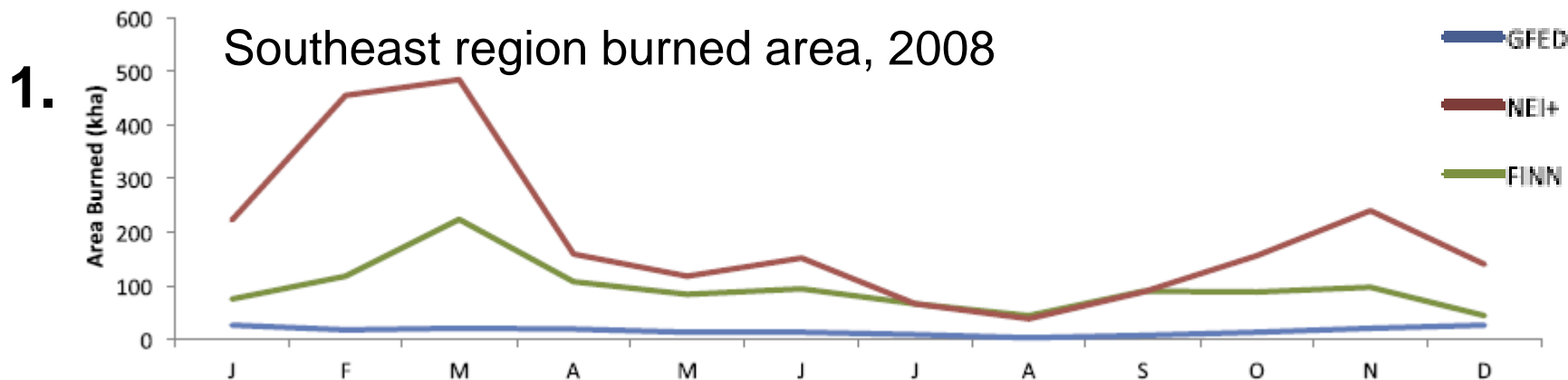
Larkin et al, 2013

2. Preliminary SAS observations?

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Biomass Burning: Not Just Winter Only?

Talk to Blanchard, Edgerton, & Baumann

3. New Kb tracer method at CTR

Running 12mo average

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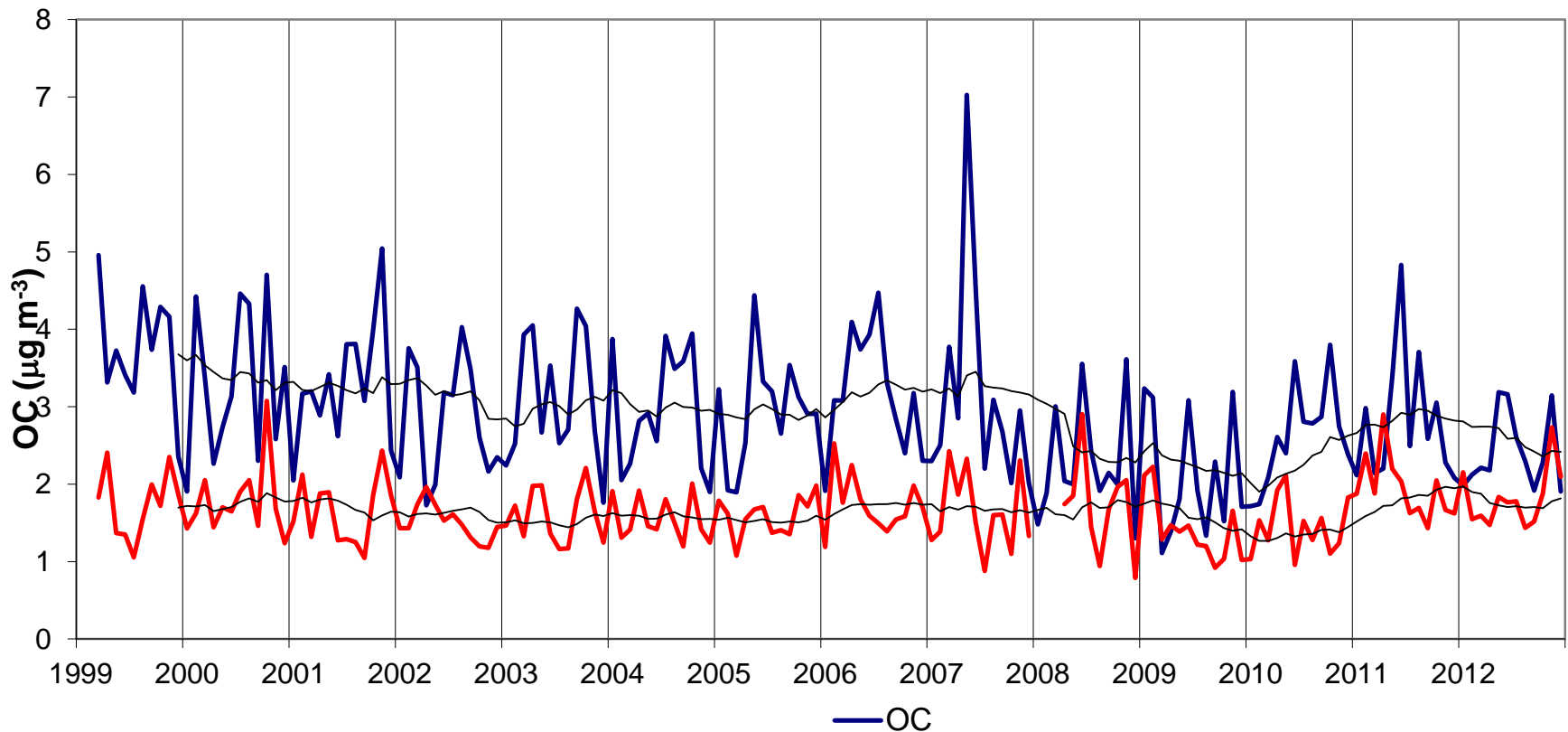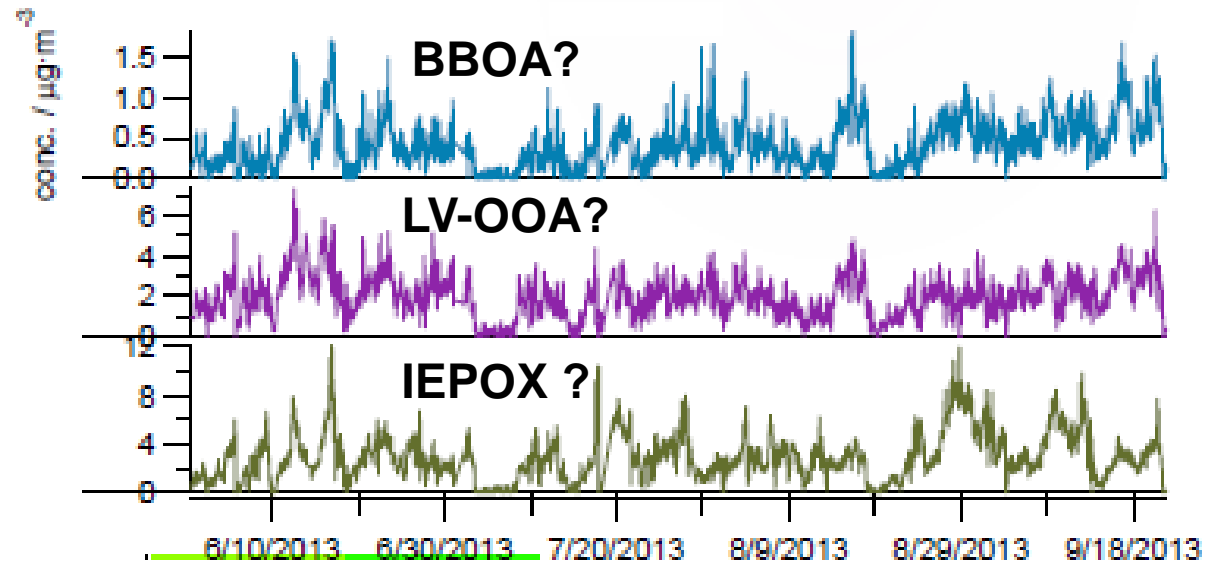
Biomass Burning: Not Just Winter Only?

4. Particulate retene at urban Atlanta
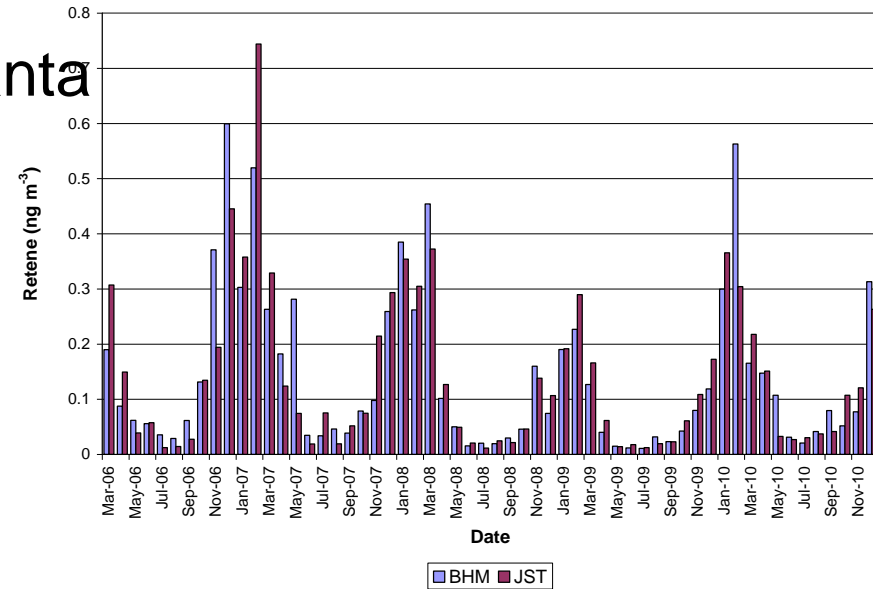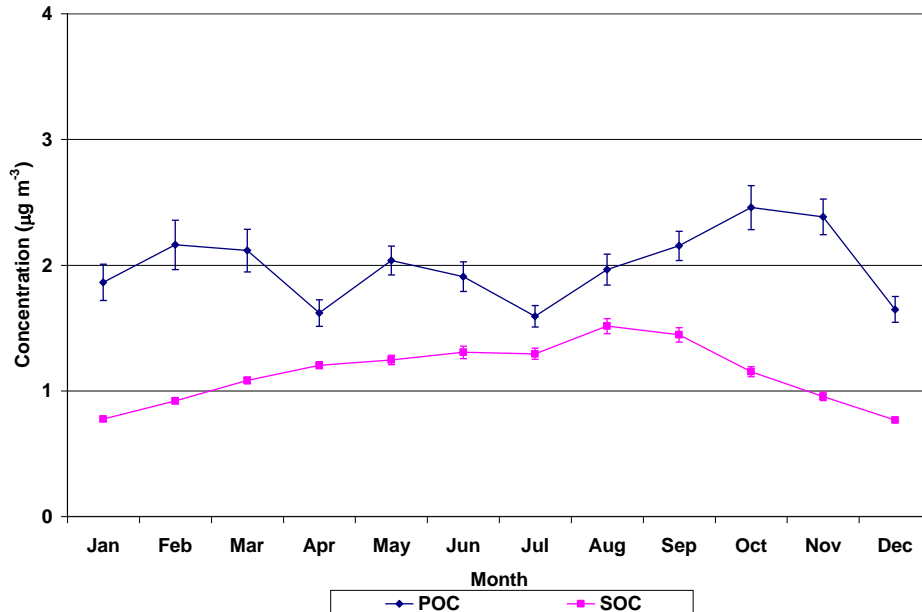
5. POC estimate (dominated by fires in rural Southeast) not very variable year round at CTR

Biomass Burning: Not Just Winter Only?

6. **ACSM at**

Look Rock

Summer 2013

Similar results in spring, fall, winter 2013 with ME-2. Factor present, but small, in all seasons. No BB tracer data yet to compare.

Minimal to no diurnal cycle. Suggestive of BBOA?

No correlation of CO with BBOA. **Is it aged, not fresh, burning?**

Do similar trends suggest aged burning signal in LV-OOA too, depending on factor analysis method?

Budisulistiorini et al.

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PRELIMINARY ¹⁴C Analyses of TC, OC & EC

See Edgerton poster

- 8 June SOAS samples suggest overall similar Fmodern in TC during SOAS (≥0.85) to 2004/2005 time frame (≥0.80)
  - **Suggests large anthropogenic reductions in OC did not drastically change modern-fossil split at CTR**

  NOSAMS facility

- **Only 2 combined samples** as yet, suggest Fmodern of EC was >0.69 during SOAS – likely biomass burning.
  - Composited samples **from 3 day period with no clear biomass burning plume** (based on CO/NOy, etc.)
  - Was possible to measure despite low [EC]
  - **What does this imply for OC from biomass burning?** 2013 and other years

Prevot, Szidat et al.

What Do We Need To Know?

- Annual and subannual trend data in biomass burning tracers
  - Recognizing undercanopy burns can be dominant
  - Tracers of very aged biomass burning from laboratory
  - How much AMS LV-OOA is from biomass burning?

- ^{14}C data on OC and EC fractions

- Any impact of anthropogenic SOA at CTR during SOAS?

- Trend estimates of vehicular SOA and isoprene SOA

- Ambient IVOC composition and subsequent SOA yields

- Role of SOA formation in power plant plumes

- What can and cannot be extrapolated to other seasons

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Role of Anthropogenic Source Changes in OC Trends?

- Mobile emissions trends suggest substantial fraction of OC drop in Southeast region is from fuel and tailpipe regulations *(Blanchard et al. talk yesterday)*

- Could anthropogenic sources impact CTR? Is it bigger than a breadbox?

  – Suggestions of aged urban 20-30hrs from BHM and Tuscaloosa during SOAS; includes aromatics *(Koss et al.)*

  – HOA not a dominant HR-AMS factor summer 2013? Would aged primary OC still look like HOA after a day?

  – Early ^{14}C data suggest role for fossil C *(Prevot, Szidat, et al.)*

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