

# Air Quality at Centreville, AL in June-July A Historical Perspective for SOAS at CTR

SAS Data Analysis Workshop  
March 31 – April 2, 2014

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# Question

How do the air quality conditions encountered at CTR during SOAS period 6/1-7/15 2013 fit into the long-term trend observed by SEARCH?

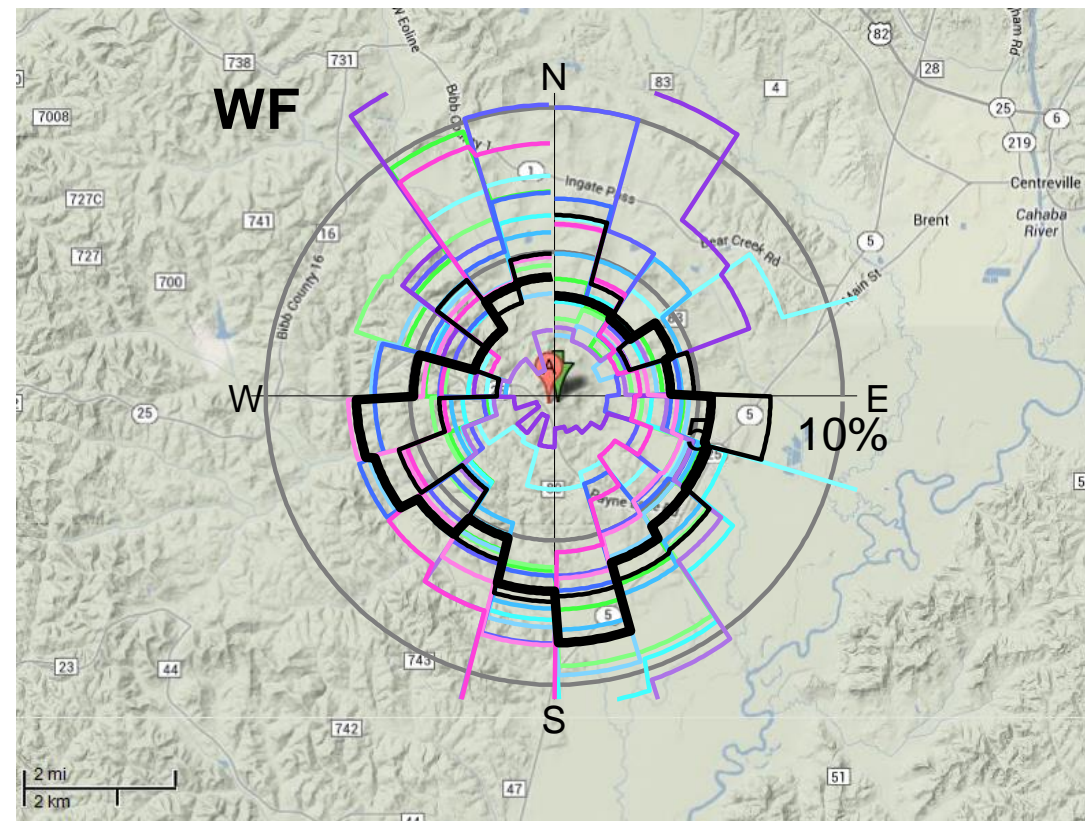




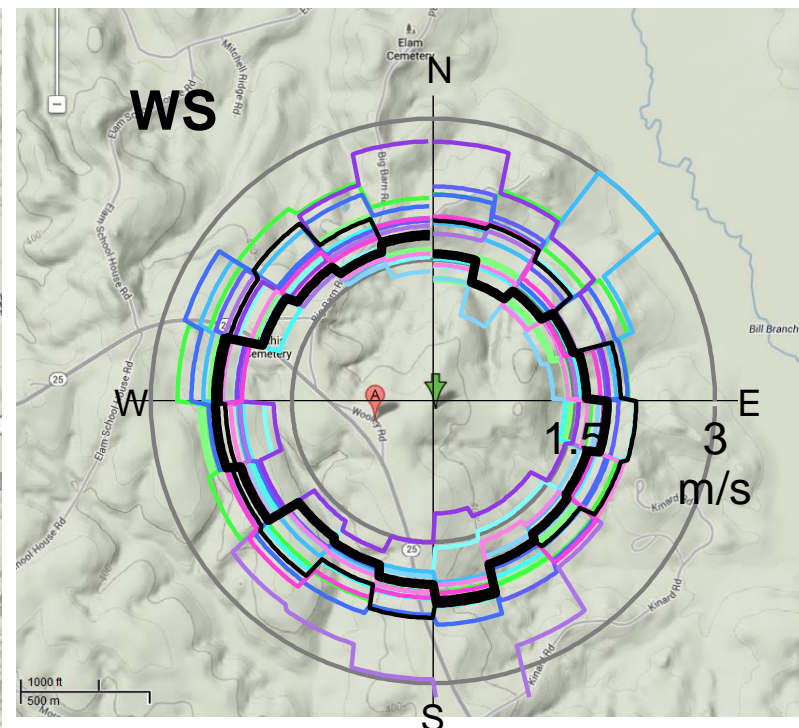
# Air Mass Transport 2000-2013

CTR-ARA 45-Day Period June 1 - July 15

2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013

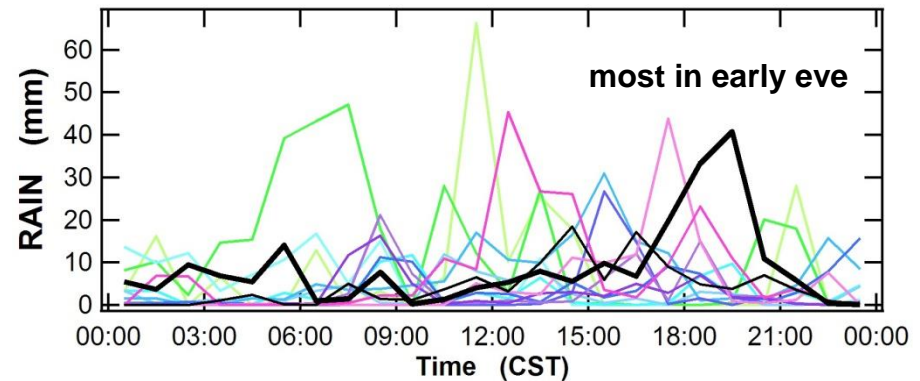
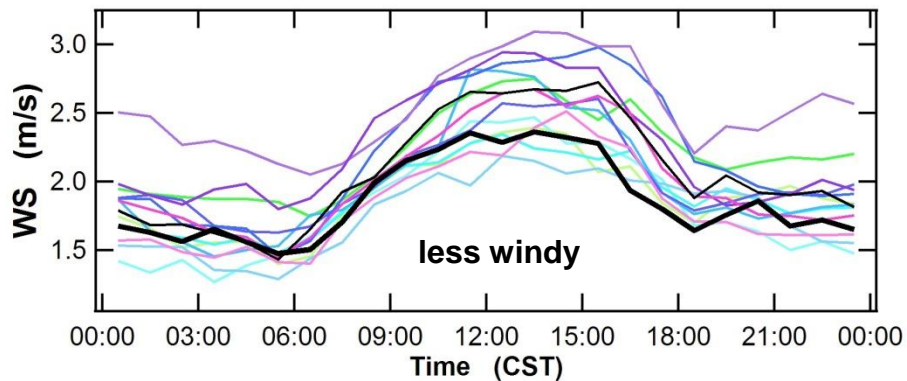
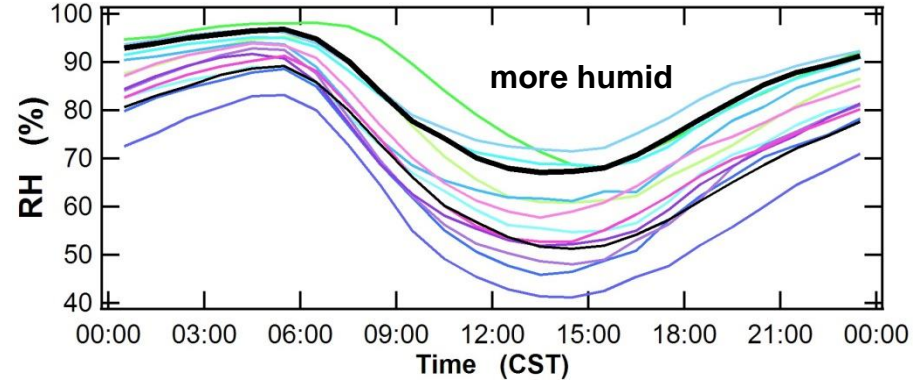
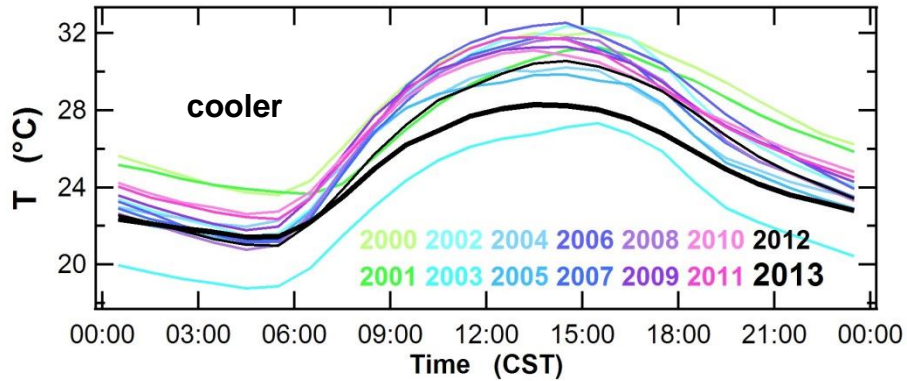
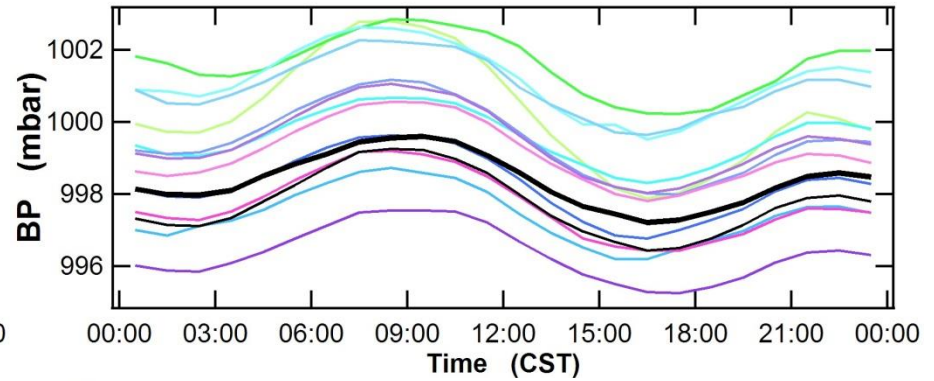
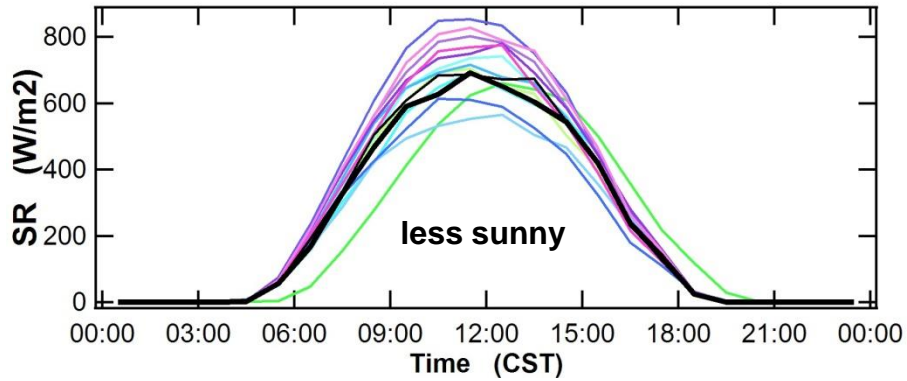


**Less northerly and more westerly component flow than in previous years!**



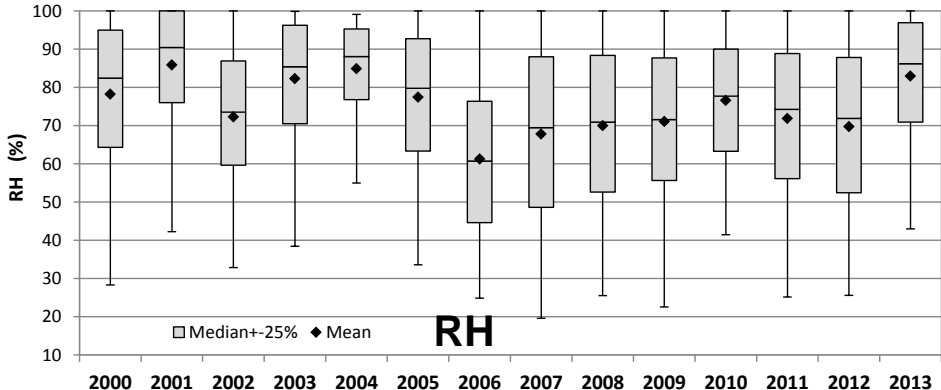
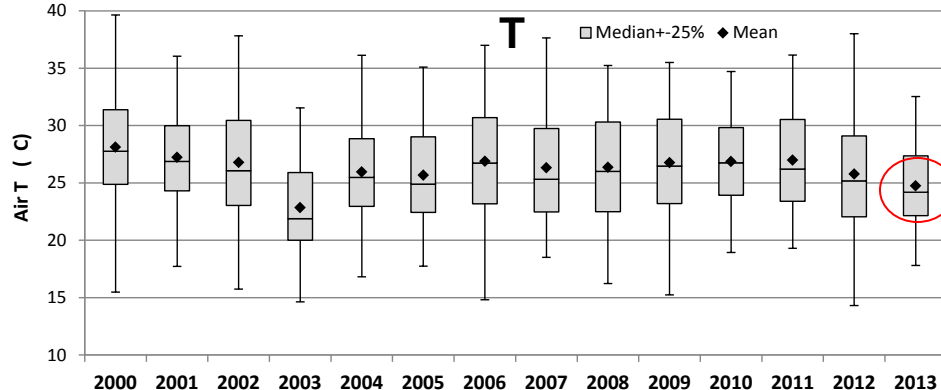
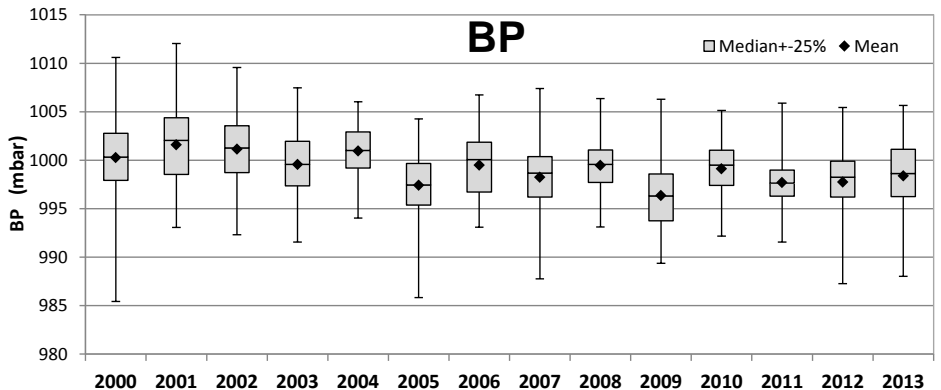
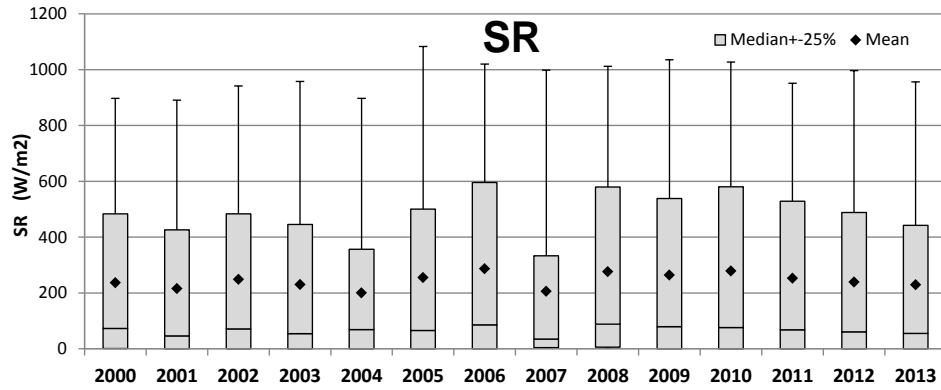
**Westerly winds are consistently strongest (excl. 2008), indicating influence by synoptic p-gradient.**

# Diurnal Met Parameters 2000-2013

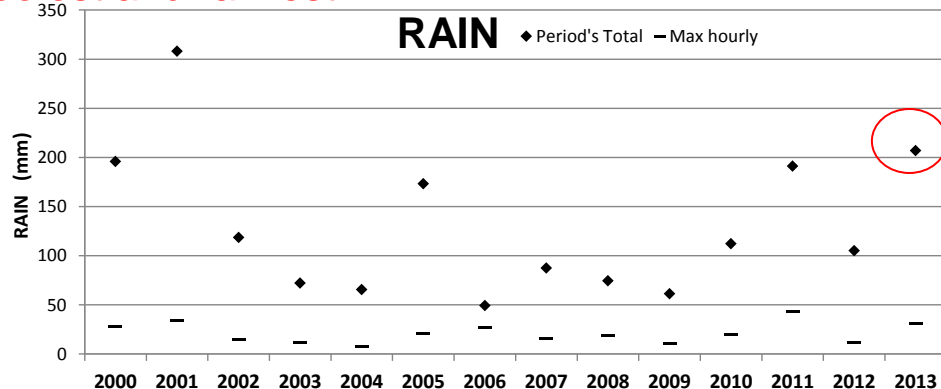
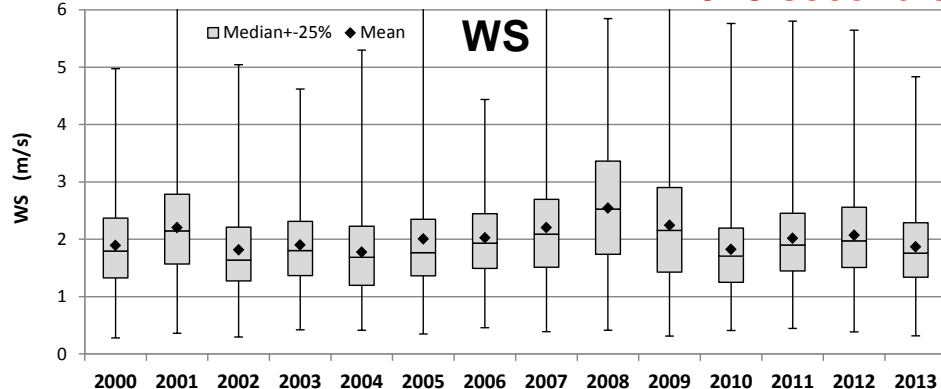


RAIN (mm) shows sum for each hour in 6/1-7/15 period

# Met Statistics 2000-2013

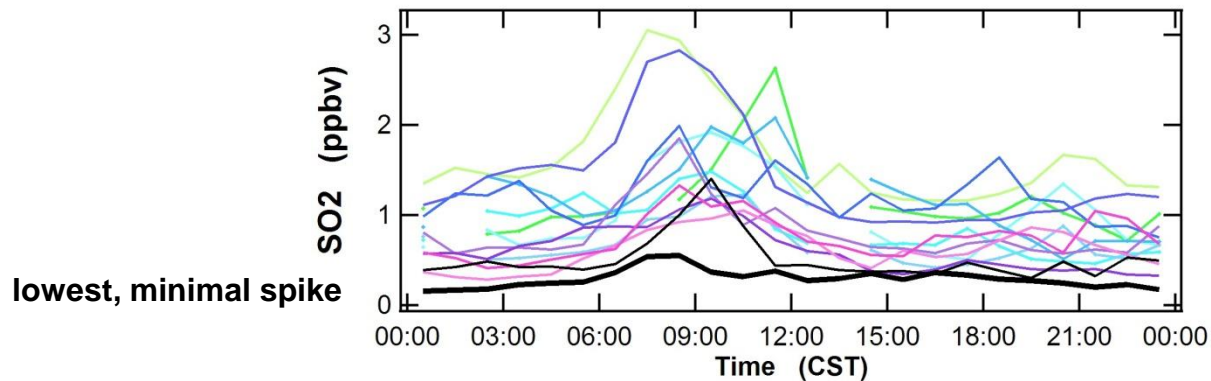


2013 second coolest and rainiest

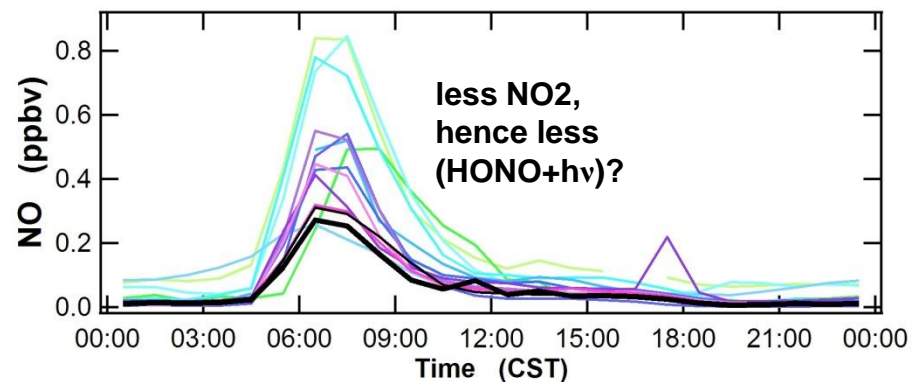
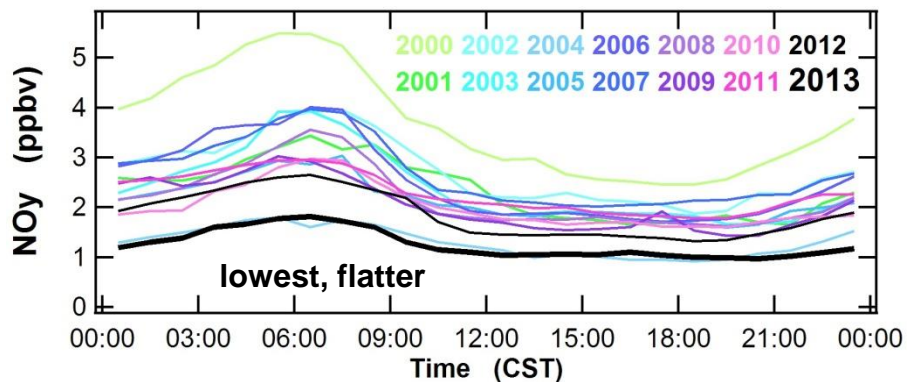
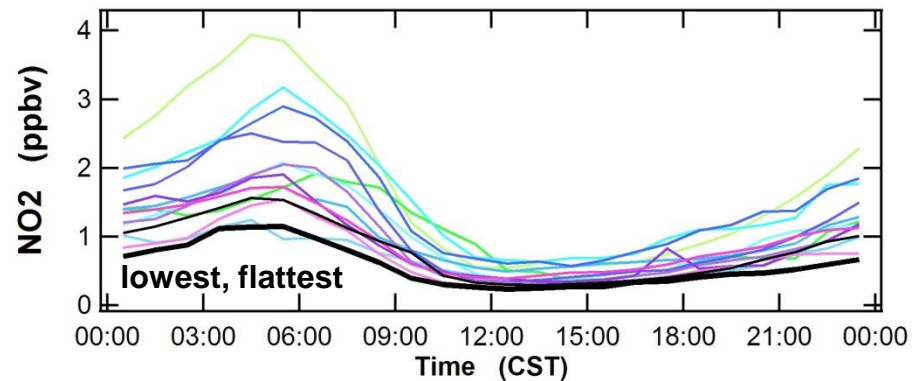
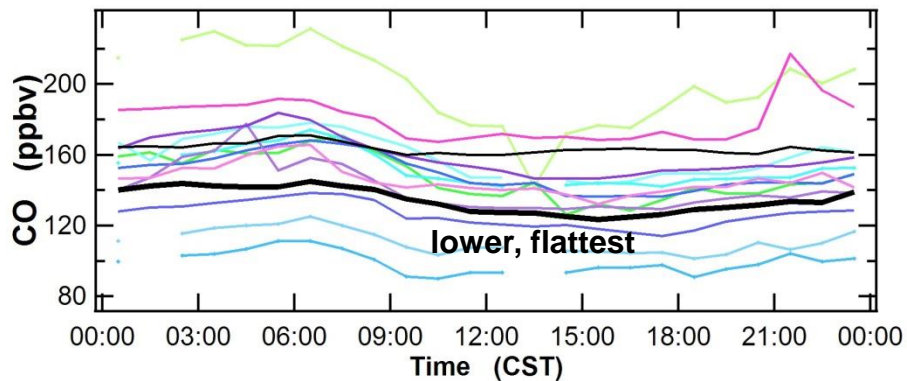




# Diurnal Primary Gases 2000-2013

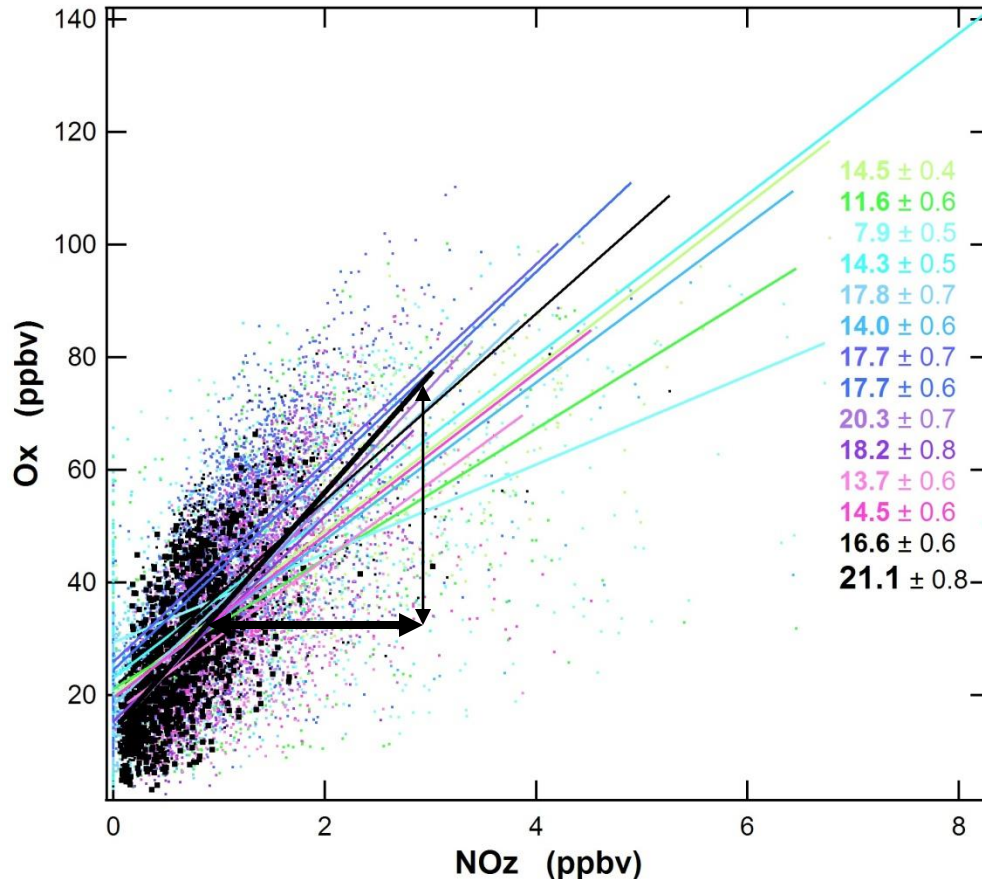
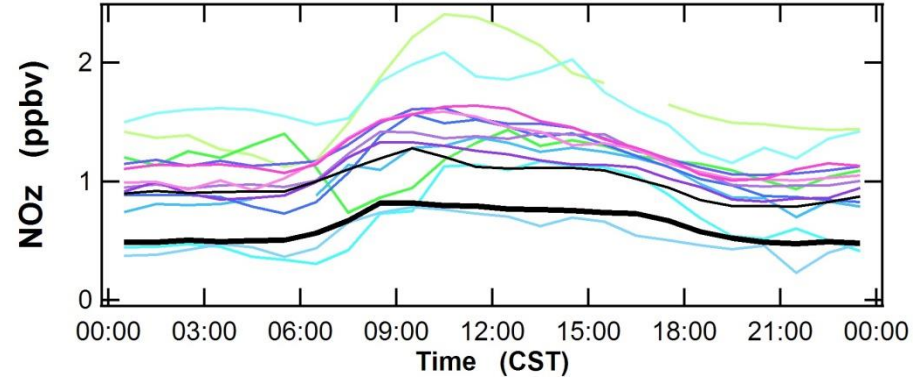
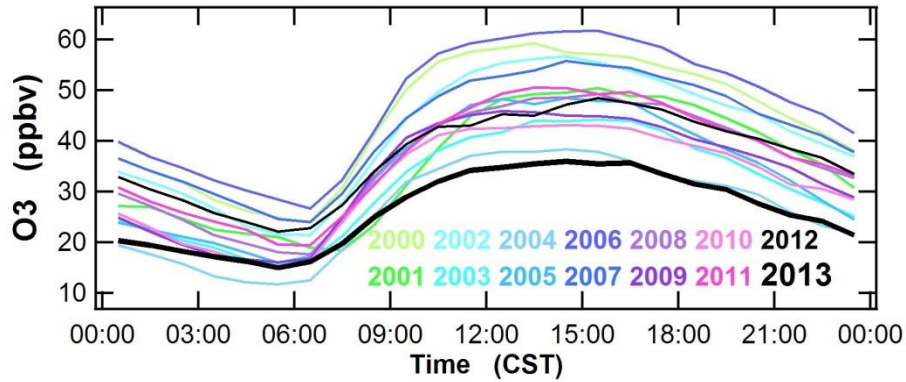


Spikes in morning SO<sub>2</sub> due to down-mixing of occasional SO<sub>2</sub> plume aloft with breakup of nocturnal inversion and development of CBL



Spike at 1700 in 2009 NO<sub>x</sub> and NO<sub>y</sub> due to singular event

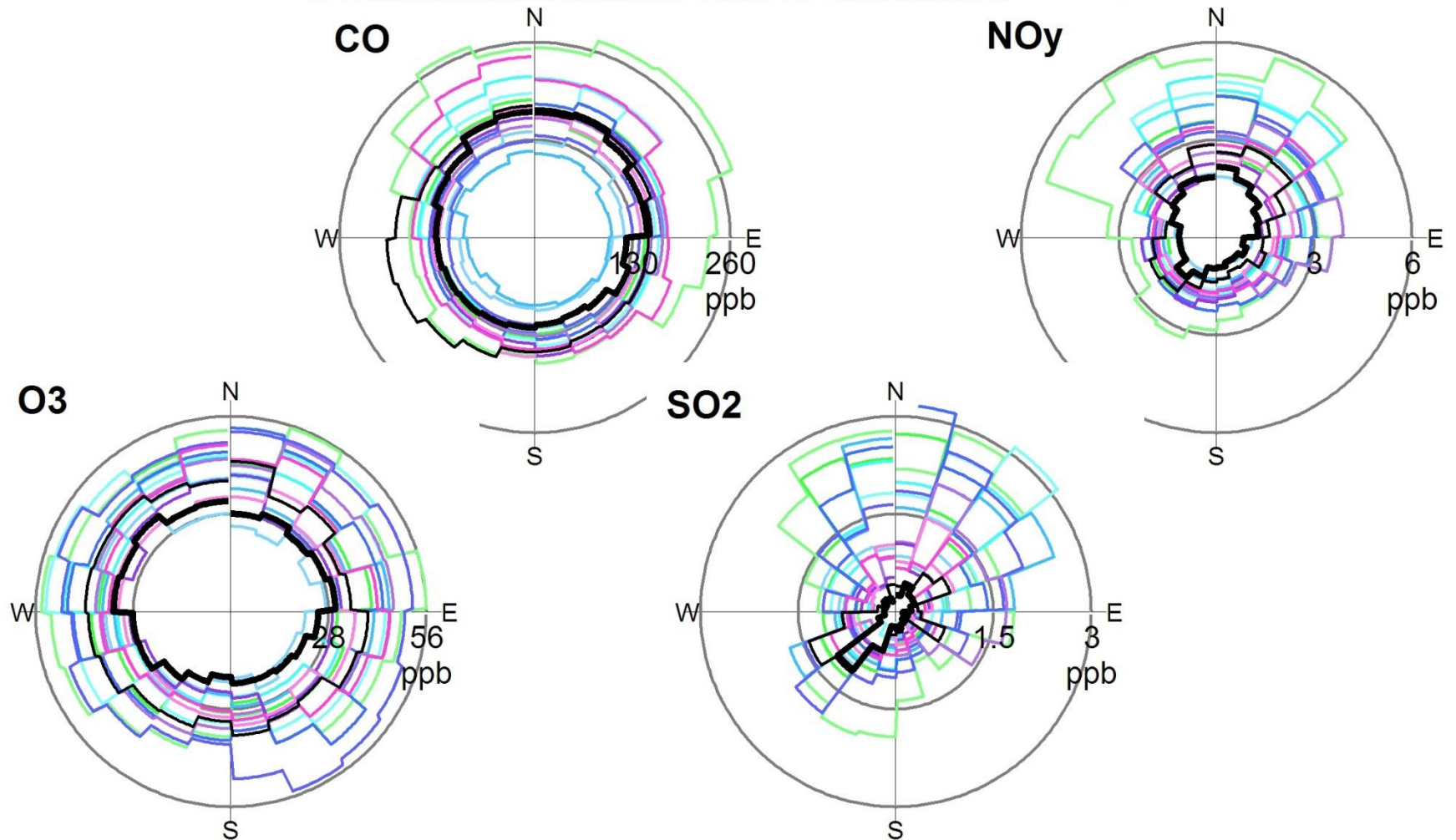
# Diurnal Secondary Gases 2000-2013



**In 2013:**  
 More O<sub>3</sub> produced per  
 NO<sub>x</sub> oxidized.  
 or:  
**Less NO<sub>x</sub> removed for  
 same ΔO<sub>3</sub> produced.**  
*Did NO<sub>x</sub> recycle more  
 often or more efficiently  
 in 2013?*

# Gaseous AP Transport 2000-2013

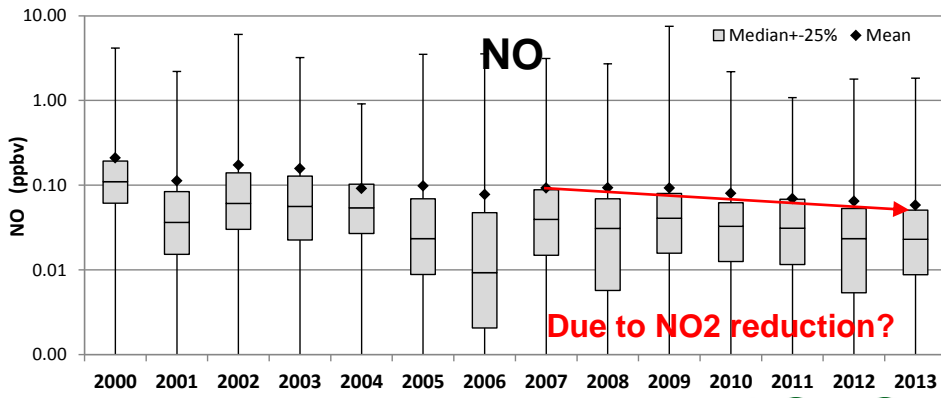
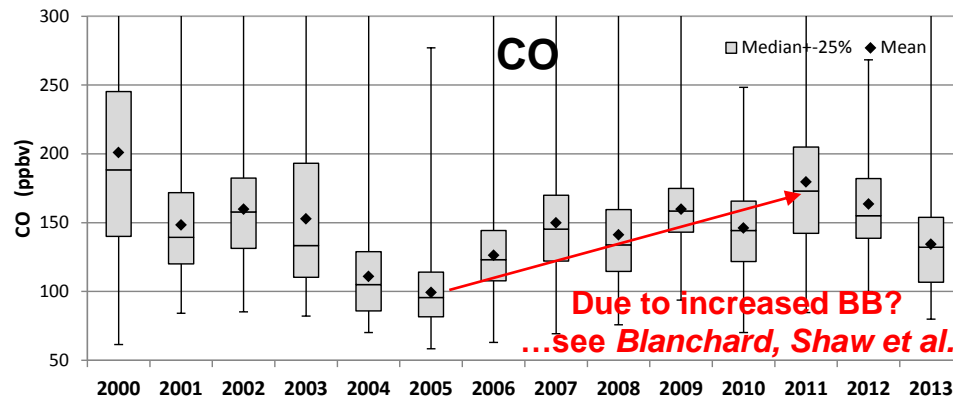
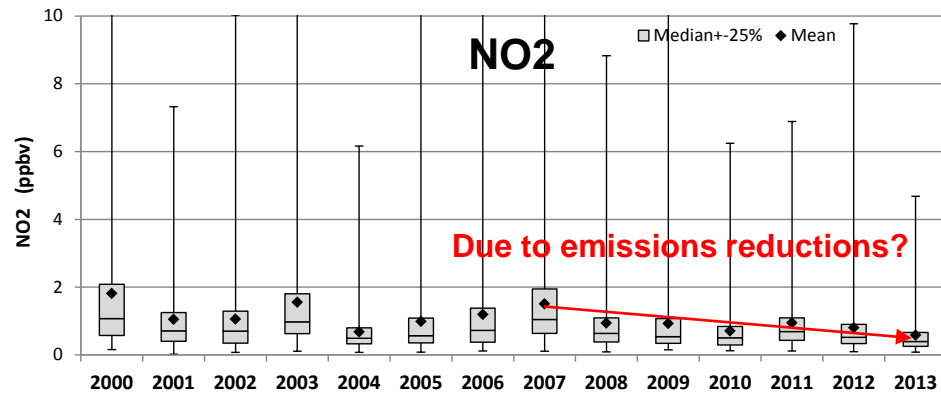
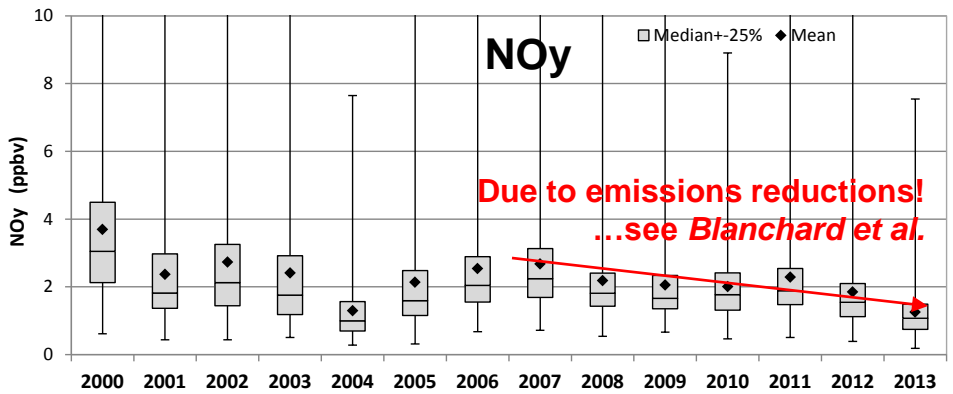
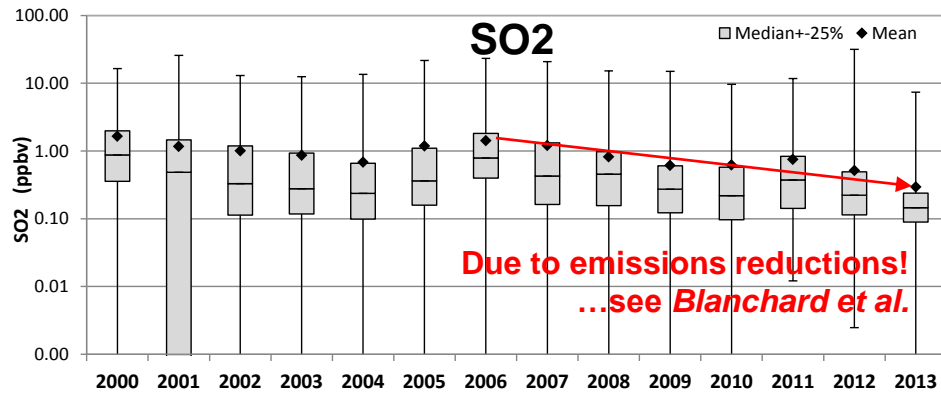
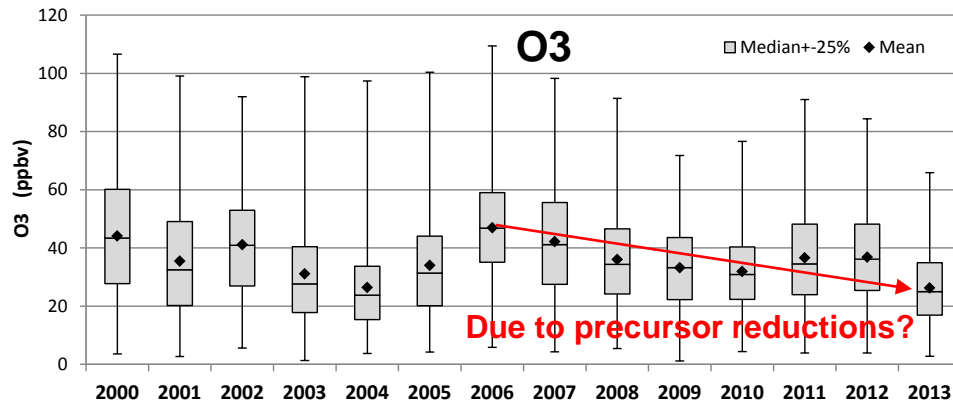
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013



- In general, O<sub>3</sub> and CO appear more regional than NO<sub>y</sub> and esp. SO<sub>2</sub>!
- Northerly flow generally transports more APs to the site than southerly flow.
- In 2013, northern SO<sub>2</sub> influence is gone, and SW influence largely reduced.

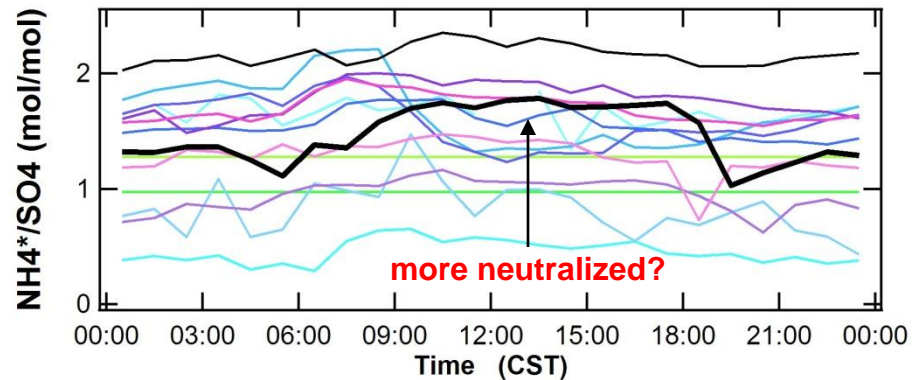
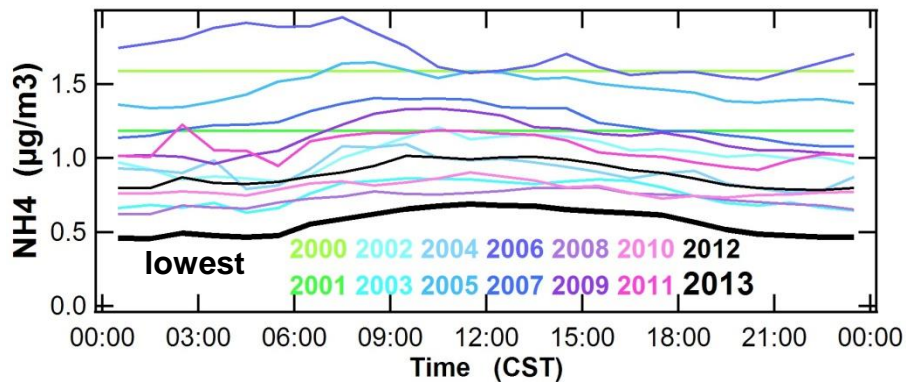
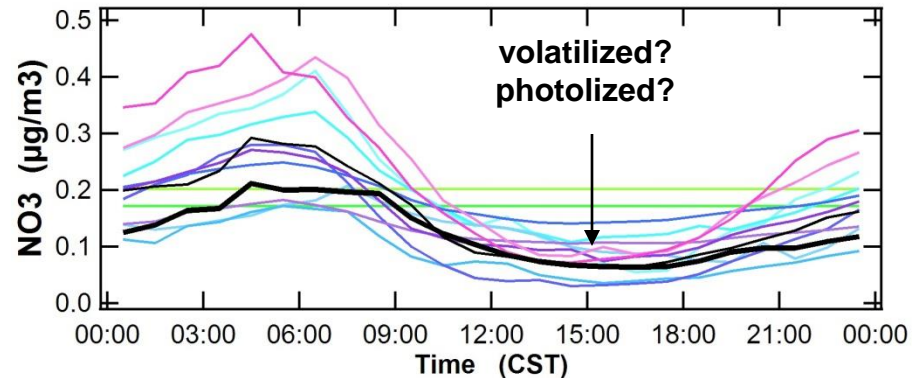
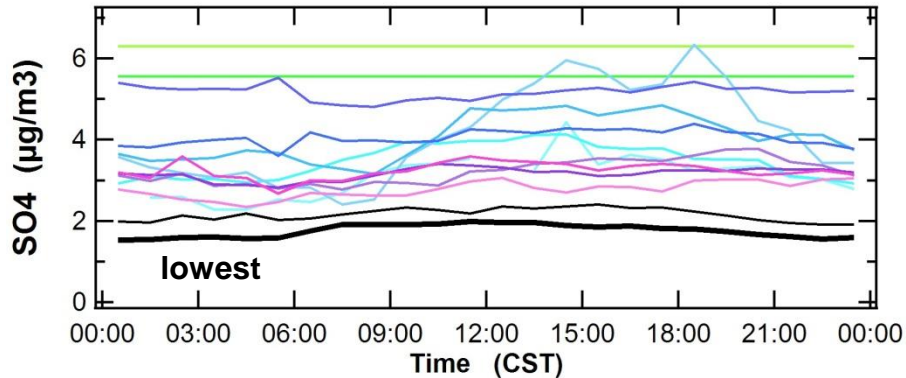


# Gaseous AP Statistics 2000-2013



# Diurnal Ionic PM<sub>2.5</sub> 2000-2013

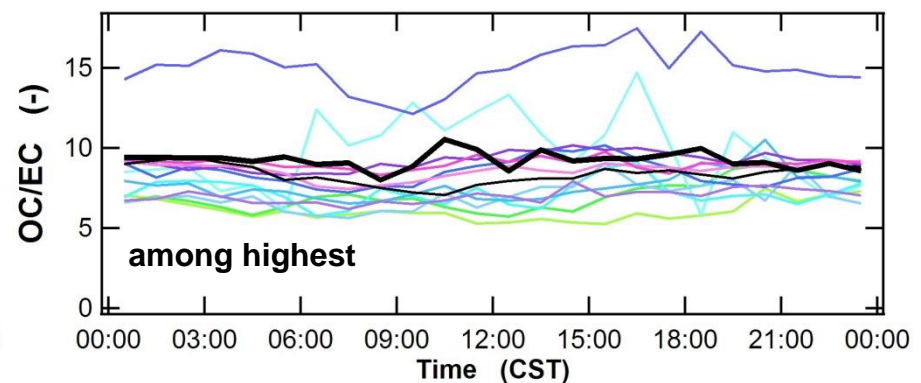
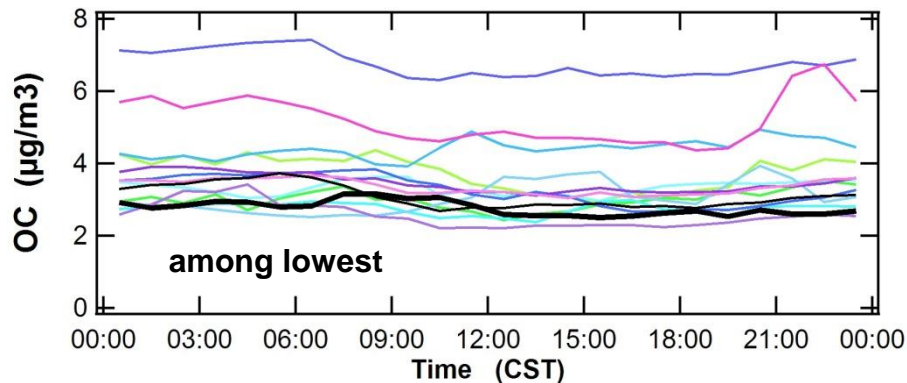
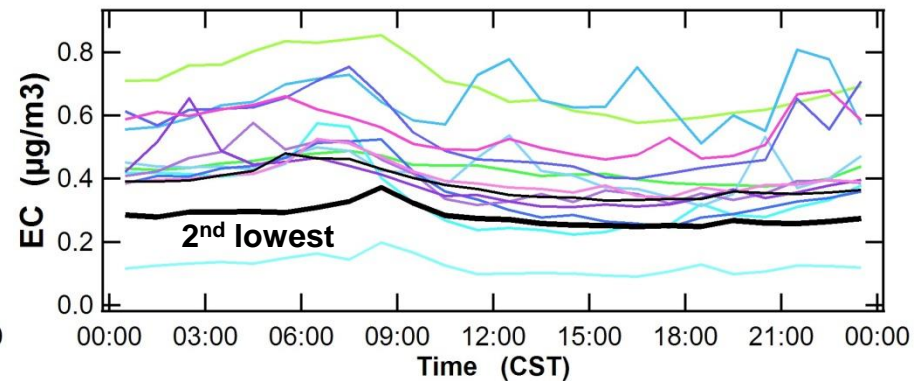
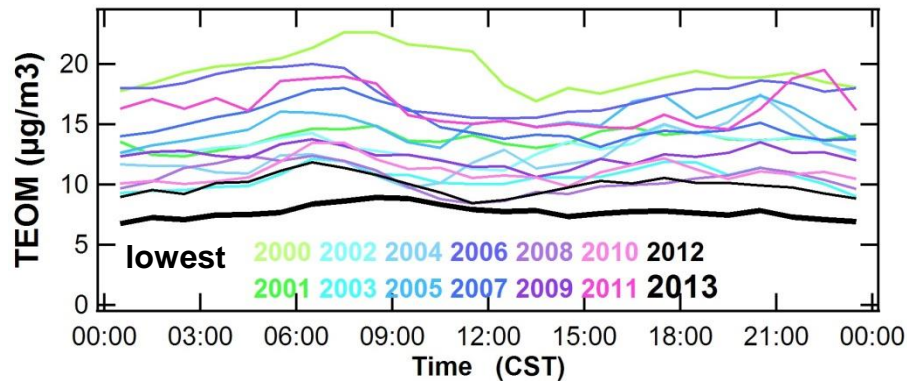
2000+01 SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> are from 24h FRM filters



NH<sub>4</sub><sup>\*</sup> = available post-NH<sub>4</sub>NO<sub>3</sub>

- Clear year-to-year downward trend in SO<sub>4</sub> and NH<sub>4</sub>.
- SO<sub>4</sub> daytime highs become shallower over time.
- NO<sub>3</sub> loss (volatilization) during midday, while NH<sub>4</sub> more retained.
- **SO<sub>4</sub>-neutralization has barely changed region wide; see Hidy et al. poster**

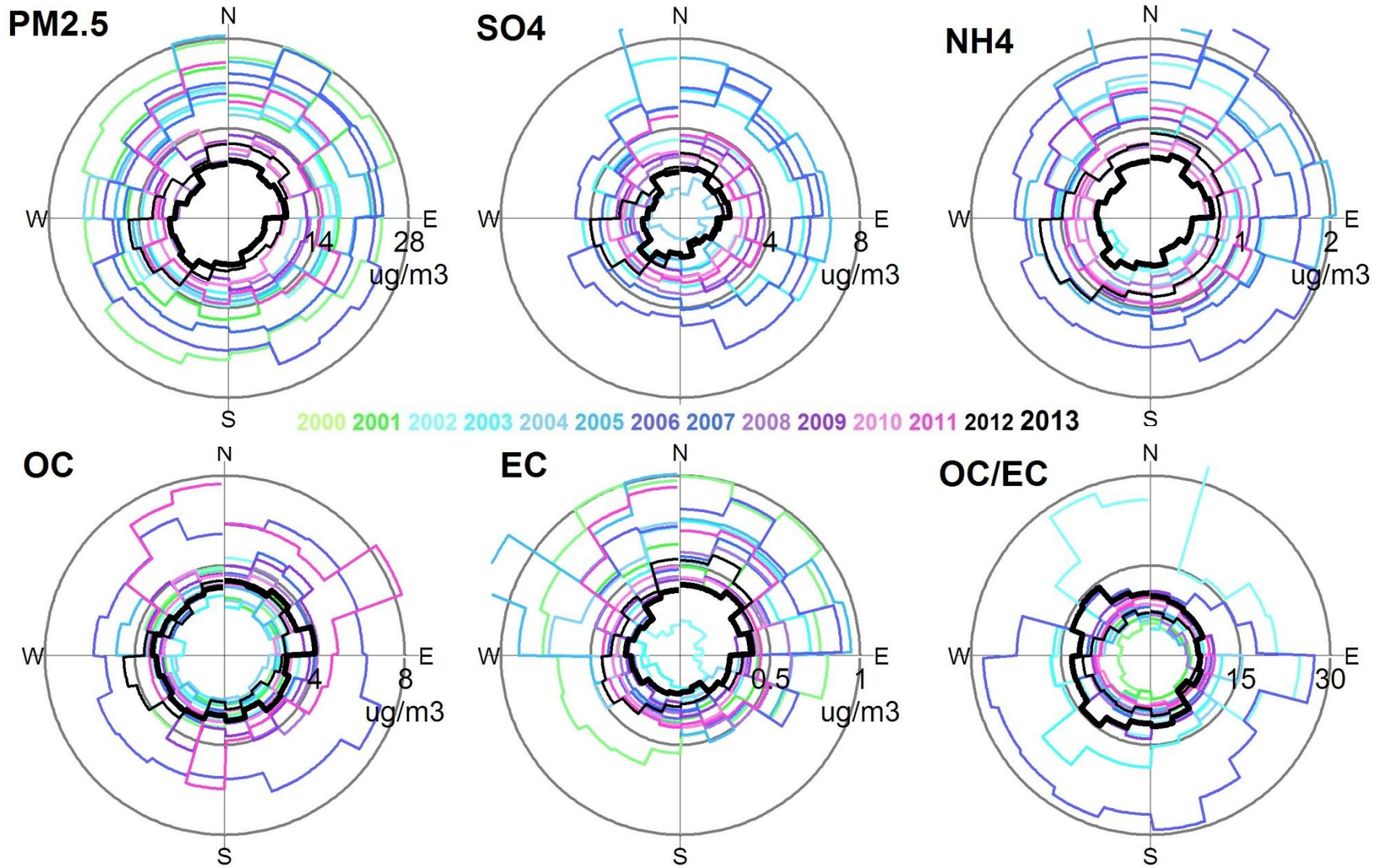
# Diurnal PM<sub>2.5</sub> Mass + Carbon 2000-2013



- PM<sub>2.5</sub> mass clearly lowest in 2013; OC and EC less clear.
- Diurnal profile flatter in 2013 for PM<sub>2.5</sub> mass, OC and EC.
- OC/EC ratio in 2013 among highest.
- Random spikes in OC/EC point to sporadic nearby BB influence.

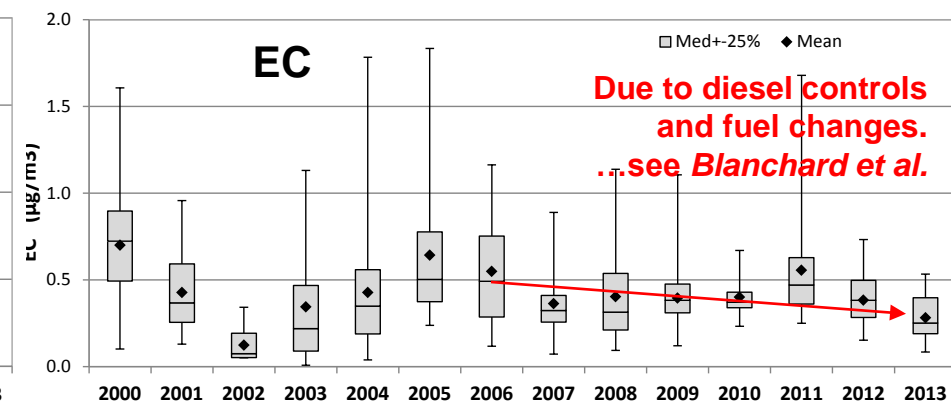
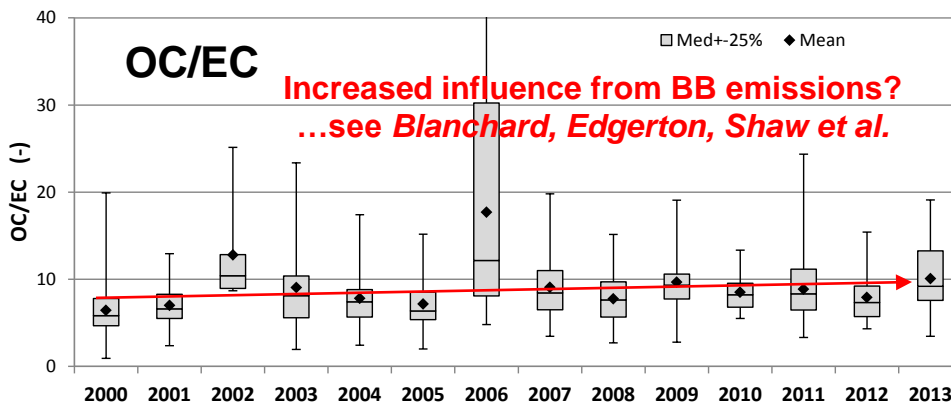
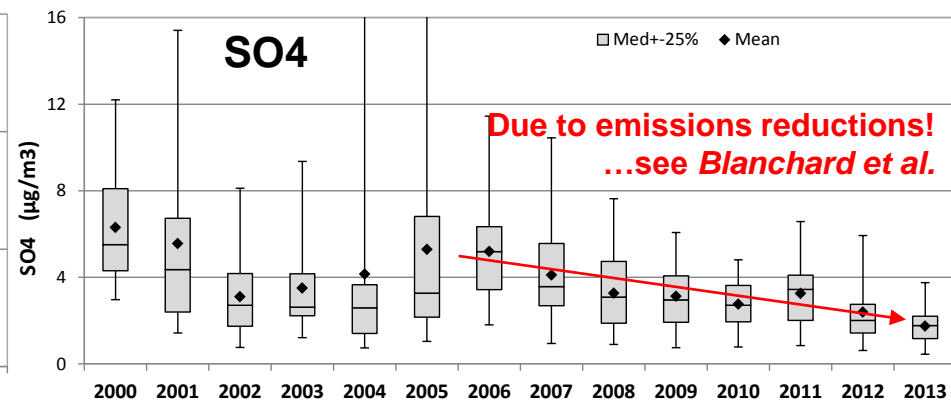
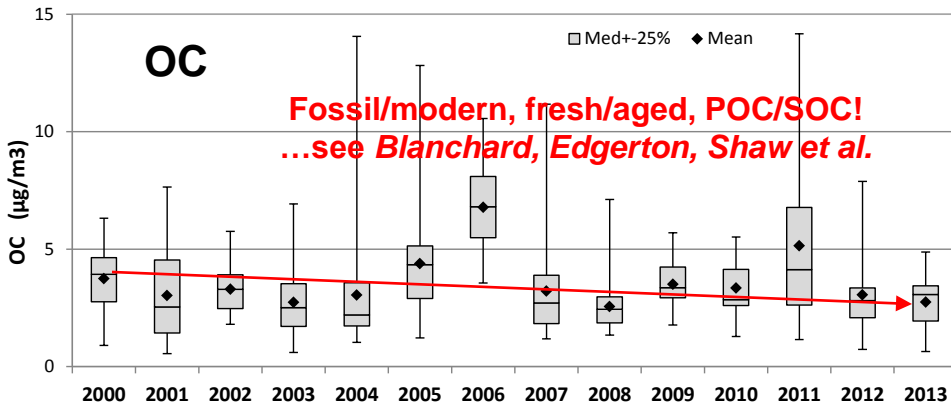
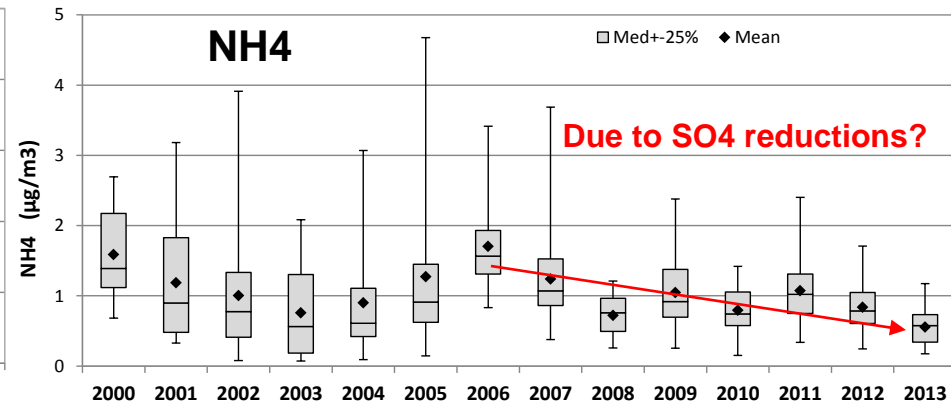
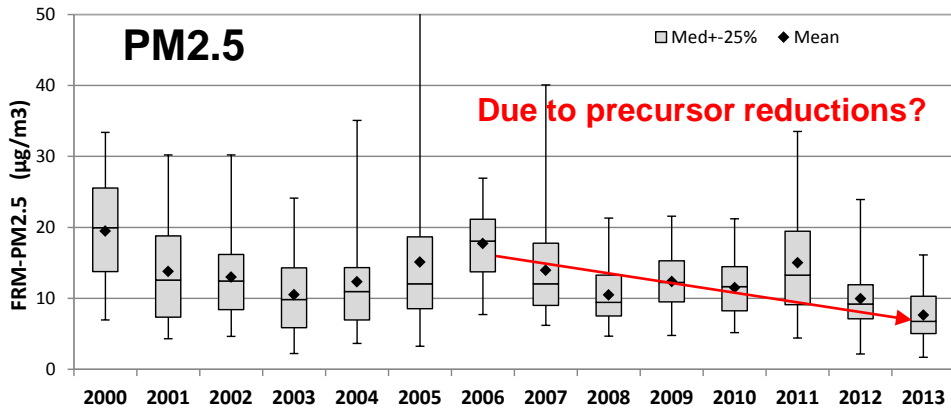


# Fine PM Transport 2000-2013



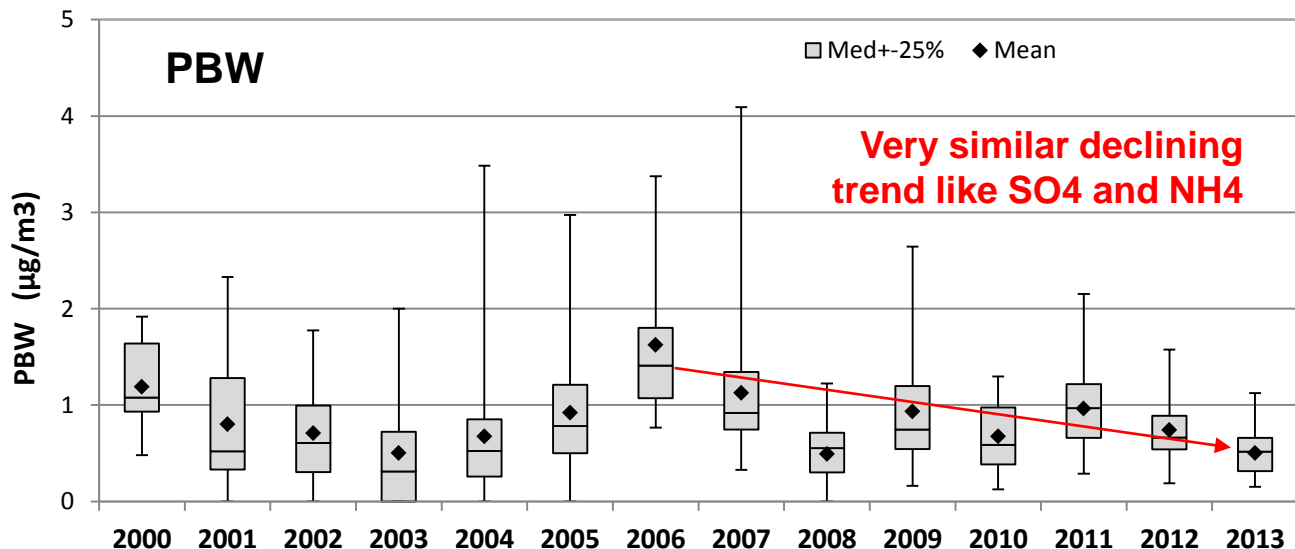
- **PM2.5 mass and components in 2013 appear more regional (concentric).**
- **OC/EC in 2013 point to nearby BB influence from NW and SW (more so in 2002 and 2006).**

# Fine PM Statistics 2000-2013



# PBW Associated with Ionic PM2.5 at CTR

- **Particle bound water estimated using SMAT\* approach based on AIM model (Clegg, 1998)**
  - Inputs are NH<sub>4</sub>, SO<sub>4</sub>, NO<sub>3</sub> adjusted to FRM
  - Assumed 35% RH and 21° C (FRM weighing conditions)
- **Derived empirical equation to describe relationship**
  - **PBW** =  $-0.002618 + 0.980314 \cdot \text{nh4} - 0.260011 \cdot \text{no3} - 0.000784 \cdot \text{so4} - 0.159452 \cdot \text{nh4}^{**2} - 0.356957 \cdot \text{no3} \cdot \text{nh4} + 0.153894 \cdot \text{no3}^{**2} + 0.212891 \cdot \text{so4} \cdot \text{nh4} + 0.0444366 \cdot \text{so4} \cdot \text{no3} - 0.048352 \cdot \text{so4}^{**2}$



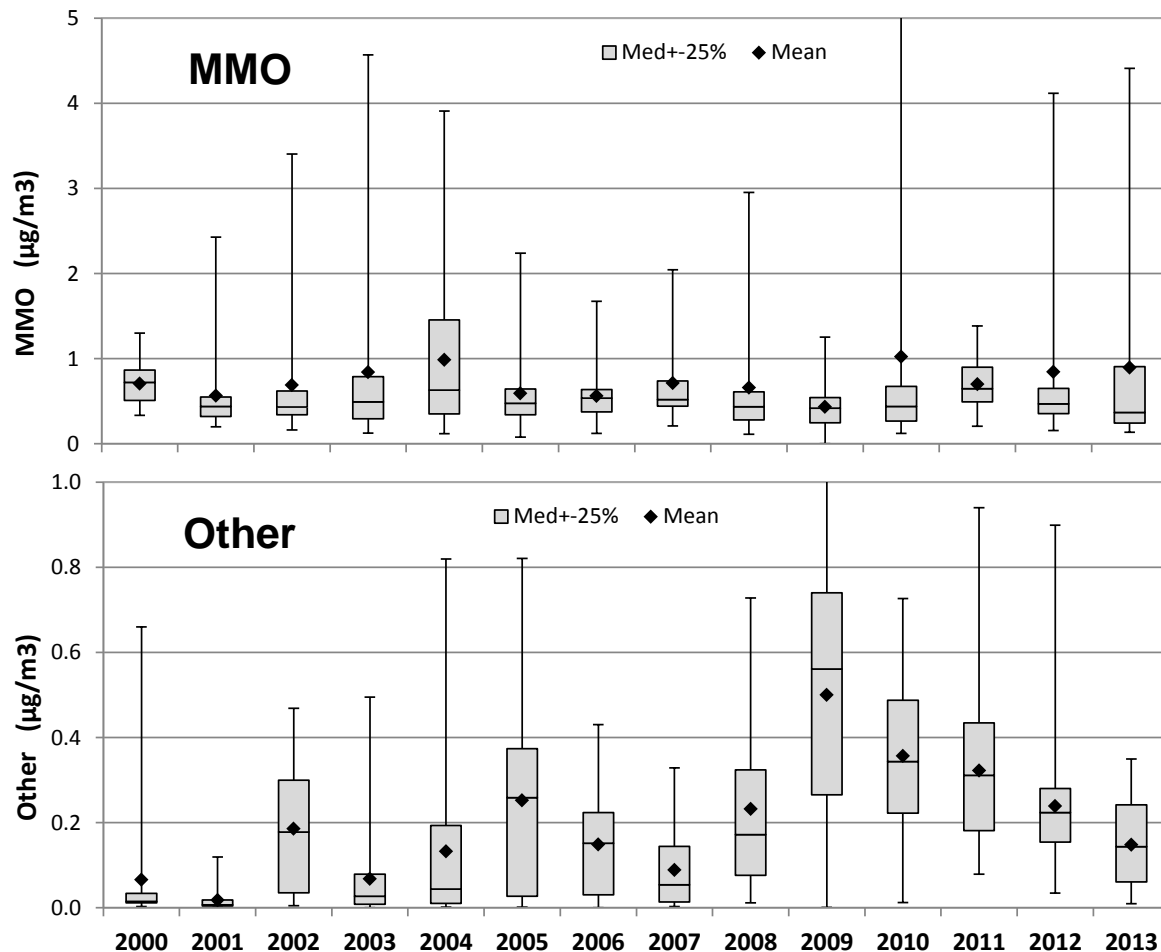
**GA Tech will double-check these numbers via ISORROPIA !**

\*) Speciated Model Attainment Test team, B. Timin, B. Cox, N. Frank, T. Rao, B. Hubbell, EPA/OAQPS, VISTAS Joint Workgroup Meeting, September 23, 2005.



# MMO and Other Elements in PM2.5 at CTR

- Major Metal Oxides based on ED-XRF of FRM filters
  - **MMO** =  $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{K}_2\text{O} + \text{CaO} + \text{TiO}_2 + \text{Fe}_2\text{O}_3$
  - **Other** =  $\text{Na} + \text{Mn} + \text{Zn} + \text{nonSO}_4\text{-S}$  (i.e.  $\text{XRF-S} - \text{SO}_4/3$ )

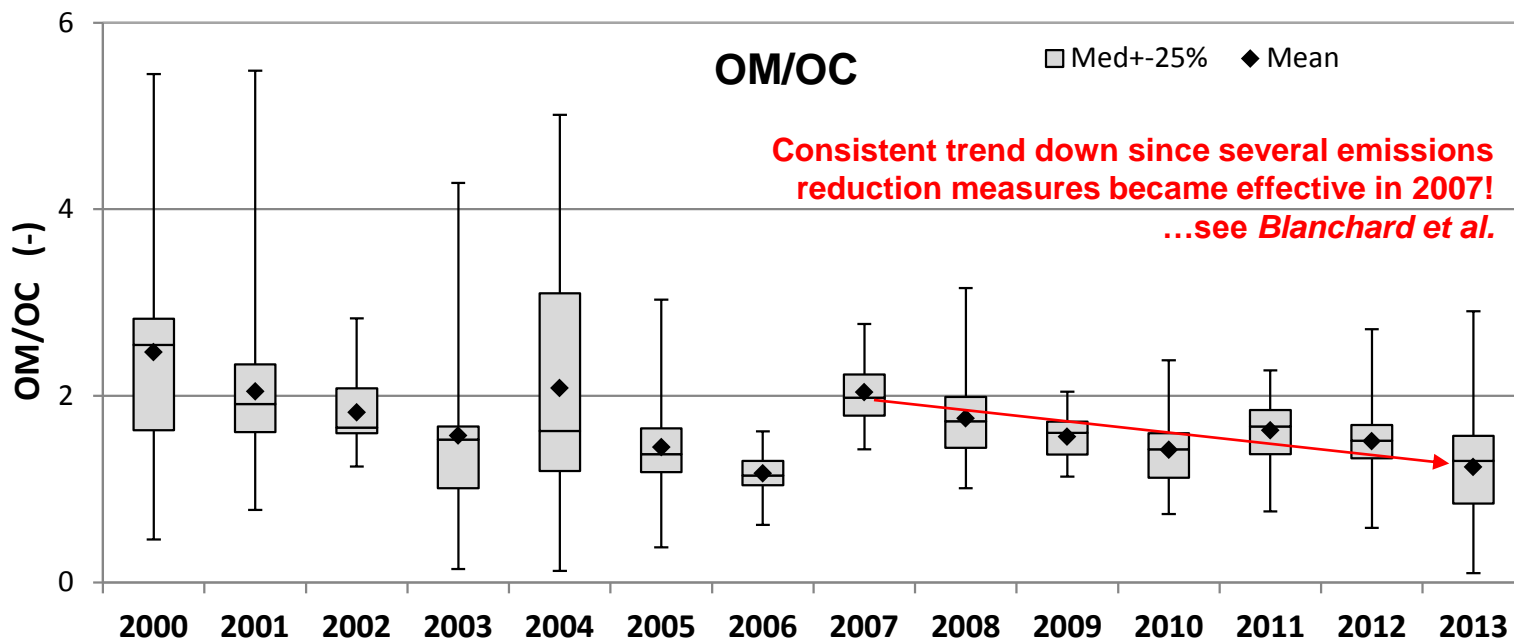


Sporadic high MMO due to mineral dust from local or distant sources. 2013 saw two events suggesting long-range transport from N-Africa.

- **PM2.5 contributions from both MMO and Other are not negligible.**
- **Other elements consistently decline since 2009.**

# OM from PM2.5 mass Balance at CTR

- Organic Mass upper limit estimated from PM2.5 mass balance:
  - $OM = PM2.5_{FRM} - EC - SO4 - NH4 - NO3 - PBW_{ions} - MMO - Other$



- What are the implications or causes of this downward trend?
- How much water is associated with OM?
- Has aerosol hygroscopicity declined?
- Has the oxidative capacity of the atmosphere decreased and with it SOA formation?
- What role does biomass burning play in this trend?

How do the air quality conditions encountered during SOAS fit into the long-term trend?

## “Answer”

- Fewer northerly winds, calmer, cooler, and moister.
- Less O<sub>3</sub> and less NO<sub>x</sub> removed per O<sub>3</sub> produced.
- Less NO<sub>y</sub>, SO<sub>2</sub>, SO<sub>4</sub>, and EC in line with reduced emissions trend (Blanchard et al.).
- SO<sub>4</sub>-neutralization has barely changed (also region wide; see Hidy et al. poster).
- PBW<sub>ions</sub> in line with declining SO<sub>4</sub> and NH<sub>4</sub> (ISORROPIA check pending).
- Less OC but higher than what mobile source OC reductions would suggest.
- OC/EC in 2013 point to nearby BB influence from NW and SW.
- BB seems to play an increasingly important role in SOA formation.

## Open Questions

- Has aerosol hygroscopicity declined?
- Has the oxidative capacity of the atmosphere decreased and with it SOA formation?
- What role does biomass burning play in this?