# CHEMICAL CLIMATOLOGY IN THE SE US: 1999-2012

SEARCH

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SAS-SOAS WORKSHOP
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ATMOSPHERIC RESEARCH & ANALYSIS

ENVAIR

## Why is Chemical Climatology a Concern?

- **Establish a long-term context for 2013 campaigns**
  - **Recognize the changing chemical environment of region and rural conditions**
  - **Reinforce relationship with pre-2012 research and expectations for experimental studies**
- **Framework for interpretation of campaign results and their generalization**
  - **Document the representativeness of aerometric conditions for SAS-SOAS campaigns**
  - **Relate or "integrate" contemporary hypotheses of photochemistry and airborne particles with basic regional and local field observations**

## Elements of Chemical Climatology

- Overall development of the Southeast and its climatology
- Trends in emissions
- Meteorological features of importance
  - **T, RH, SR, WS, WD; summer synoptic conditions**
- Comparison of trends in ambient concentrations for gases and particles
  - **Gases—SO2, NOy, NH3, NMOC, especially isoprene**
  - **Particles—mass, composition, especially SO4, NH4, OC, EC**
- Considerations for chemical indicators relevant to SOAS objectives
  - **Reaction products—O3, SO4, NOz, SOC; OH-RO2…**

## Southeastern Chemical Climatology, 1999-2012

- Basic measurements of urban and rural contrasts in a large SE region from the Gulf of Mexico to the north central Alabama and Georgia
- Complements presentations of carbon (Blanchard ), Representativeness (Baumann) , SOC constraints and consistencies (Shaw), and Summer 2013 carbon including isotopes (Edgerton)
- Provides a framework for interpreting SAS-SOAS data in the light of changing chemical environment in the SE and long-term annual and seasonal averages since 1999.

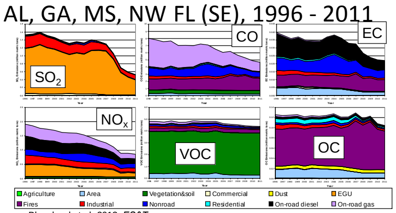
## Southeastern Chemical Climatology – Approach and Summary

- Organized in sequence of emissions to indicators of ambient chemistry
- Annual anthropogenic emissions show changes in "forcing" of chemistry in a subtropical continental setting
- Ambient chemistry regionally and locally affected by meteorology, especially thermodynamic properties and air mass mixing and transport
- Indicators of photochemistry, including O3 and precursors, aerosol composition show a mix of variation and systematic changes consistent with "general" expectations, but unresolved questions raised in details of trends.

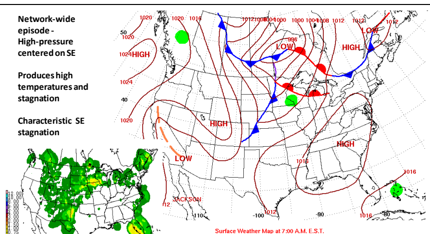
## Emissions and Meteorology

- **Emission trends**
  - **Emissions estimated from National Emissions Inventory**
  - **Annual anthropogenic emissions declined from 1999-2012**
  - **Summer diurnal emission patterns for regional EGUs and transportation**
  - **Summer EGU SO2 and NOx emissions by state show daytime maximum with rise about 0600 hrs. trends similar to the NEI**
  - **Transportation similar daily maximum during the day, rising at ~0600 hrs with weekday and weekend morning differences**
  - **Natural emissions of isoprene rise with T and SR; terpenes sensitive to T; rise in morning; summer rise about 0600 hrs.**
- **Meteorological Features**
  - **Summer T, RH, SR, WS and WD trends indicate small variations; 2013 tends cooler and warmer than previous years**
  - **Synoptic patterns common for regional stagnation and accumulation of pollution**
  - **Vertical mixing associated with diurnal changes - morning breakup coincides with emissions increase**

## Decreasing Anthropogenic Emissions in AL, GA, MS, NW FL (SE), 1996 - 2011




Blanchard et al. 2013, *ES&T*.

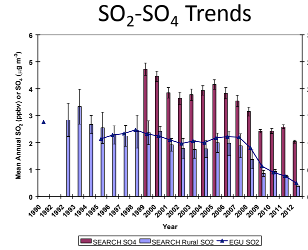



NOAA Daily Weather Map July 21, 2004
http://www.hpc.ncep.noaa.gov/dailywxmap/

## Ambient Concentration Trends

- **Annual concentration trends for chemicals of primary origin decline with emissions for both urban sites and rural sites**
  - **Inorganic species show major reductions associated with targets to meet NAAQS**
  - **NMOC in Atlanta area generally follows motor vehicle emission reductions, but groups of species show variable trends**
  - **Isoprene trend appears to "modestly" increase over 2000-2012**
- **Secondary products show downward concentration trends dependent on reactant reductions, but have tended to level out since about 2007**
  - **Sulfate tracks ambient SO2, but levels relative to emissions after 2007**
  - **Ozone shows a consistent less than 1:1 proportionality with both VOC and NOx decrease**
  - **OC-EC track one another—Implications for biogenic OC?**

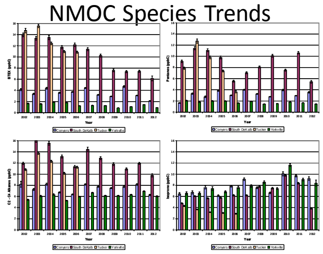
## $SO_2$-$SO_4$ Trends




## Changes in NMOC

- **Summer NMOC concentration trends different for groups of species**
  - **Use PAMS Atlanta (3 sites) and YRK (upwind) examples**
  - **Groups—C2-C4; pentanes; BTEX; and isoprene**
- **Annual trends indicate Atlanta anthropogenic change**
  - **Urban C2-C4 decline but pentanes mixed; isoprene increase**
  - **Rural anthropogenic concentrations much lower; isoprene similar to urban sites**
- **Midday history of rural sites in Southeast (1990-2012)**
  - **Shows decline in concentrations across the SE in anthropogenic and in isoprene**
  - **Tempered by meteorology and reactivity, especially isoprene**
  - **Isoprene consistently much higher in concentration than pinenes**
  - **Isoprene at YRK appears near midday levels at western Alabama site from 1990**

## NMOC Species Trends

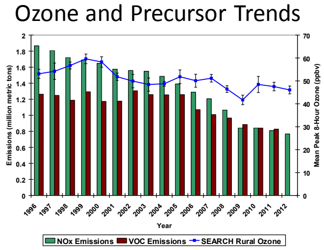


## Midday Rural NMOC Species History (ppbvC)

**Show anthropo- presence, but strong isoprene influence**

| Species Group | West AL (1990) | Oak Grove, MS (1994) | CTR, AL (1994) | YRK, GA (1994) | YRK, GA (2002) | YRK ,GA (2012) |
|---|---|---|---|---|---|---|
| $C_2$-$C_4$ | -- | 9.81 | 8.3 | 8.95 | 3.9 | 5.5 |
| Pentanes | 0.7 | 25.7 | 7.42 | 12.1 | 1.3 | 1.2 |
| BTEX | 0.2 | 5.57 | 2.34 | 8.5 | 0.75 | 0.60 |
| Isoprene | 5.6 | 11.2 | 21.1 | 9.80 | 7.5 | 6.5 |
| Pinenes | 0.3 | 5.8 | 3.0 | 2.2 | -- | -- |

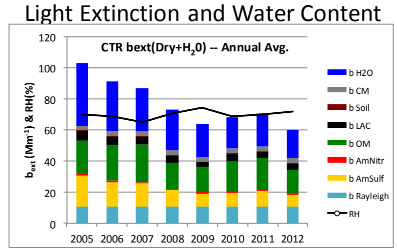
## Ozone and Precursor Trends



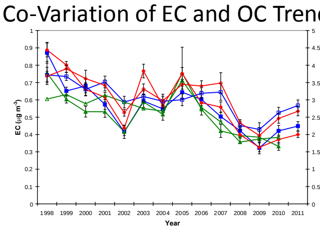

## Presence of Water in Aerosols

- **Variety of evidence indicates that water is a major fraction of ambient aerosols**
  - **At equilibrium, condensed water in particles depends on relative humidity; equilibration occurs such that more water is in particles at night than during the day**
- **There is sufficient water available for heterogeneous chemical reactions to produce SOC**

## Light Extinction and Water Content




## Co-Variation of EC and OC Trends

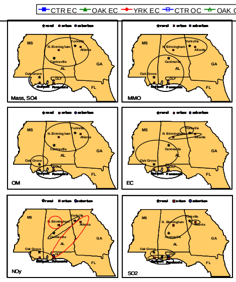



## Spatial Variation of Pollutants

- **Differences in urban-rural concentrations decreased for O3, and OM, while SO4 remains the same; inland-coastal gradients for SO4 essentially disappeared, weakened for OM and remained the same for O3 between '99-'02 vs. '09-'12. Other species of gases and particles show gradients between rural-urban and inland-coastal sites**
  - **The homogeneity of average O3, OM and SO4 concentrations indicates the importance of the regional component of chemistry**
- **Application of Empirical Orthogonal (factor) Analysis adds insight into average spatial distributions relative to emissions**
  - **Major spatial factors differ for different species**
- **Major EOF factor for inland sites is strongly coupled with temperature change and transport distance**
  - **This coupling is more variable for the coastal sites**

## Urban-Rural Contrasts

| Species | Inland Sites 1999-02 CTR | Inland Sites 1999-02 BHM | Inland Sites 2009-12 CTR | Inland Sites 2009-12 BHM | Coastal Sites 1999-02 OAK | Coastal Sites 1999-02 GFP | Coastal Sites 2009-12 OAK | Coastal Sites 2009-12 GFP |
|---|---|---|---|---|---|---|---|---|
| $PM_{2.5}$ (microg $m^{-3}$) | | | | | | | | |
| Mass | 14.17 | 20.62 | 8.89 | 11.88 | 12.77 | 12.15 | 9.61 | 8.58 |
| **$SO_4$** | **4.16** | **4.95** | **2.20** | **2.66** | **3.66** | **3.75** | **2.33** | **2.31** |
| $NO_3$ | 0.38 | 1.00 | 0.29 | 0.50 | 0.35 | 0.44 | 0.33 | 0.36 |
| $NH_4$ | 1.32 | 1.83 | 0.73 | 0.96 | 1.11 | 1.23 | 0.74 | 0.75 |
| EC | 0.58 | 2.05 | 0.63 | 1.04 | 0.52 | 0.74 | 0.36 | 0.43 |
| **OM** | **4.70** | **7.32** | **3.48** | **3.96** | **4.24** | **3.97** | **2.65** | **2.75** |
| MMO | 0.36 | 0.97 | 0.41 | 0.92 | 0.45 | 0.48 | 0.67 | 0.59 |
| $PM_{10-2.5}$ (microg $m^{-3}$)[c] | | | | | | | | |
| Mass | 5.62 | 13.60 | 5.01 | 12.19 | NA | NA | 6.23 | 8.26 |
| $SO_4$ | 0.21 | 0.29 | 0.18 | 0.34 | NA | NA | 0.21 | 0.31 |
| $NO_3$ | 0.40 | 0.46 | 0.37 | 0.48 | NA | NA | 0.46 | 0.69 |
| $NH_4$ | 0.05 | 0.02 | 0.03 | 0.004 | NA | NA | 0.02 | 0.07 |
| MMO | 1.38 | 4.47 | 1.24 | 4.10 | NA | NA | 1.76 | 2.04 |
| Gases (ppbv) | | | | | | | | |
| **$O_3$** | **36.97** | **23.27** | **32.93** | **24.74** | **37.05** | **31.81** | **33.15** | **32.96** |
| CO | 182.3 | 502.3 | 164.7 | 296.4 | 169.8 | 270.3 | 138.7 | 179.3 |
| $SO_2$ | 2.02 | 4.87 | 0.76 | 2.44 | 1.65 | 2.31 | 0.73 | 1.17 |
| NO | 0.43 | 19.97 | 0.15 | 7.54 | 0.21 | 3.63 | 0.09 | 1.10 |
| $NO_2$[d] | 2.76 | 14.37 | 1.51 | 12.03 | 1.41 | NA | 1.02 | 4.55 |
| $NO_y$ | 5.04 | 38.16 | 2.72 | 21.21 | 3.37 | 11.91 | 1.89 | 6.46 |
| $NO_z$ | 1.76 | 5.98 | 1.19 | 2.04 | 1.42 | NA | 0.77 | 0.89 |
| $NH_3$[e] | NA | NA | 0.32 | 2.16 | NA | NA | 0.31 | 0.77 |



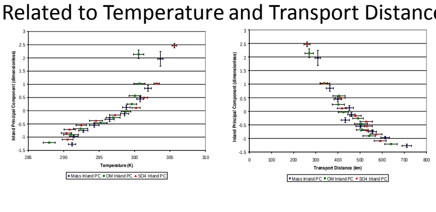

**PCA (EOF) Results**

Inland – Coastal Contrasts: Mass, $SO_4$, MMO

Both Inland – Coastal + Urban – Non-urban Contrasts: OM and EC

More complex: $NO_y$ and $SO_2$

## Major EOF Factor for Inland Data Strongly Related to Temperature and Transport Distance




## So What to Look for?

- **What are the implications of the continued declines of reactants and products of photochemical processes?**
- **How do the long-term annual or seasonal averages inform the details of chemistry leading to oxidants and SOC in the southeastern environment?**
- **Are there consistencies or inconsistencies in long-term measurements that constrain the importance of SOC formation mechanisms in the SE semitropical-continental rural or urban environments?**