Anthropogenic and Biogenic Emissions, and their Contributions to Summertime Haze in the Southeast U.S.: Results from the NOAA SENEX Study in 2013

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and the SENEX Science Team

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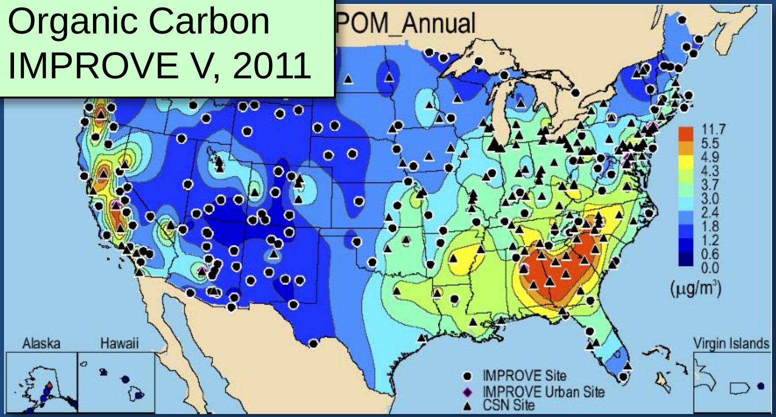
CIRES, Univ. of Colorado at Boulder

- The NOAA SENEX mission in summer 2013
- Lessons learned so far about the interactions between anthropogenic and biogenic emissions to form secondary pollutants
- Other results: biomass burning, emissions from oil and gas production, ethanol refining

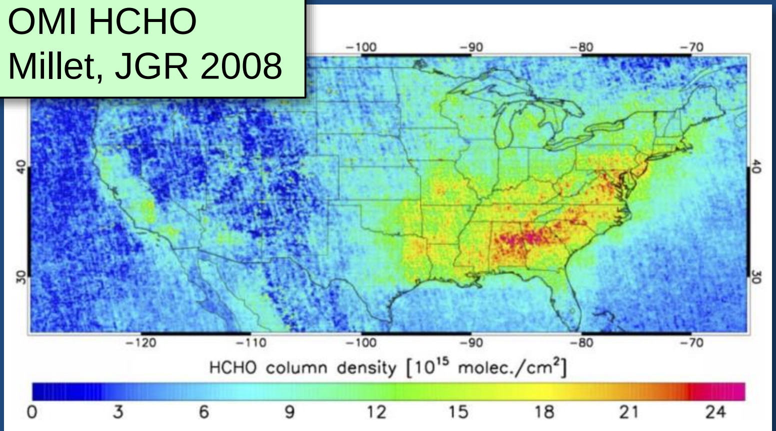
Atmospheric Chemistry in the Southeast U.S.

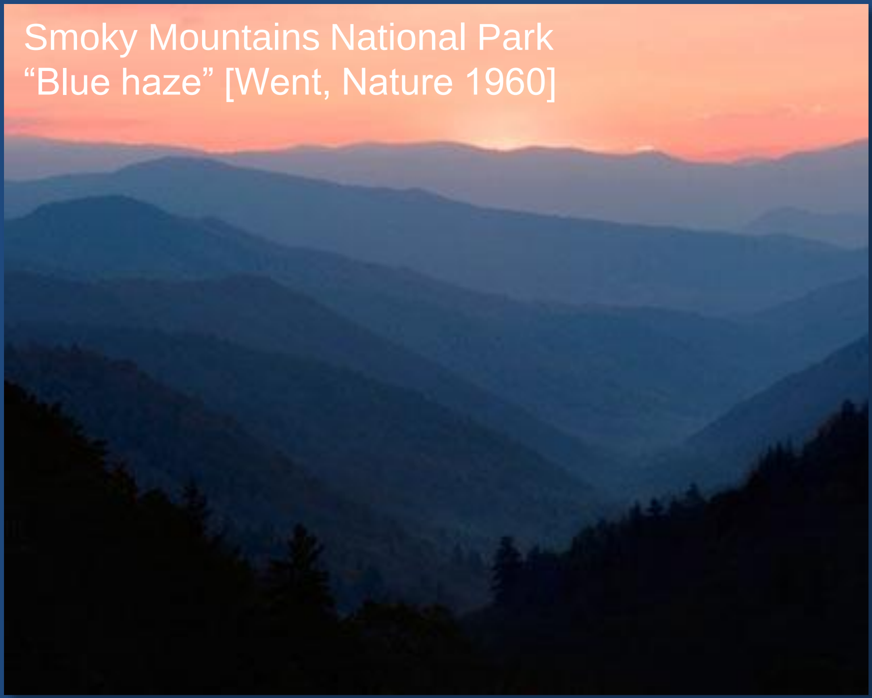
- The Southeast has the highest biogenic VOC emissions in the U.S., and also high pollutant emissions, photochemistry and cloudiness
- How do anthropogenic and man-made emissions combine to form secondary pollutants?

Organic Carbon
IMPROVE V, 2011



OMI HCHO
Millet, JGR 2008

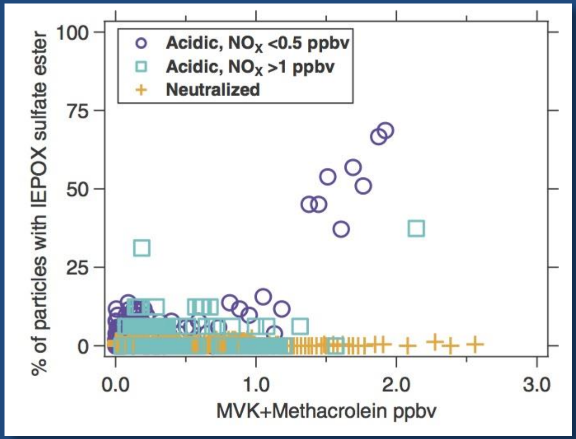




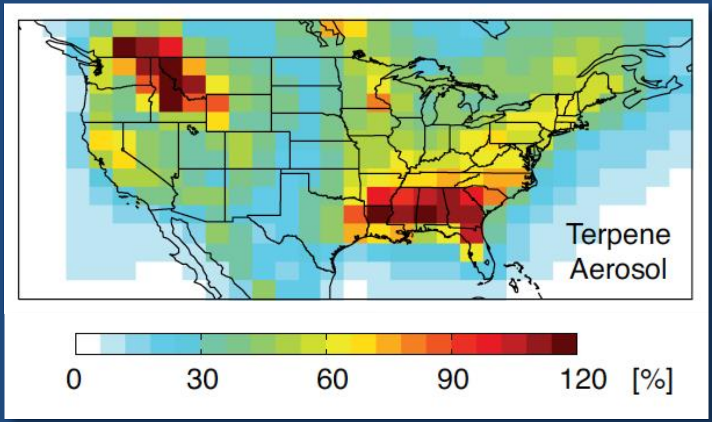
To what extent is haze in the Southeast natural vs. caused by man-made emissions?

SOA Formation from Natural and Man-Made Emissions

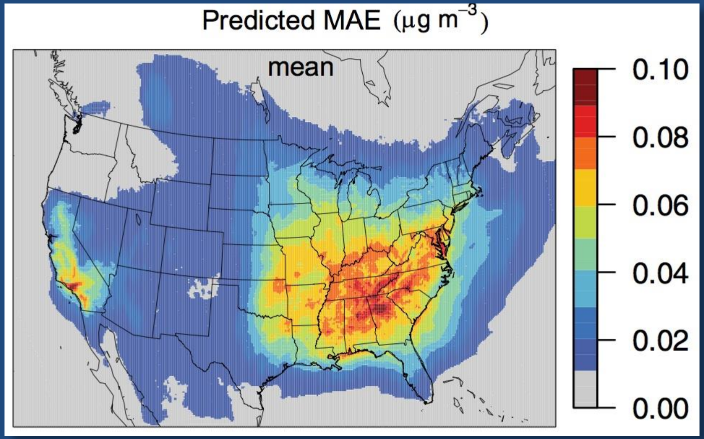
Isoprene organosulfates (low NOx, acidic aerosol) e.g. Froyd [PNAS 2010]



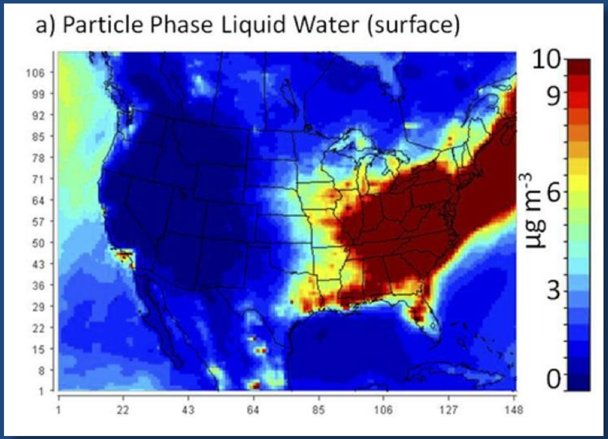
Nighttime oxidation of biogenic VOCs (high NOx) e.g. Pye [ACP 2010]



High-NOx oxidation of isoprene to form SOA e.g. Lin [PNAS 2013]



Particle water as a reactive medium controlled by sulfate e.g. Carlton [ACP 2013]



Studying the Interactions Between Natural and Anthropogenic Emissions at the Nexus of Air Quality and Climate Change

SENEX Science Questions:

1. **What are the emissions of aerosol, aerosol precursors and greenhouse gases?**
   - Biogenic emissions
   - Anthropogenic emissions (point sources, urban, shale gas extraction)
   - Biomass burning emissions

2. **What is the composition and distribution of aerosol?**

3. **What are the formation mechanisms of secondary species (ozone, sulfate, organics)?**
   - Interaction between biogenic and anthropogenic emissions
   - Net effect of aqueous-phase chemistry
   - Nighttime production

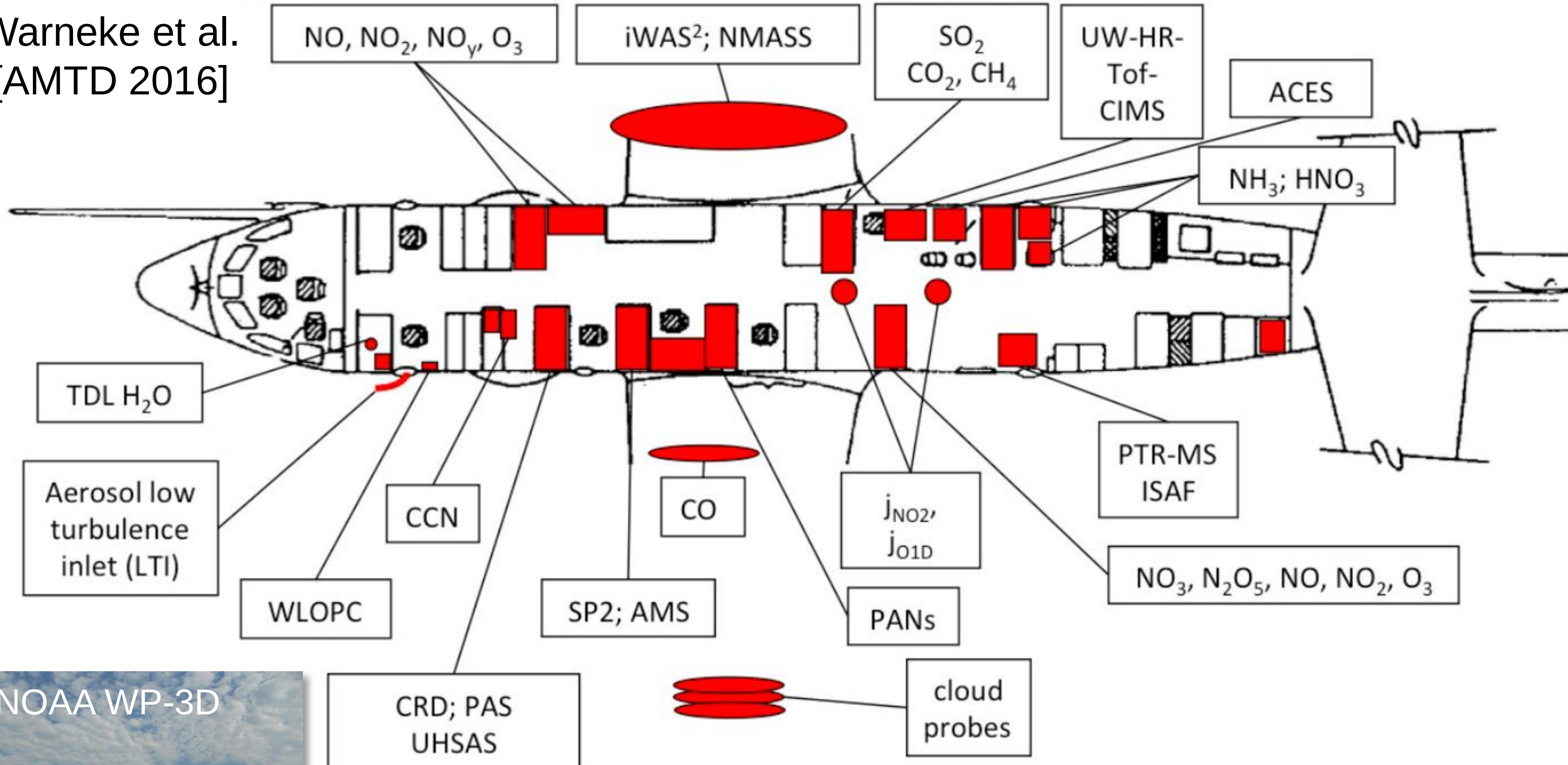
4. **Which deposition processes are critical for determining atmospheric concentrations of trace gases and aerosol?**

5. **What are the climate-relevant properties of aerosol?**
   - Extinction, absorption and CCN properties

Photo: L. Gratz

NOAA SENEX Study in the Southeast U.S.

Warneke et al.
[AMTD 2016]

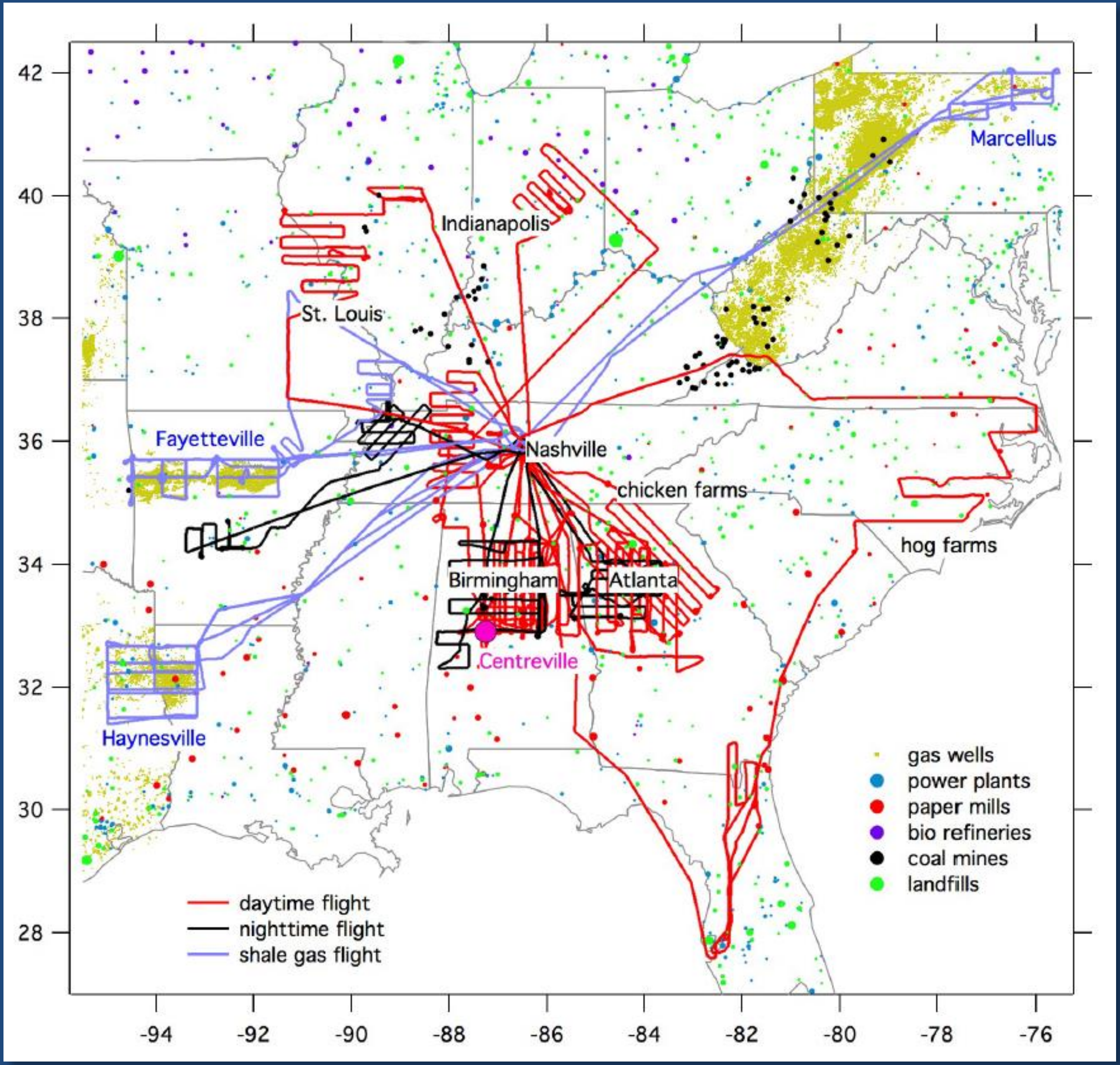


Extensive payload to measure the gas and aerosol composition

Two EPA STAR-funded collaborators:
Thank you!

Thanos Nenes CCN
Frank Keutsch HCHO

NOAA SENEX Study in the Southeast U.S.



- 19 flights in June-July of 2013 operated out of Smyrna, TN
- Data publicly available at esrl.noaa.gov/csd/projects/senex/
- Instruments and flights described in Warneke et al. [AMTD 2016]

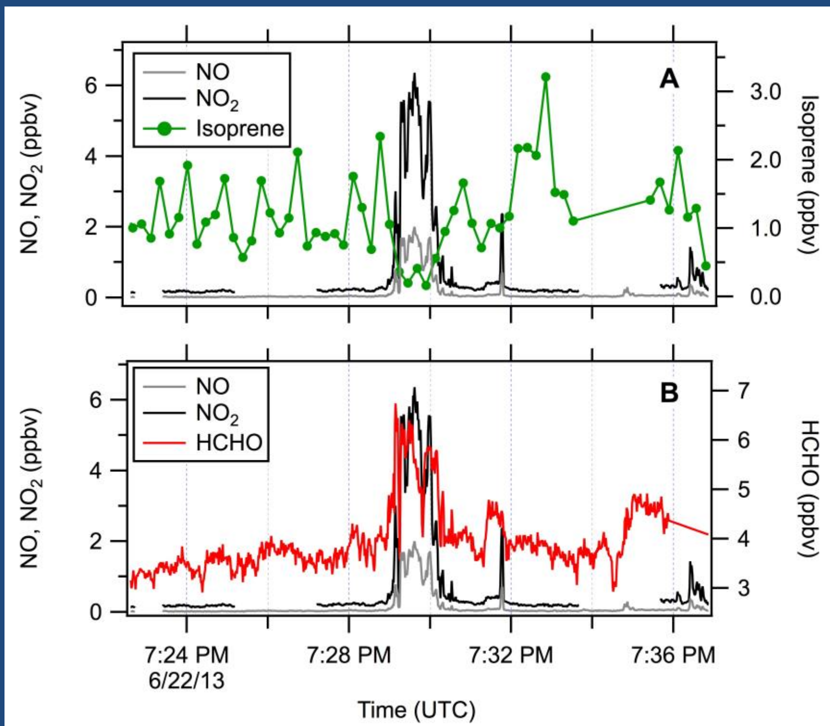
SENEX = Part of Southeast Atmosphere Study

Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications

Nitrogen Oxides Control Photo-Oxidation Rates

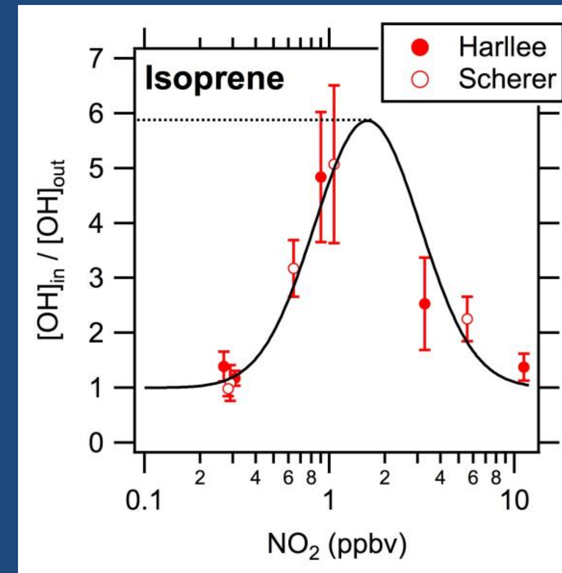
de Gouw et al. [in preparation]

A. Isoprene is depleted in power plant plumes, as OH is enhanced at higher NOx

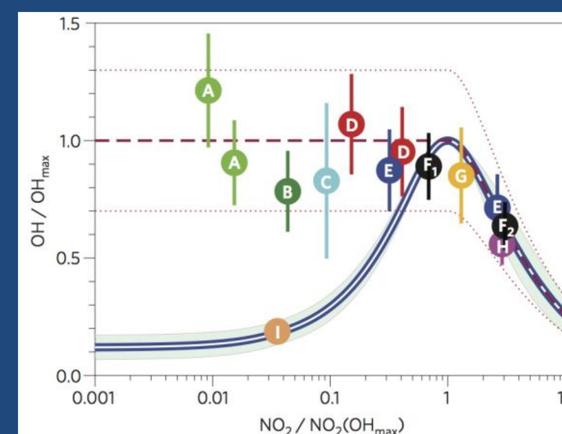


Can explain correlation between products from biogenic VOCs and anthropogenic emissions

B. NO_2-dependence of OH is as expected

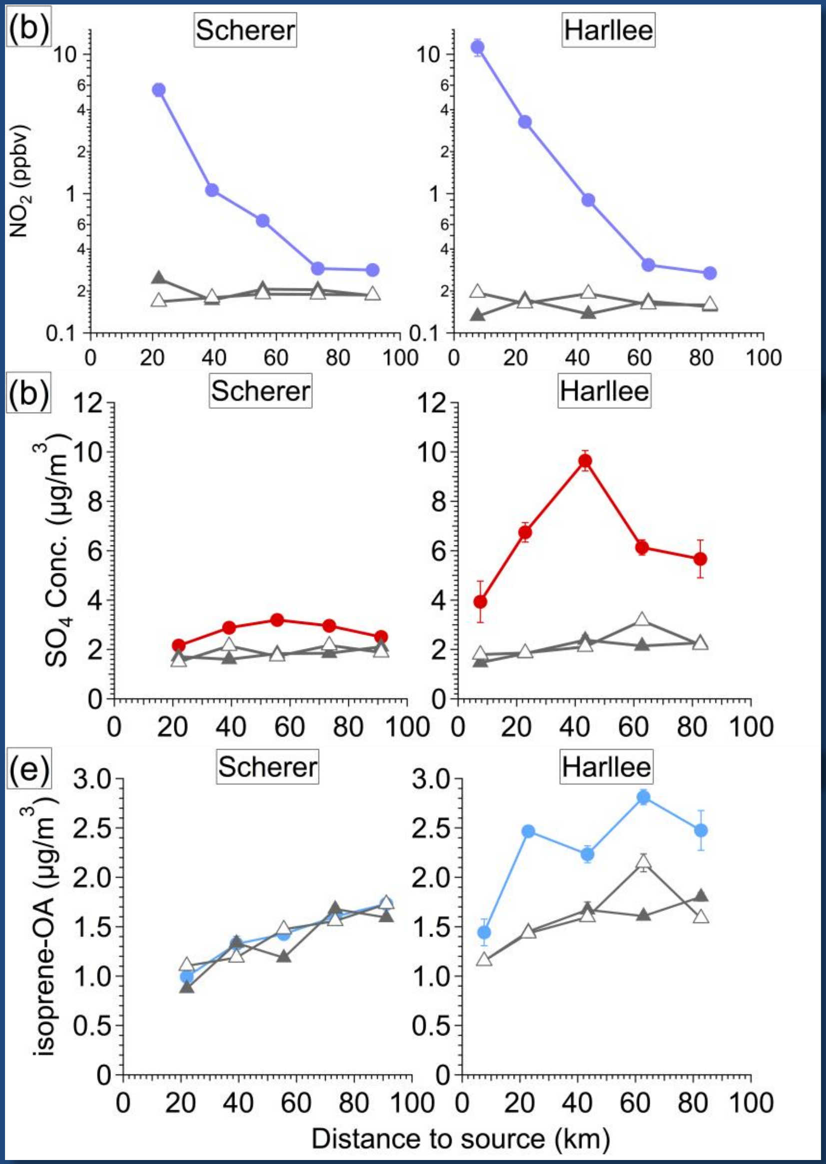


C. But different from direct OH measurements [Rohrer, NGEO 2014]



Aerosol Formation from Isoprene in Power Plant Plumes

Xu, Ng, Middlebrook et al. [in preparation]

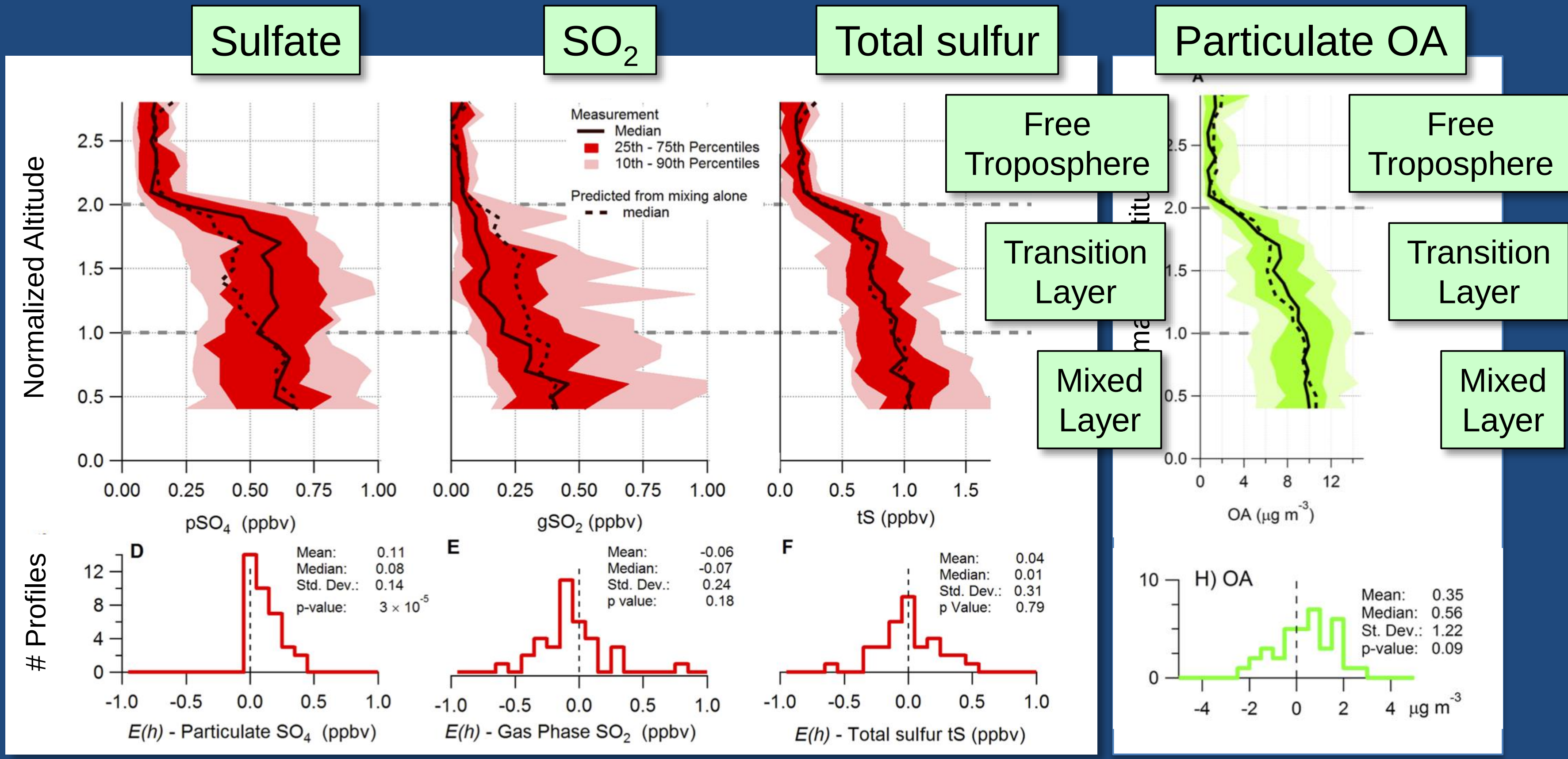


- NO_2 is similar in Scherer and Harllee plumes
- Isoprene is oxidized at similar rates in both plumes
- Harllee Branch plume contains more sulfur and forms more sulfate
- Isoprene SOA is only formed in the Harllee plume

June 16 flight over Atlanta, and Scherer and Harllee Branch power plants

Effects of Aqueous-Phase Chemistry

Wagner et al. [ACP 2015]

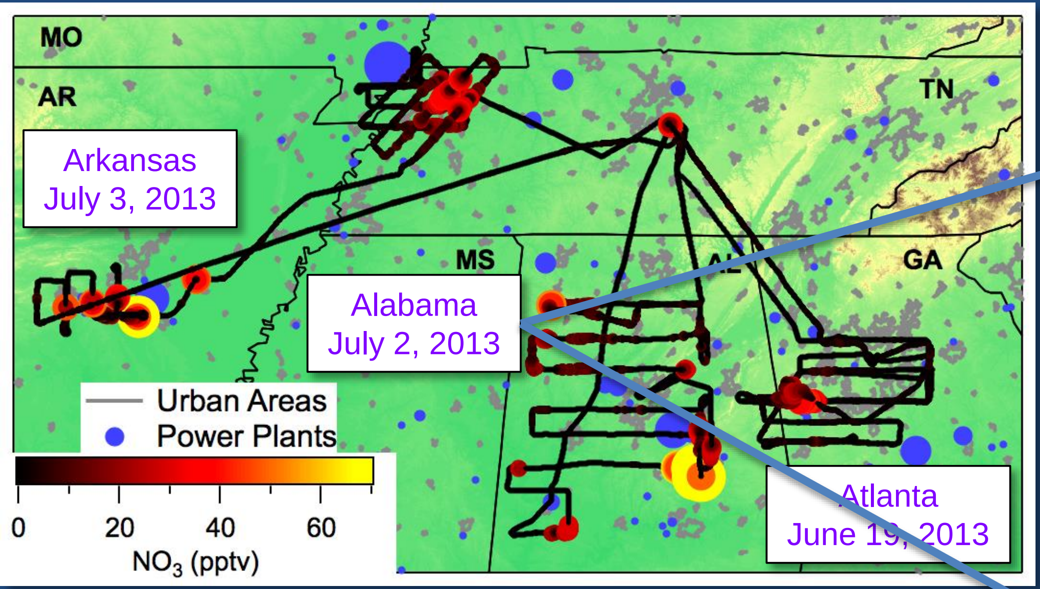


- Total sulfur and other inert trace species (e.g. BC) in the transition layer can be explained by mixing between mixed layer and free tropospheric air
- Sulfate is enhanced in the transition layer possibly due to cloud chemistry
- Enhancement of OA in the transition layer is not statistically significant

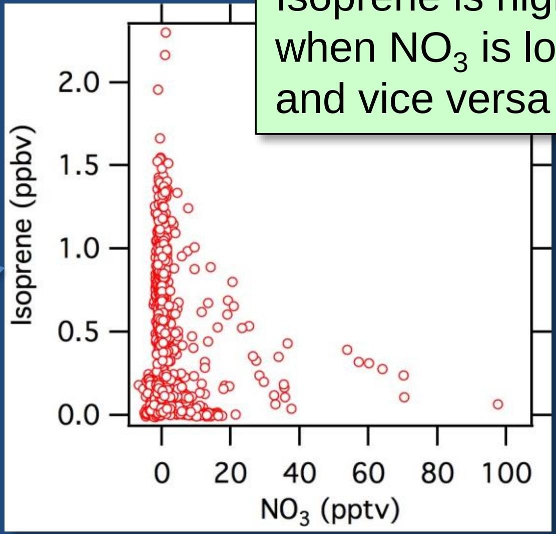
Biogenic VOC – Nitrate Chemistry

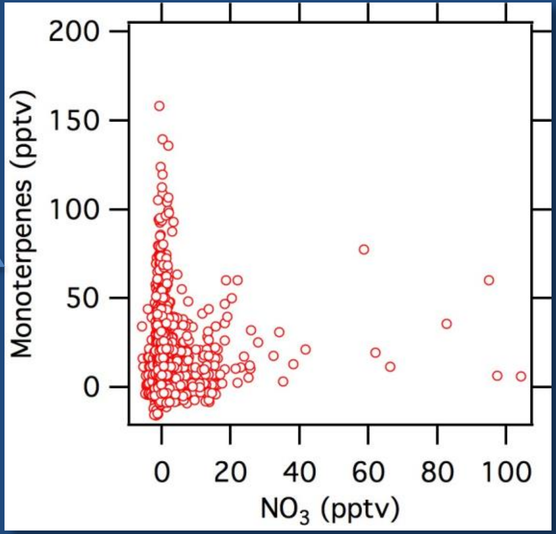
Edwards, Fry, Brown et al.

Three night flights to sample power plants, urban plumes & biomass burning



Isoprene is high when NO_3 is low and vice versa

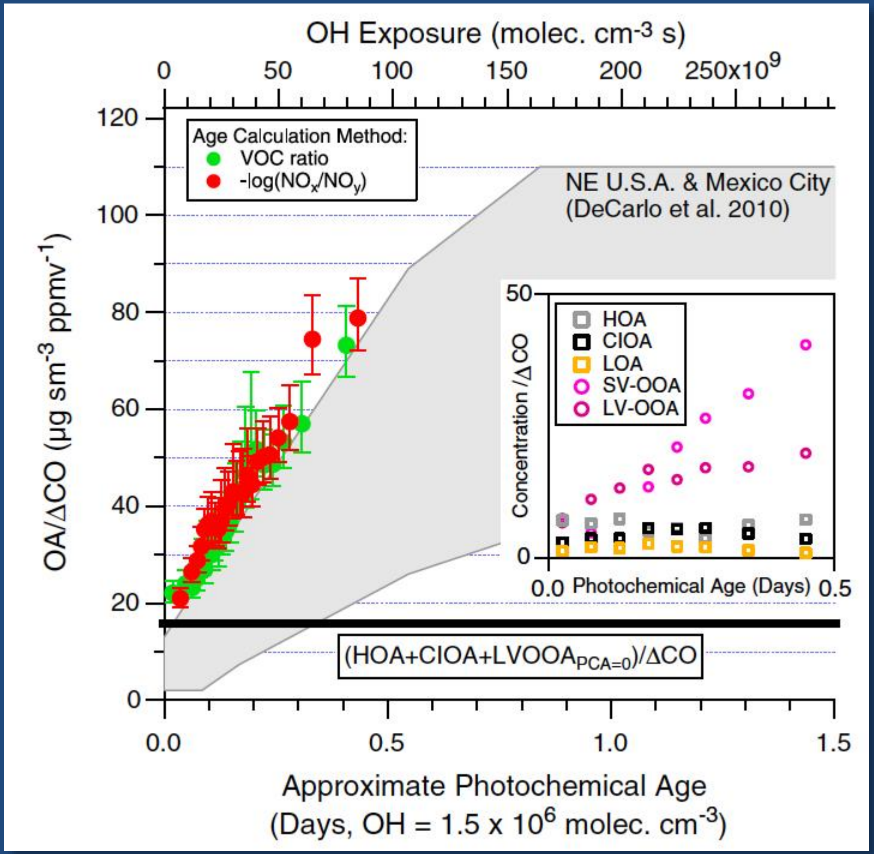




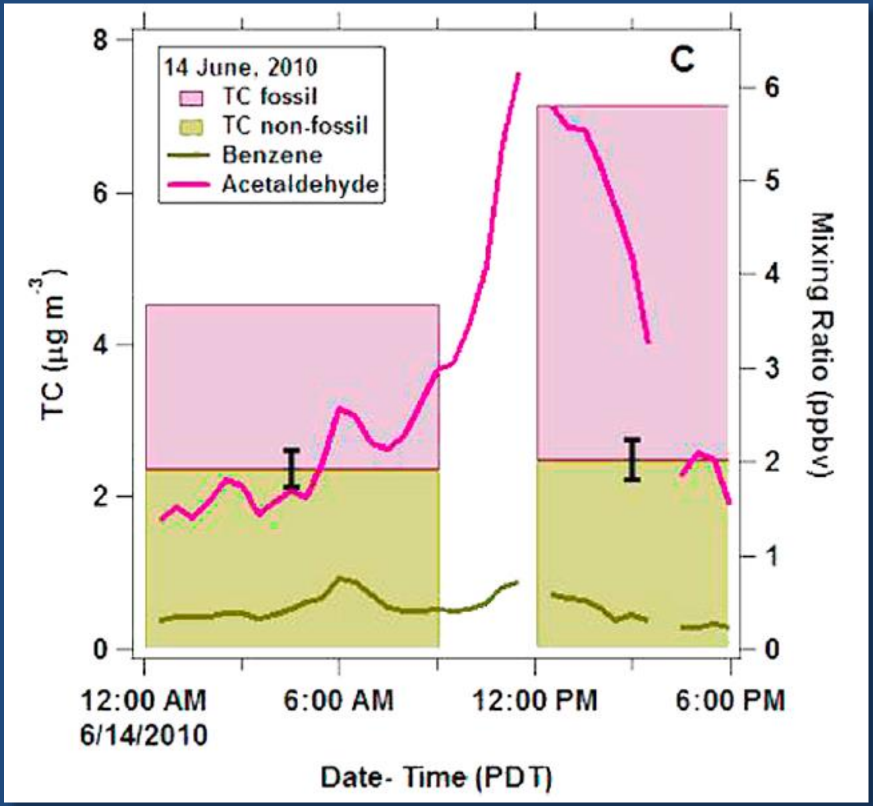
- NO_3 mixing ratios were modest due to presence of large biogenic VOC mixing ratios in the nighttime residual layer
- Nighttime BVOC oxidation dominated by NO_3 rather than O_3. Can we distinguish the products?

Does Urban SOA Contribute to Aerosol in the Southeast?

Middlebrook, Brioude et al.



Hayes et al. [ACP 2015]

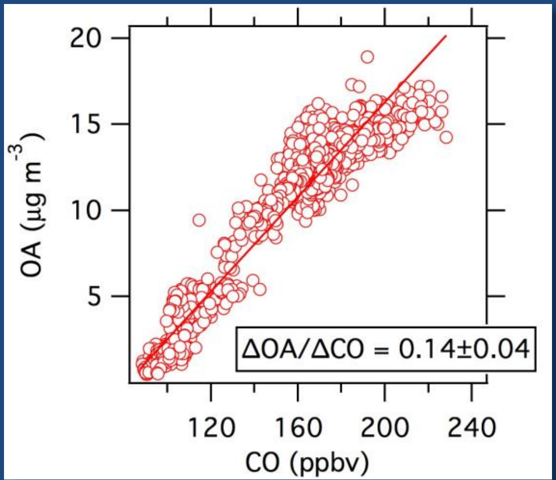


Bahreini et al. [GRL 2012]

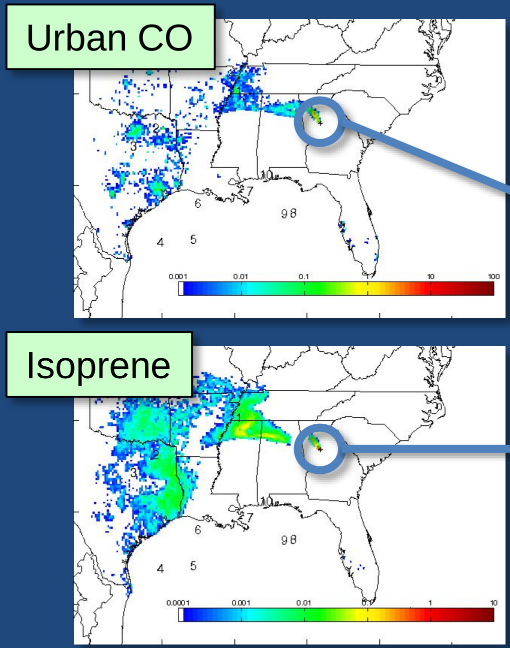
- In urban air, SOA is efficiently formed from oxidation of anthropogenic IVOCs and SVOCs
- How much does this source contribute to OA in the Southeast?

Separation of Sources Using Lagrangian Model FLEXPART

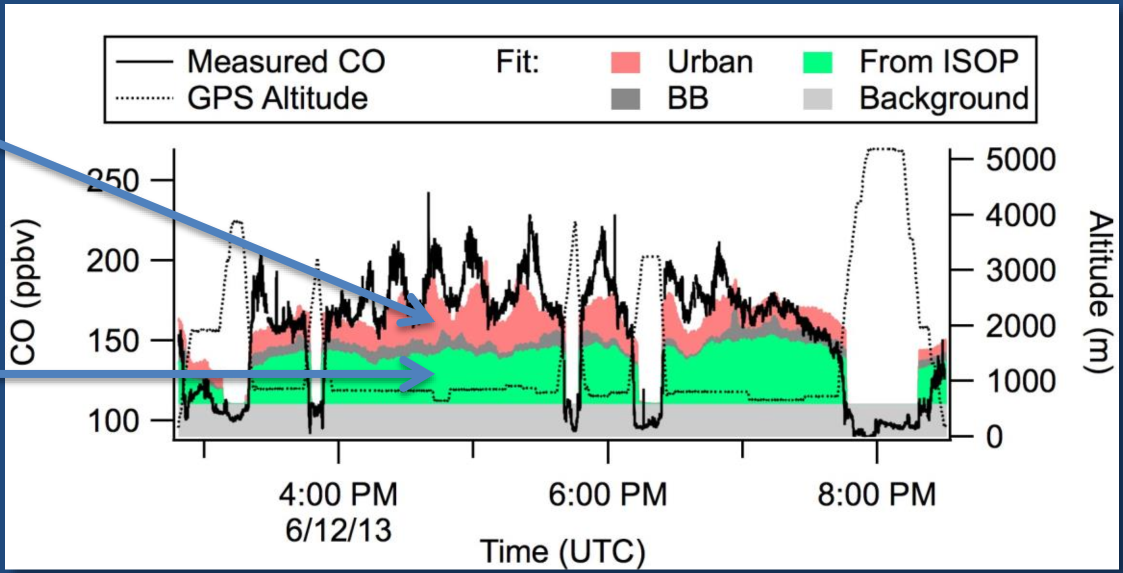
Middlebrook, Brioude et al.



- OA correlated well with CO and slope is similar between different flights
- But: CO is emitted from anthropogenic sources <u>and</u> formed from isoprene oxidation
- FLEXPART is used to separate sources by linear regression of modeled tracers



CO has mixed sources determined by linear regression



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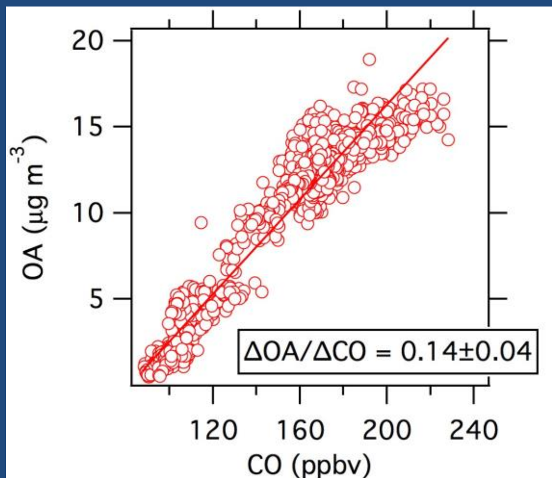

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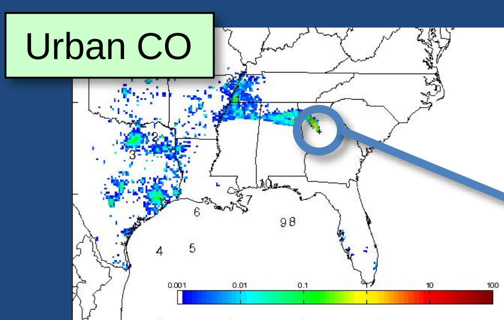

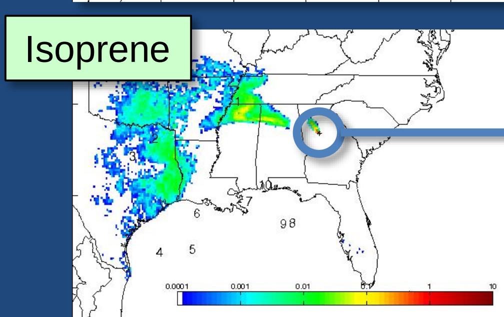

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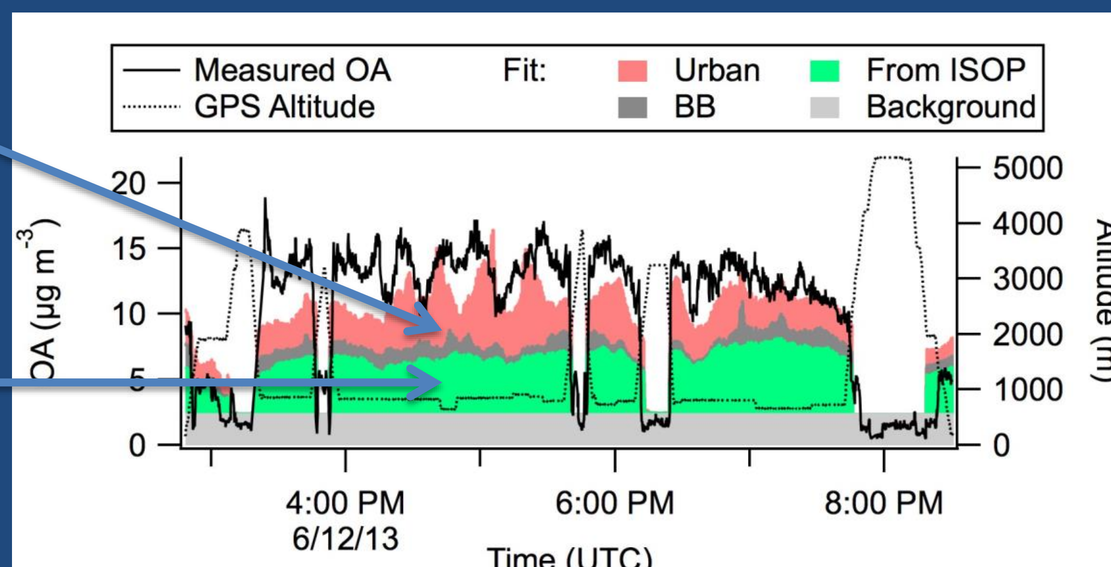
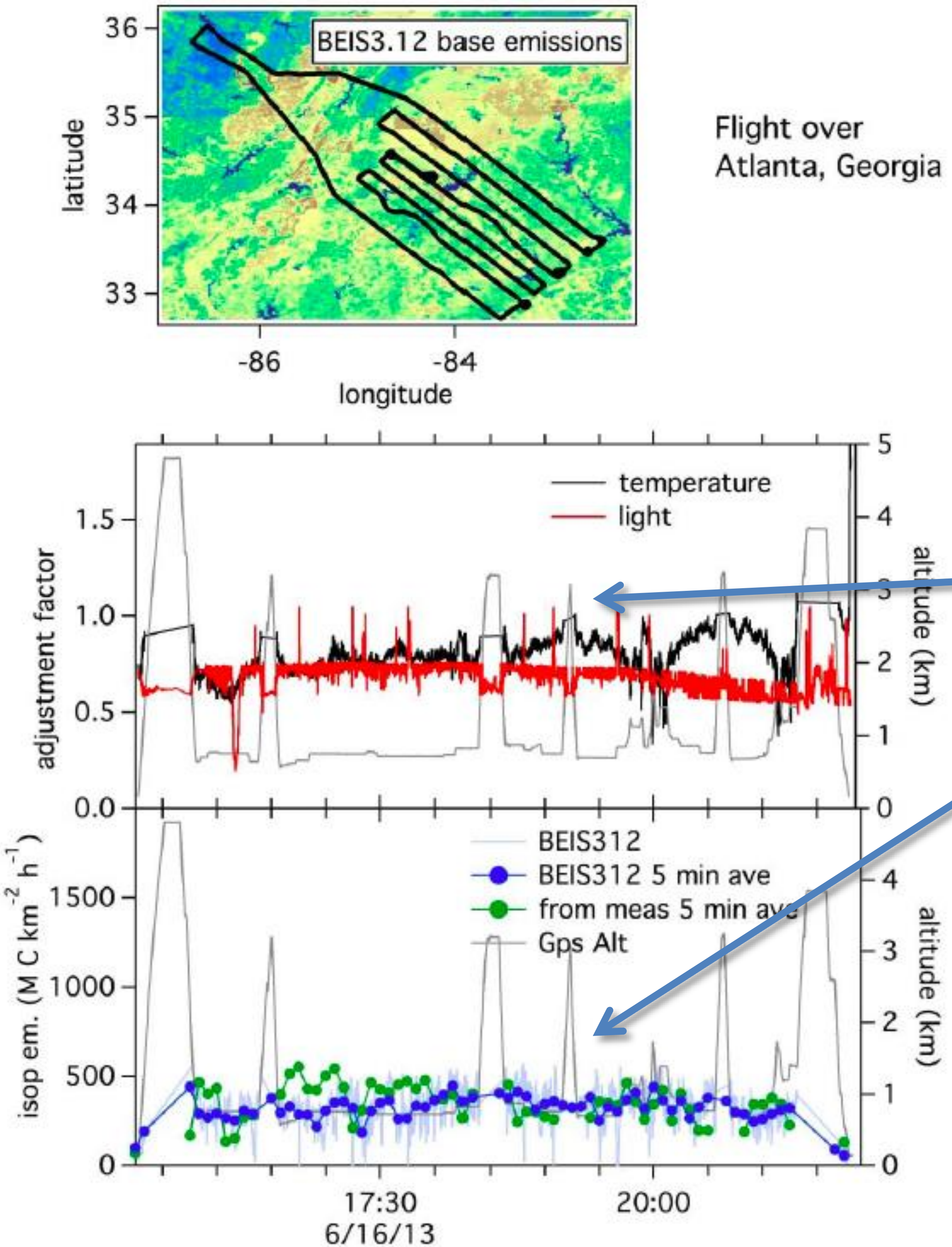


Other Results

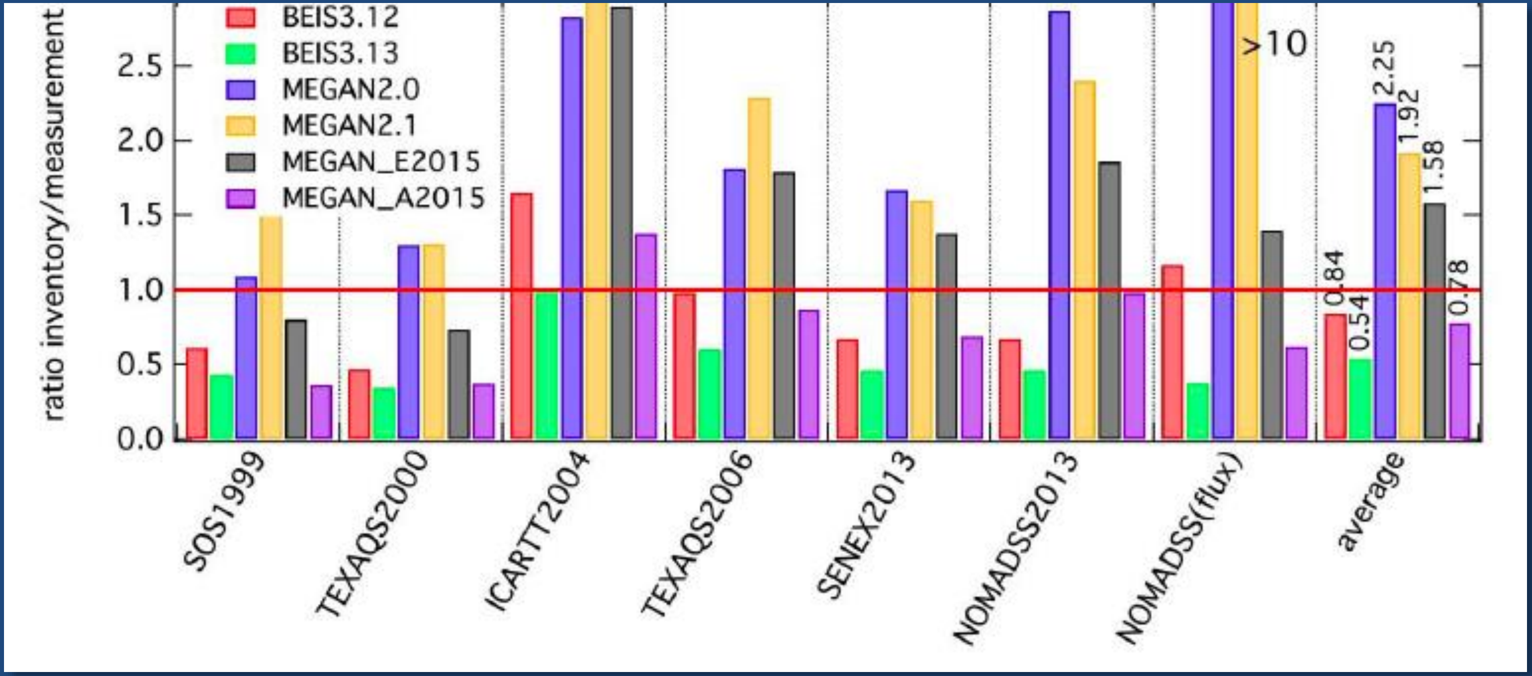
Evaluation of Isoprene Emission Inventories



- Comparison of modeled and measured isoprene require correct emissions, chemistry and meteorology
- Many relevant parameters are measured from the aircraft
- Allows the emissions to be separately evaluated

Joint project with Ramboll Environ and PNNL with support from Texas AQRP (final report, September 2015)

Evaluation of Isoprene Emission Inventories

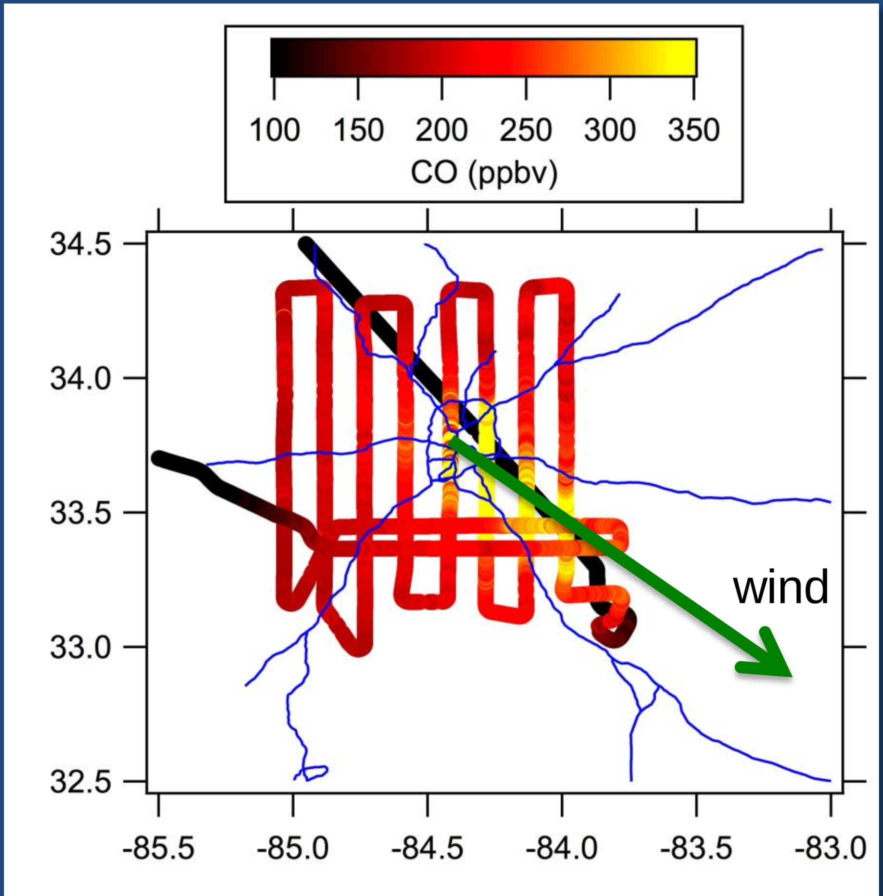


- BEIS 3.13 is lower and MEGAN is higher than emissions derived from NOAA WP-3D and NCAR C-130 measurements
- MEGAN updated with high-resolution plant functional type database <u>and</u> new emission factors derived from C-130 airborne data gives best description of the data

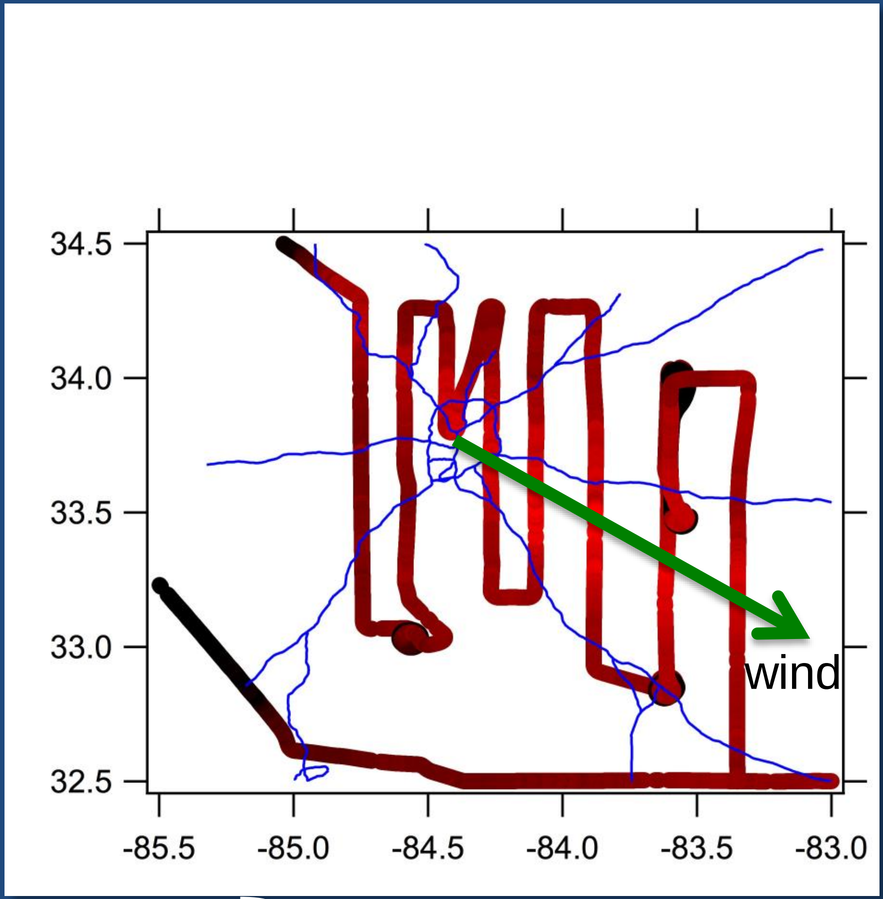
Thanks to: Carsten Warneke, Haofei Yu, Alex Guenther, Sue Kemball-Cook and Greg Yarwood

Differences in Chemistry Between SENEX and SOS-99

Atlanta, July 6, 1999 (SOS)



Atlanta, June 12, 2013 (SENEX)



- Strong decreases in emissions:
  - CO: 400-500 ppbv peaks in 1999
  - CO: 200-250 ppbv peaks in 2013
- Similar decreases for anthropogenic VOCs and NOx

Very different chemical regime

Differences in Chemistry Between SENEX and SOS-99

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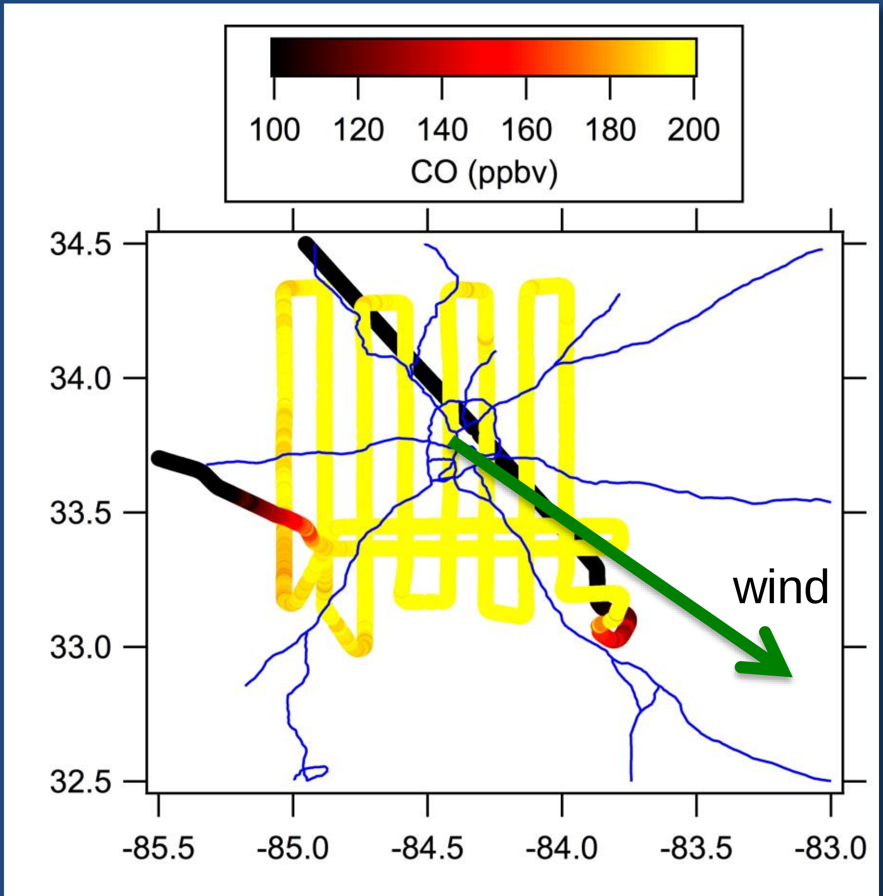

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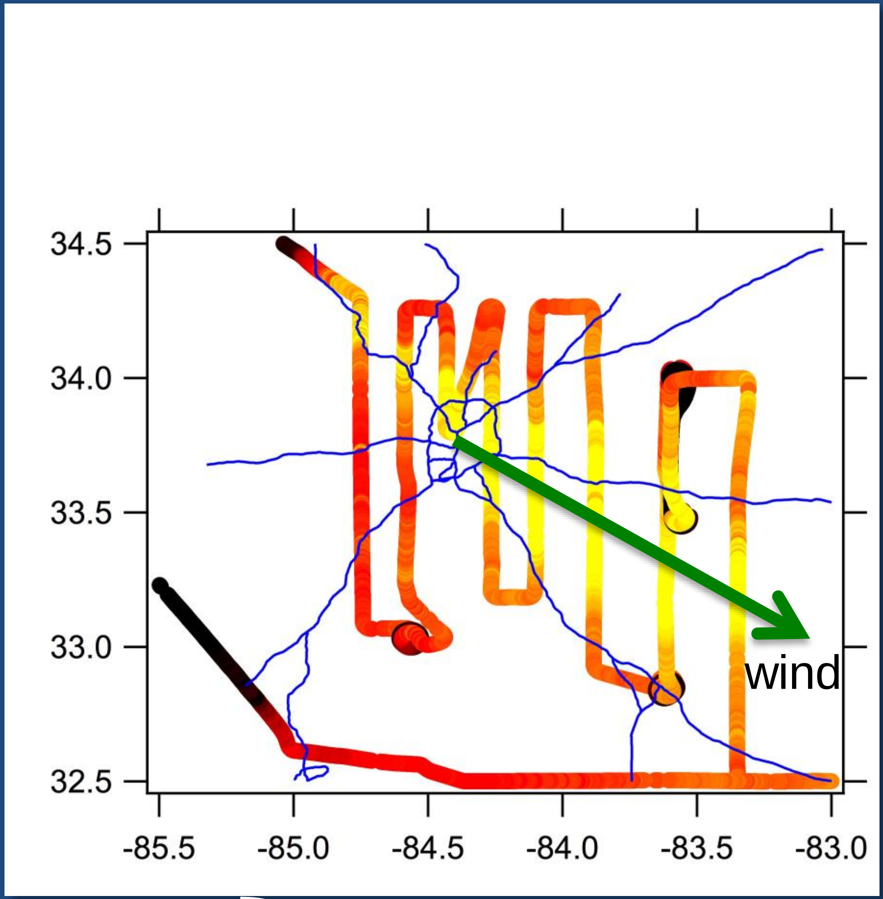

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} Very different chemical regime

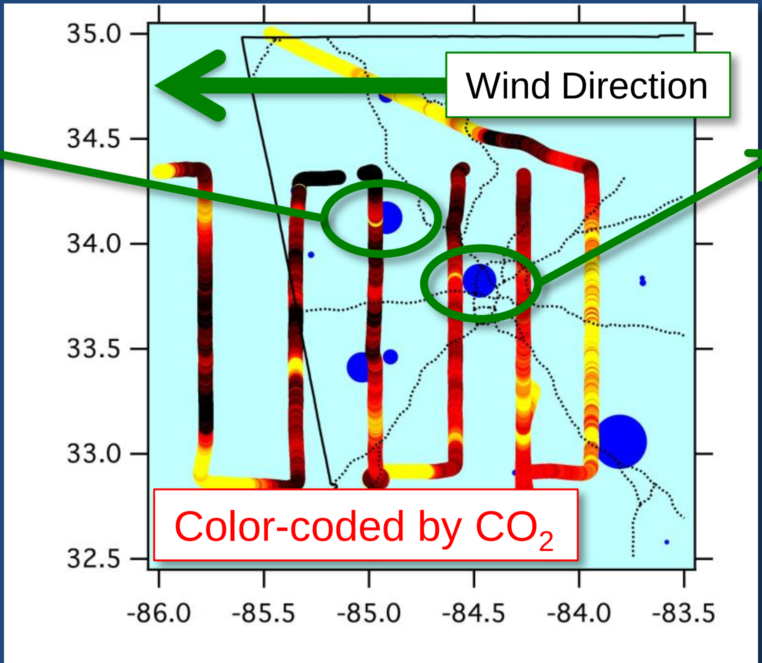
Power Plants: Coal vs. Natural Gas

Plant Bowen
Coal

1st quarter 2013:
3.3 TWh (CEMS)

Emission intensity

CO_2	930	g/kWh
NOx	0.56	
SO_2	0.20	

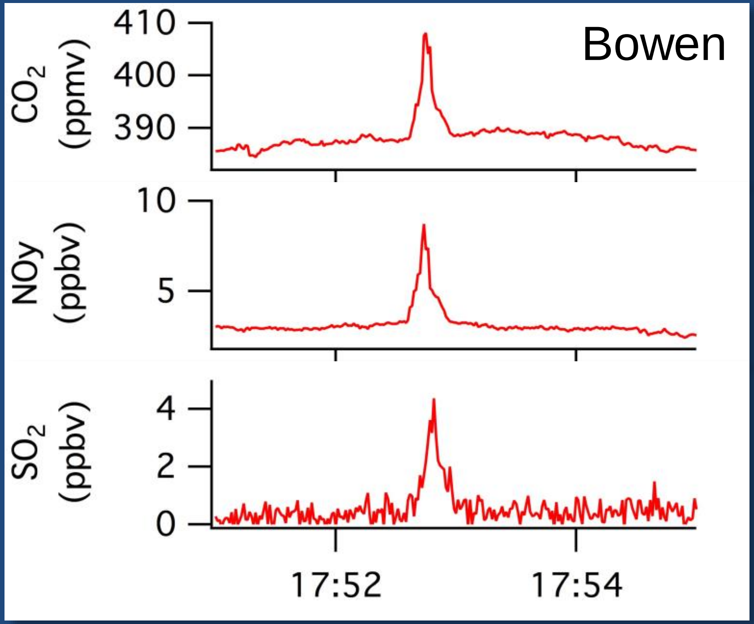


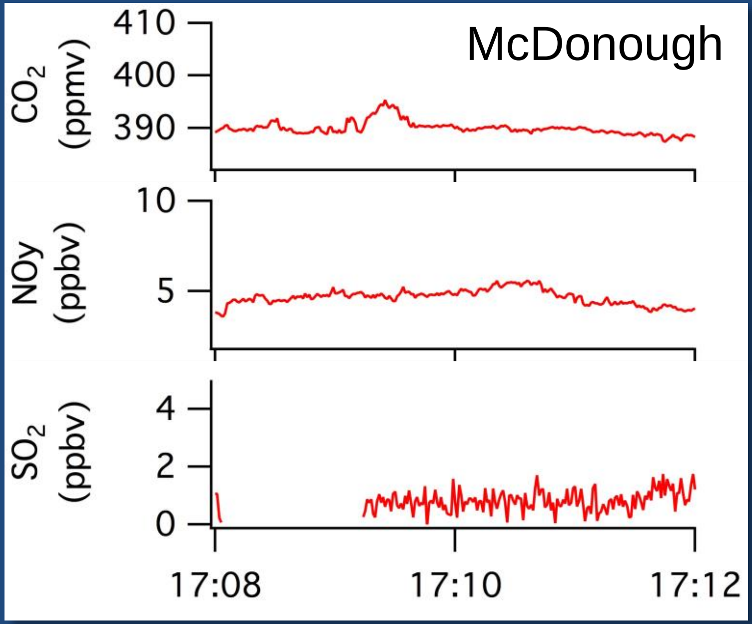
Plant McDonough
NG combined cycle

1st quarter 2013:
4.7 TWh (CEMS)

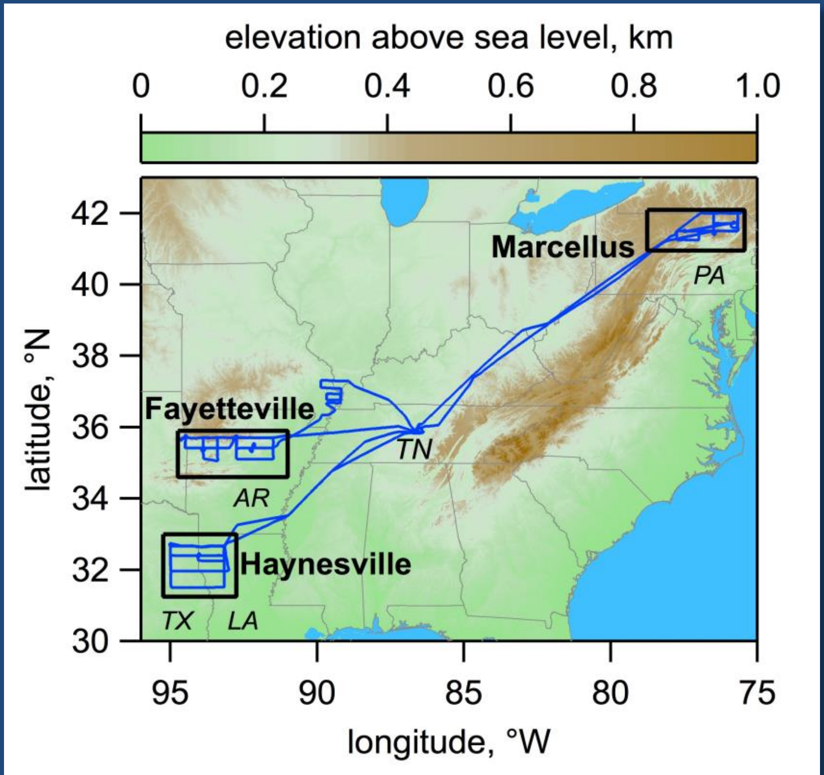
Emission intensity

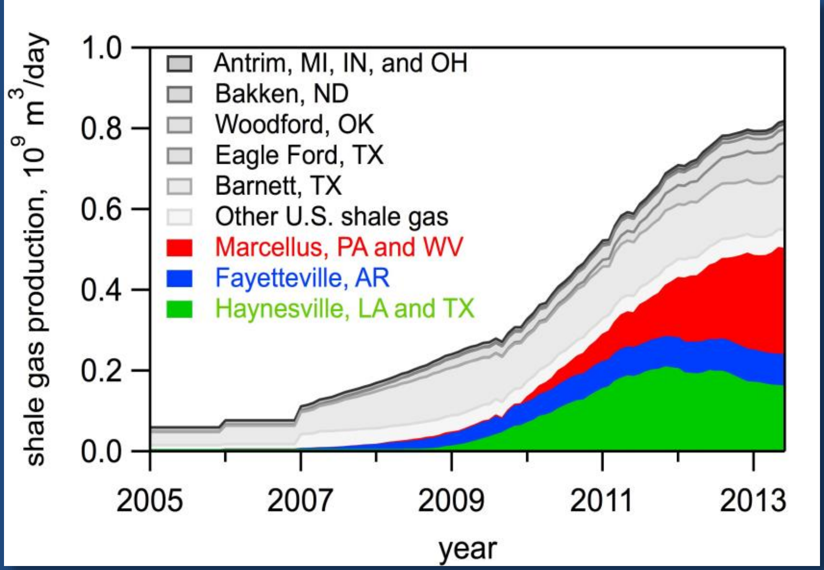
CO_2	360	g/kWh
NOx	0.018	
SO_2	0.0019	

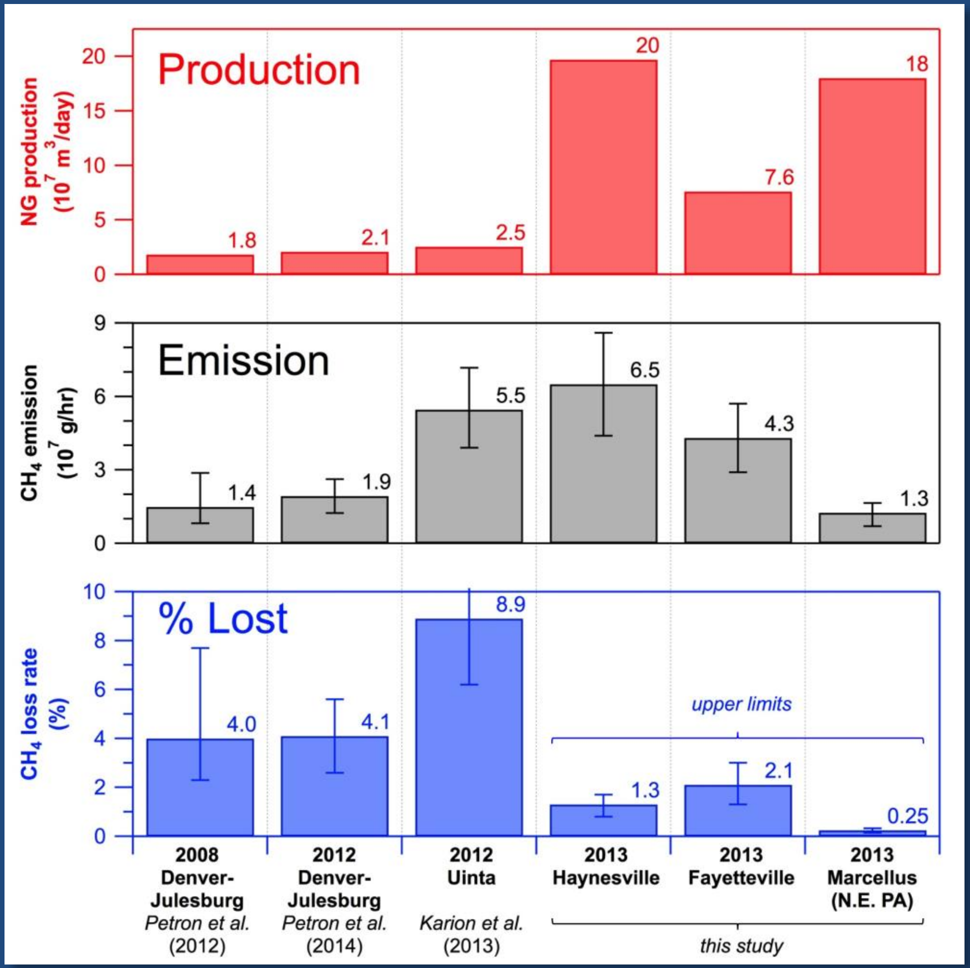




Emissions from Production of Natural Gas



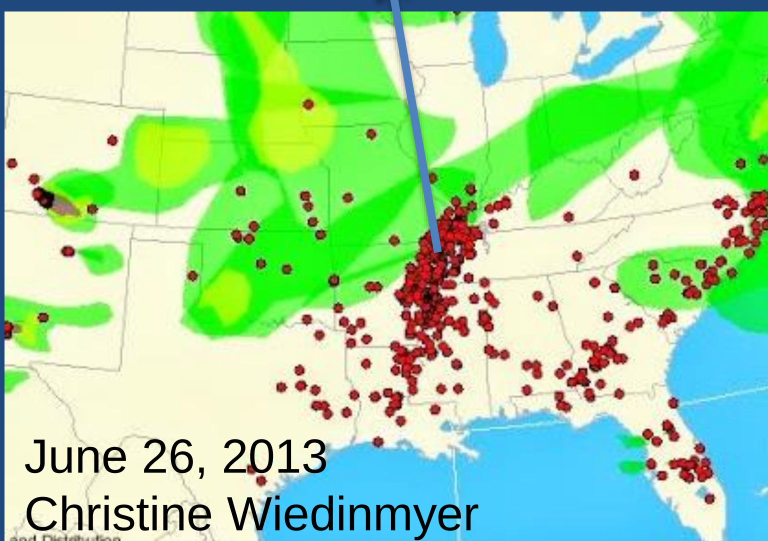




Studied basins have lower leak rates than basins in Utah and Colorado
Peischl et al. [JGR 2015]

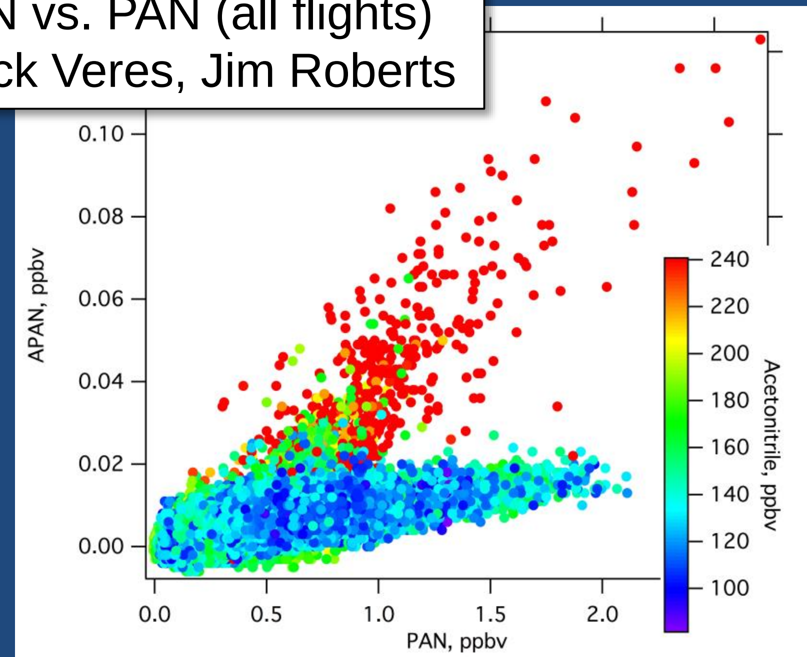
What is the Importance of Biomass Burning Emissions?

Agricultural burning in the Mississippi Delta

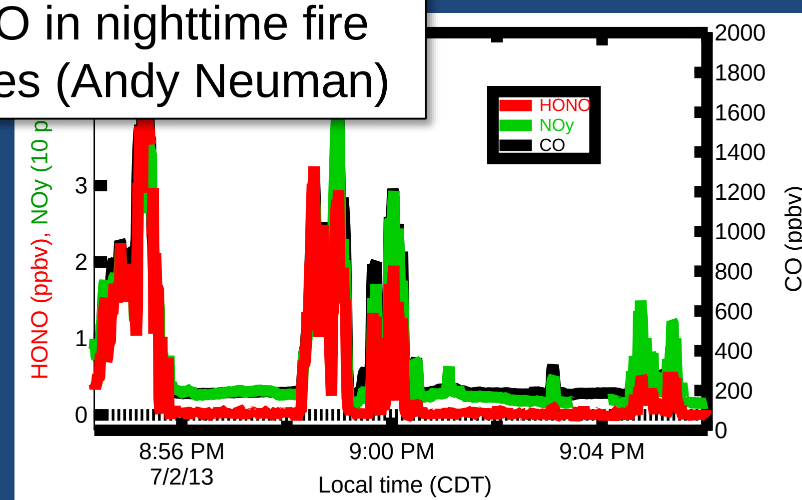


June 26, 2013
Christine Wiedinmyer

APAN vs. PAN (all flights)
Patrick Veres, Jim Roberts



HONO in nighttime fire plumes (Andy Neuman)



More work is needed

Summary

- SENEX data constrain several mechanisms that couple the emissions of biogenic and anthropogenic precursors to form secondary pollutants
- More detailed analysis is in progress to quantify the relative importance of these interactions, and determine the impact on air quality and climate

Acknowledgements

Michael Trainer, Lu Xu, Sally Ng, Nick Wagner, Pete Edwards, Julie Fry, Steve Brown, Ann Middlebrook, Jerome Brioude, Chuck Brock, Bin Yuan

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AMS	Ann Middlebrook, Jin Liao, Andre Welti
NO, NO_2	Illana Pollack, Tom Ryerson
NO_3	Peter Edwards, Steve Brown
HNO3, HONO	Andy Neuman
PANs	Patrick Veres, Jim Roberts
CO, SO_2	John Holloway
CH_4	Jeff Peischl

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