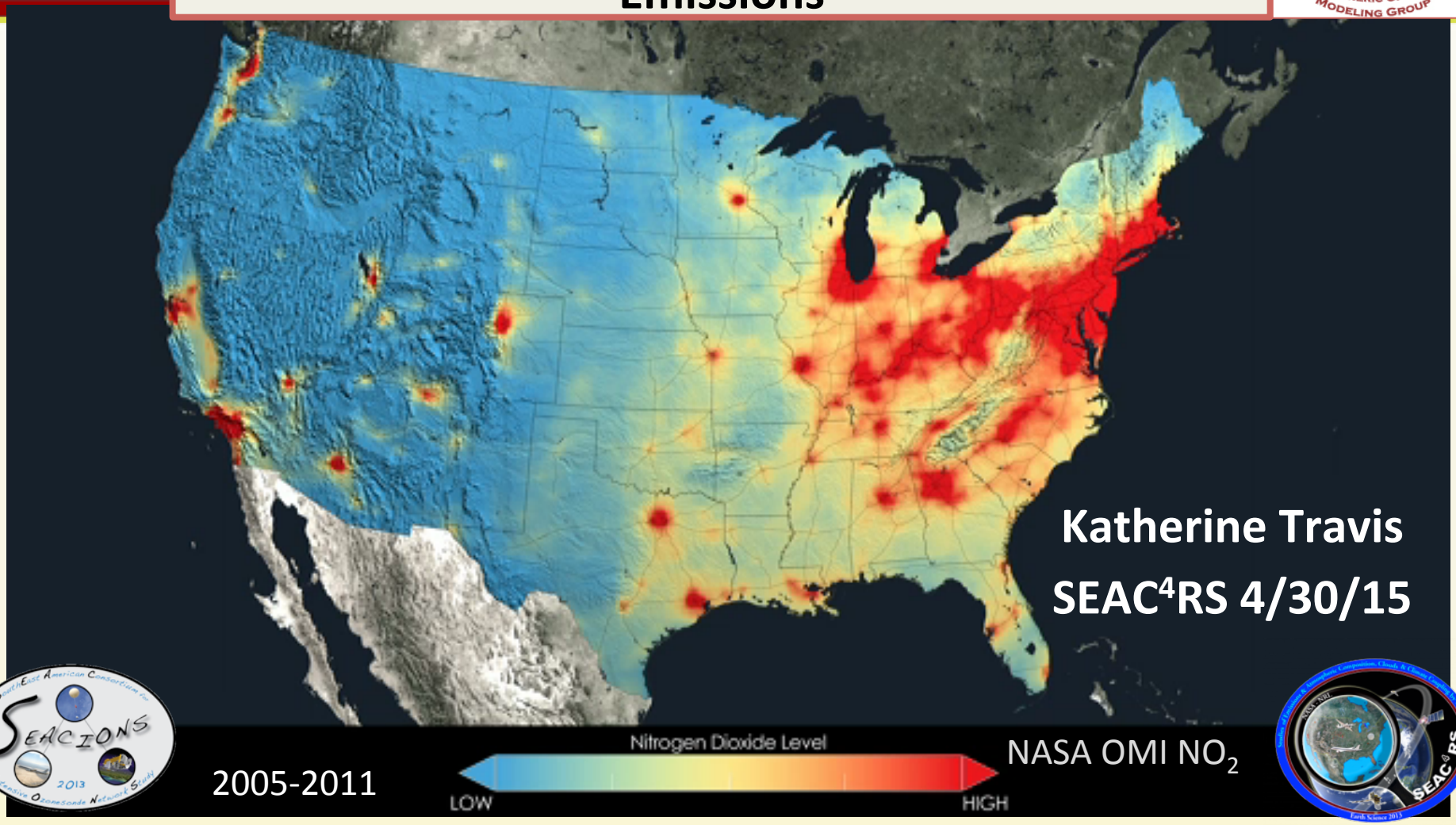
O_3-NOx-VOC Chemistry in the Southeast U.S. & the Implications of Rapidly Declining NOx Emissions

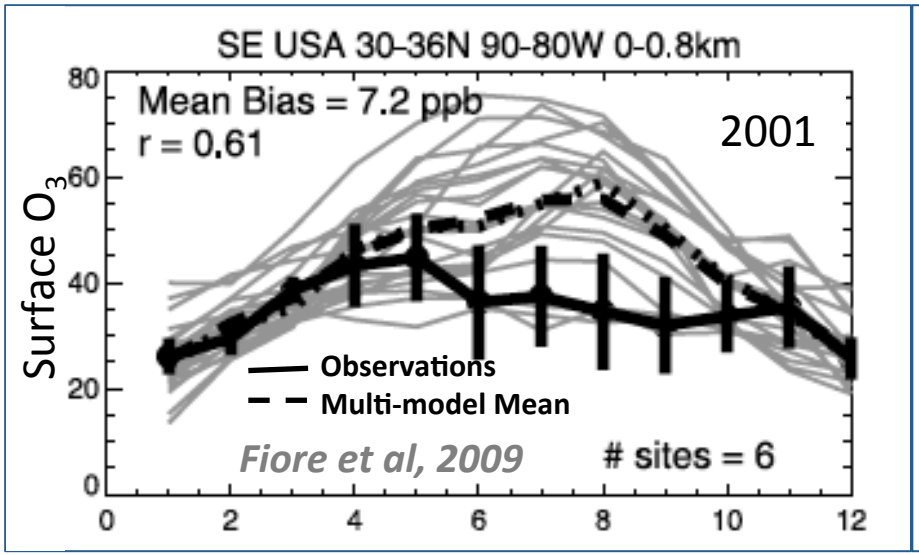


Co-authors: Daniel Jacob, Paul Wennberg, John Crounse, Anne Thompson, Thomas Hanisco, Thomas Ryerson, Jack Dibb, Greg Huey, Patrick Kim, Jenny Fisher, Lei Zhu, Eloise Marais, Chris Miller, Karen Yu, Andy Neuman, Xianliang Zhao, Bob Yantosca, Melissa Payer

HARVARD
School of Engineering and Applied Sciences

The Southeast U.S. NOx Emissions Are Rapidly Decreasing

A Modeling Trouble Spot…



In a Region of Rapidly Declining NOx

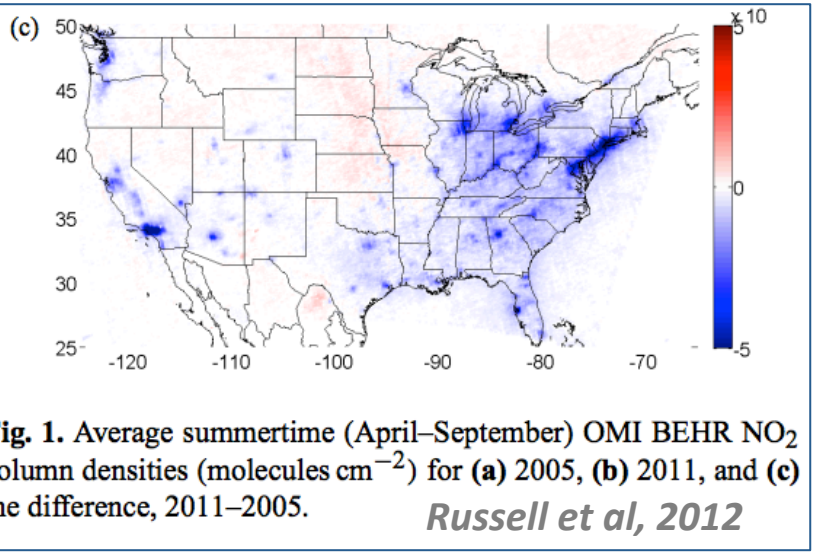


Fig. 1. Average summertime (April–September) OMI BEHR NO_2 column densities (molecules cm^{-2}) for **(a)** 2005, **(b)** 2011, and **(c)** the difference, 2011–2005.

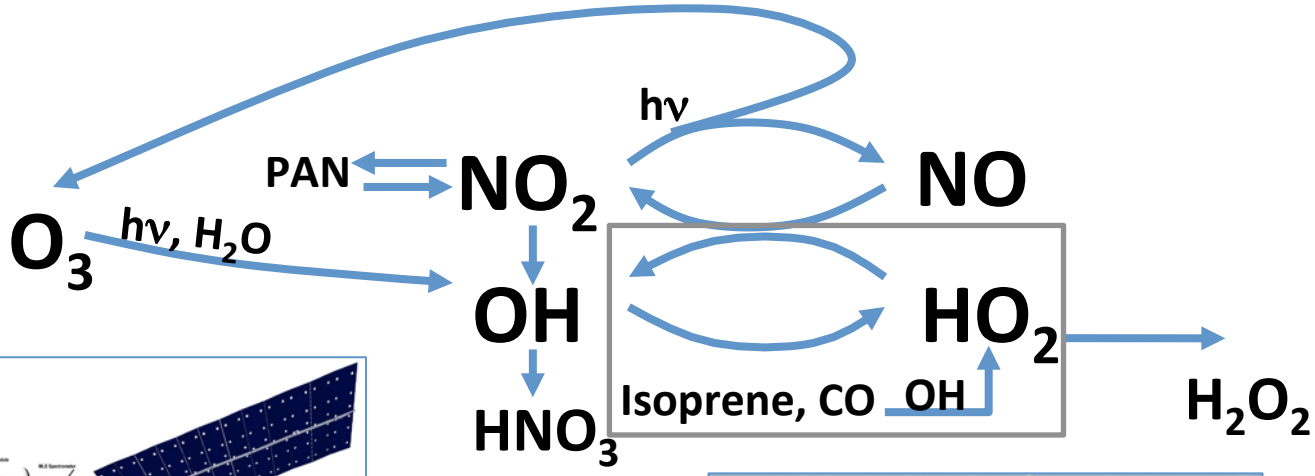
Russell et al, 2012

- Model difficulties have been attributed to uncertainties in NOx-O_3-VOC chemistry.
- Even recent studies have similar biases (Canty et al, 2015 (APCD)).

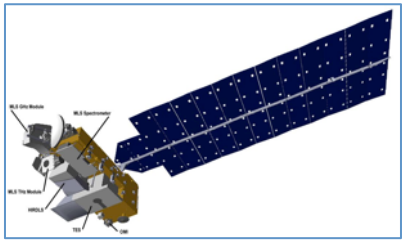
- OMI NO_2 implies a decrease from 2005 – 2011 of 32 $\pm$ 7%.
- EPA emissions indicate a decline of 28% over this period.

EPA is proposing a new 8-hour standard between 65 and 70 ppb.
How can states achieve compliance with current modeling capabilities?

We Have An Unprecedented Data Set to Constrain O_3-NOx-VOC Chemistry



Anne Thompson

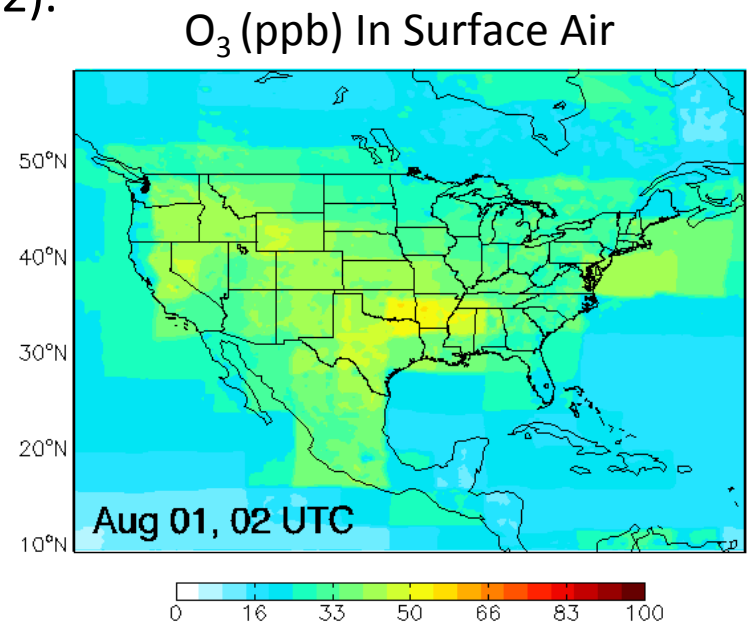


OMI NO_2

- T. Ryerson: NOx, NOy, O_3
- G. Huey: PAN
- T. Hanisco, Alan Fried: HCHO
- G. Diskin, D. Blake: CO
- R. Cohen: NO_2, PNs, ANs
- J. Dibb: HNO_3 + NO_3
- A. Wisthaler: isoprene
- P. Wennberg: HNO_3, H_2O_2, ISOPOOH, ISOPN, HPALDs

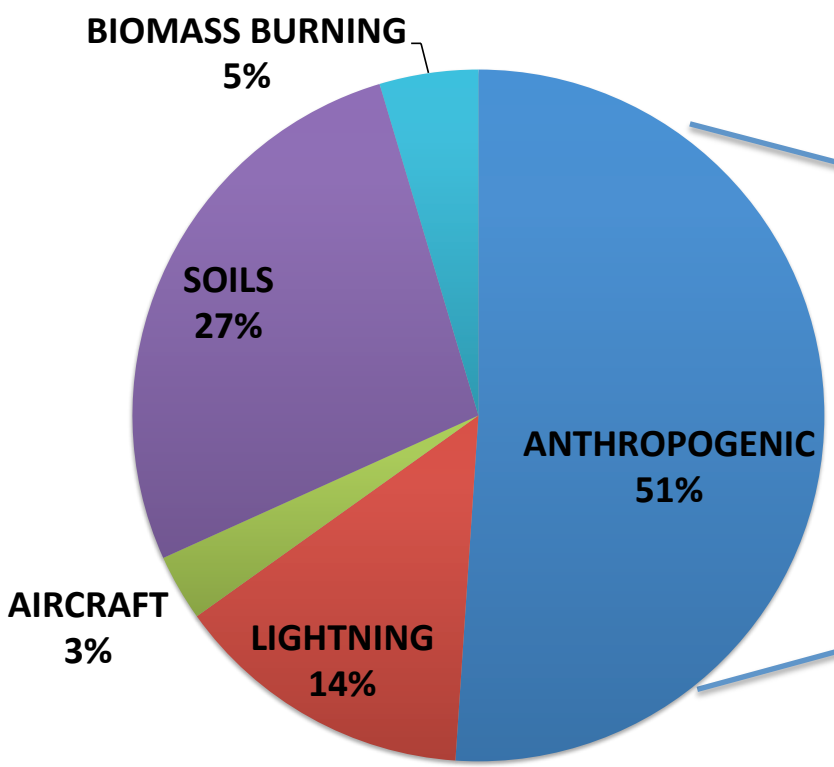
GEOS-Chem Developed to Incorporate the State-of-the-Science Relevant to this Region

- 0.25°x0.3125° nested resolution over North America.
- **Emissions:**
  - Biogenic from MEGAN (Guenther et al, 2012).
  - Soil NOx from Hudman et al (2012).
  - Lightning NOx according to Murray et al (2012).
  - Anthropogenic emissions from NEI 11v1.
- **Chemistry:**
  - Chemistry from Mao et al, 2013.
    - w/bromine chemistry (Parrella et al, 2012).
  - Improved treatment of low- and high- Nox pathways to incorporate recent lab studies.
  - Fast photolysis of carbonyl nitrates (Muller et al, 2014).
- **Physical processes:**
  - Fast deposition of isoprene oxidation products (Nguyen et al, 2015).



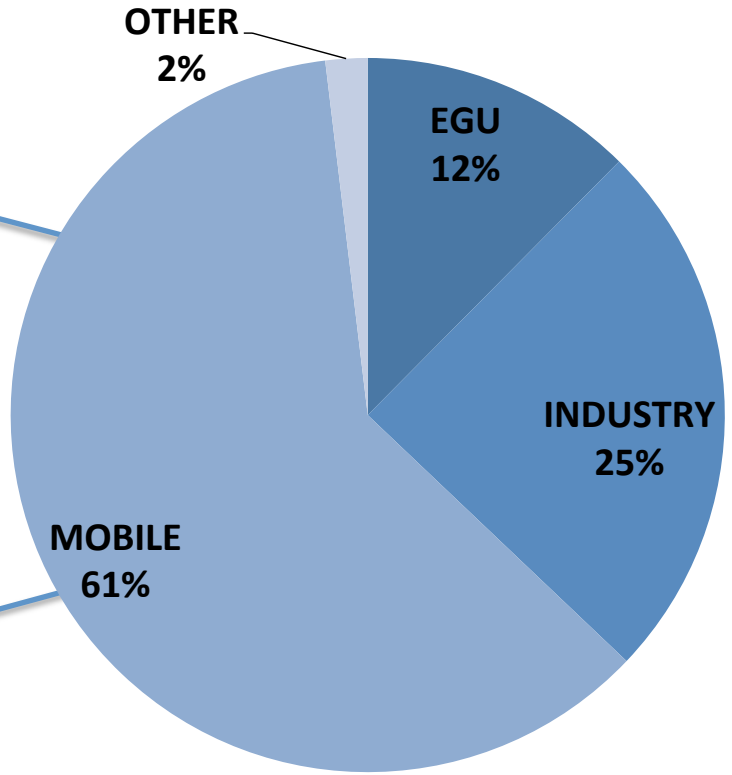
Source Contributions to NOx in the U.S.

U.S. Total Emissions During August 2013 (Tg N)



Total NOx Emission = 0.57 Tg N

Anthropogenic Emissions (NEIv11)

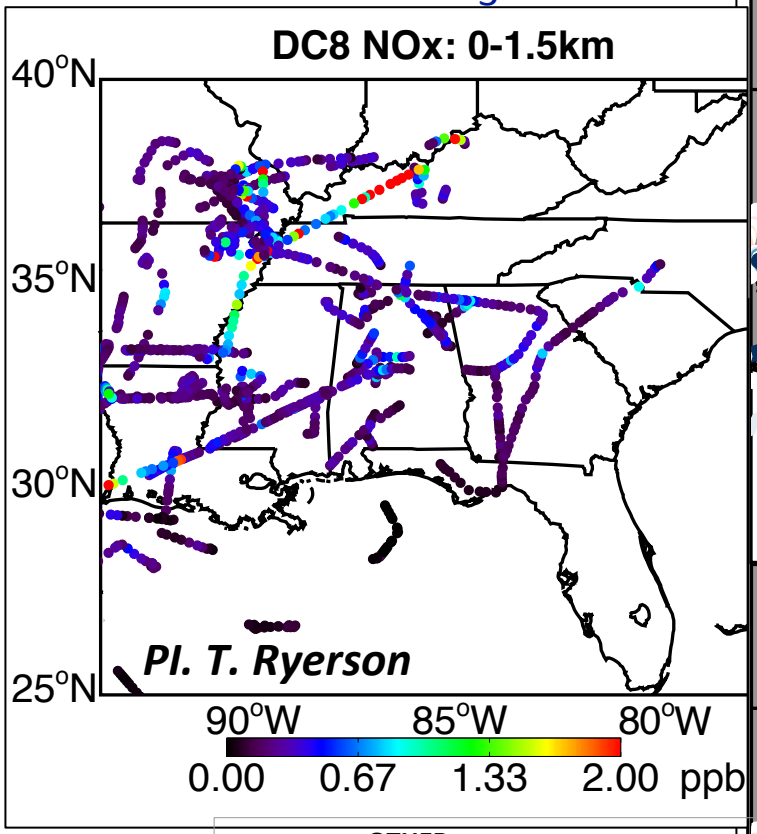


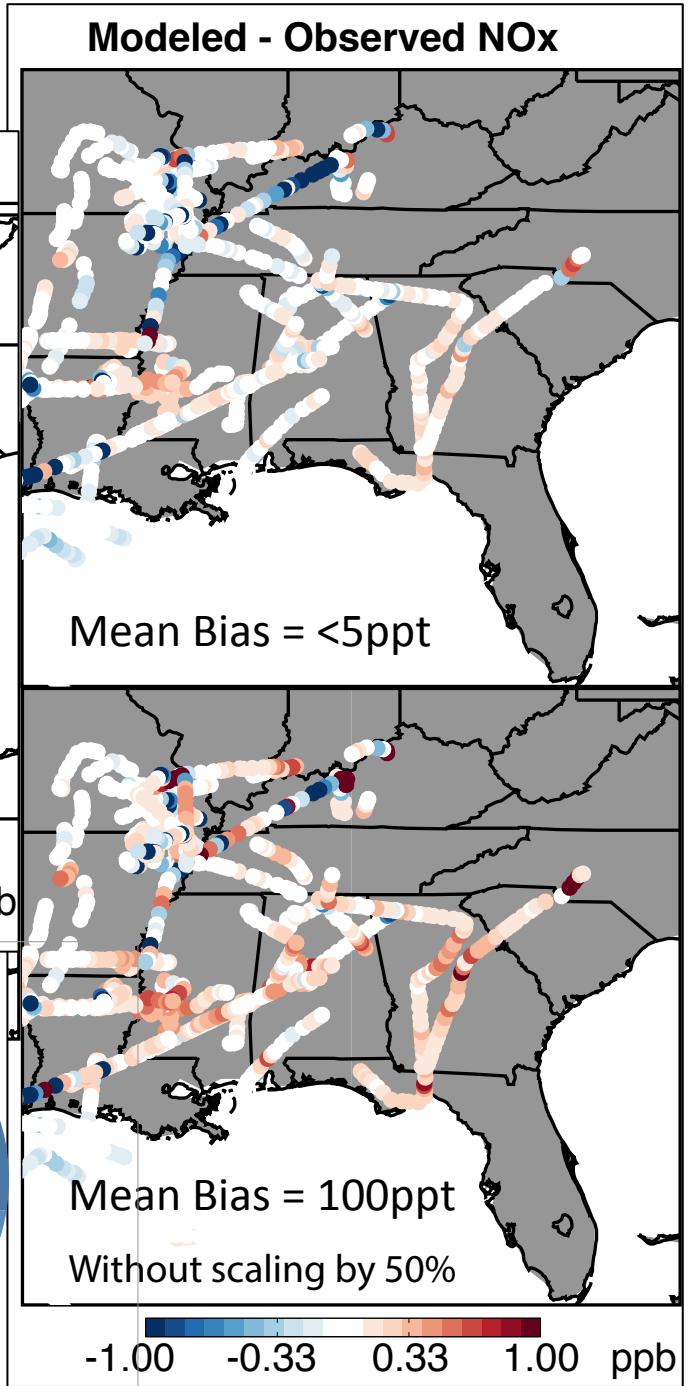
Total NOx Emission = 0.29 Tg N

**Note anthropogenic breakdown is based on Annual CONUS totals*

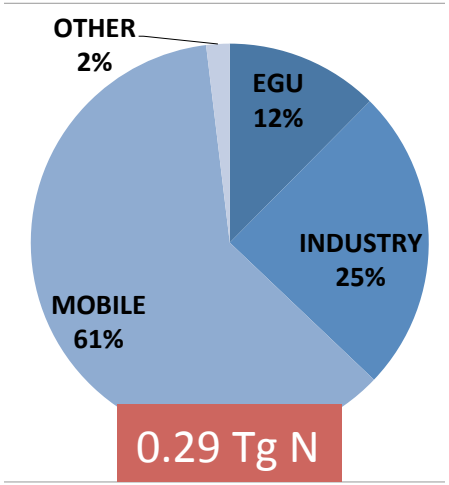
GEOS-Chem with NEI11 Overestimates Boundary Layer NOx and O_3

- We reduce the mobile NOx inventory by >50%.
- Many studies find that the NEI overestimates mobile NOx by 30-70% (Anderson et al, 2014, Brioude et al, 2013, Fujita et al, 2012, Yu et al, 2012).

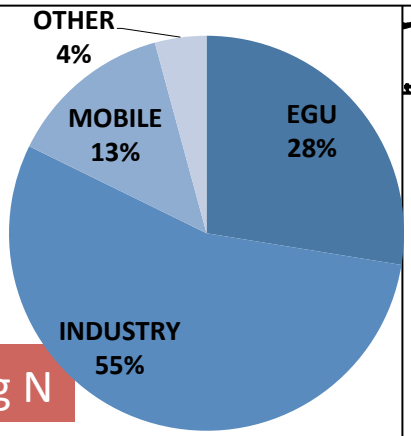




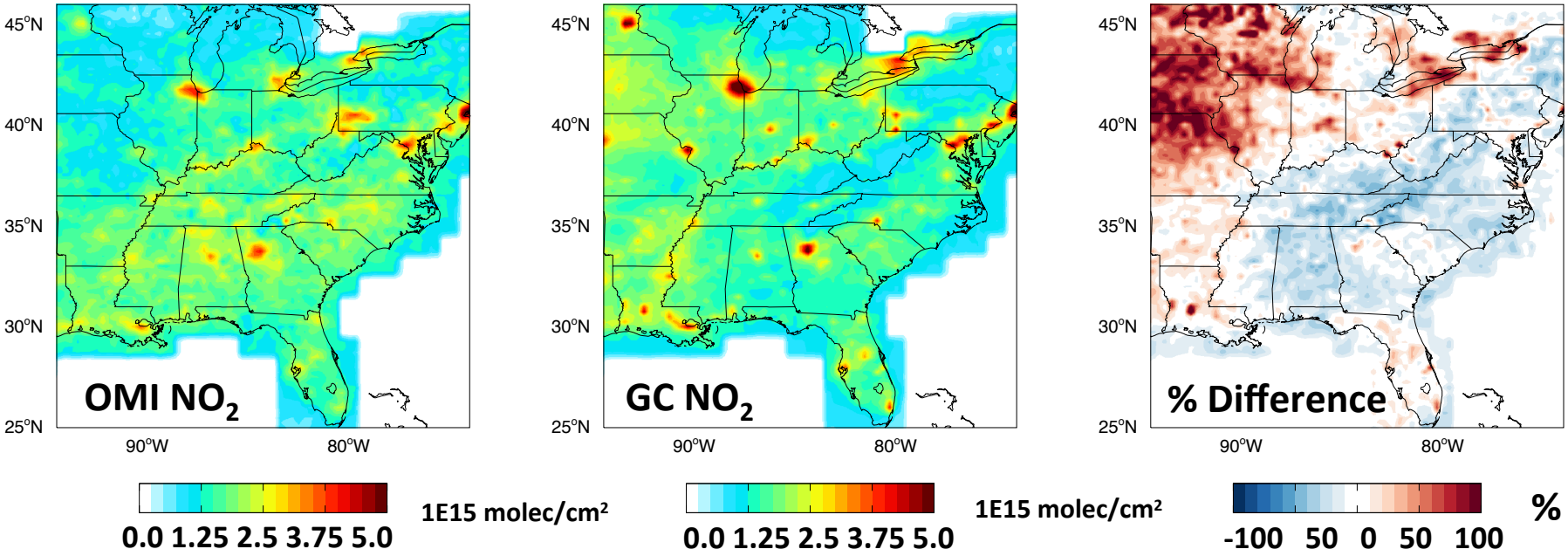
Original NEIv11



Reduced Mobile NOx

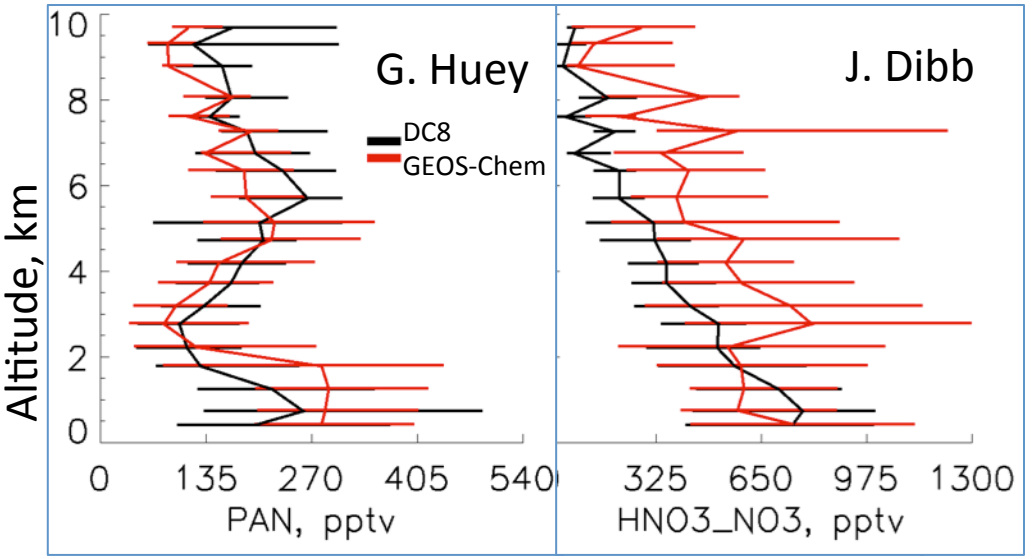


We Are Biased Low in Rural Regions Against OMI NO_2

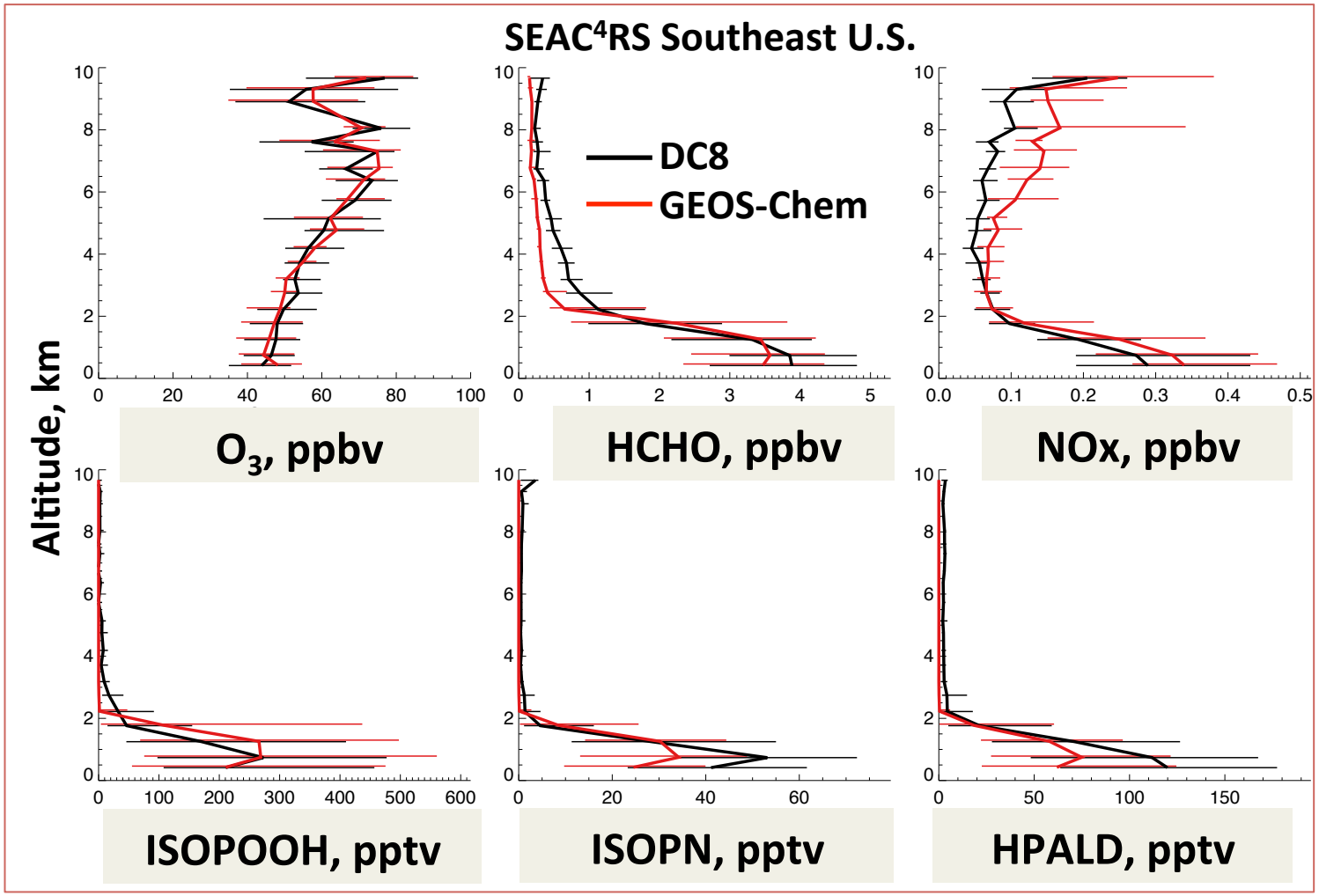


- Midwest NO_2 columns are overestimated by 2x where soil NOx dominates emissions (similar to Lamsal et al, 2014).
  - Uncertainties in the OMI AMF over polluted regions is ~20% and ~0.75E15 molec/cm^2 in rural regions
- OMI NO_2 (NASA) has known problems with urban vs. rural comparisons due to underlying coarse surface albedo maps.
- Cutting soil NOx will only be a small part of improving our model in the southeast.

NOx reservoir species are well-captured

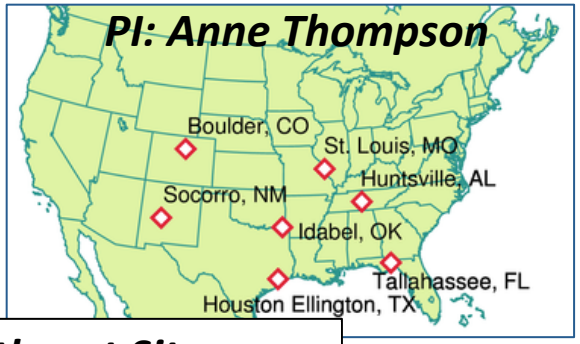


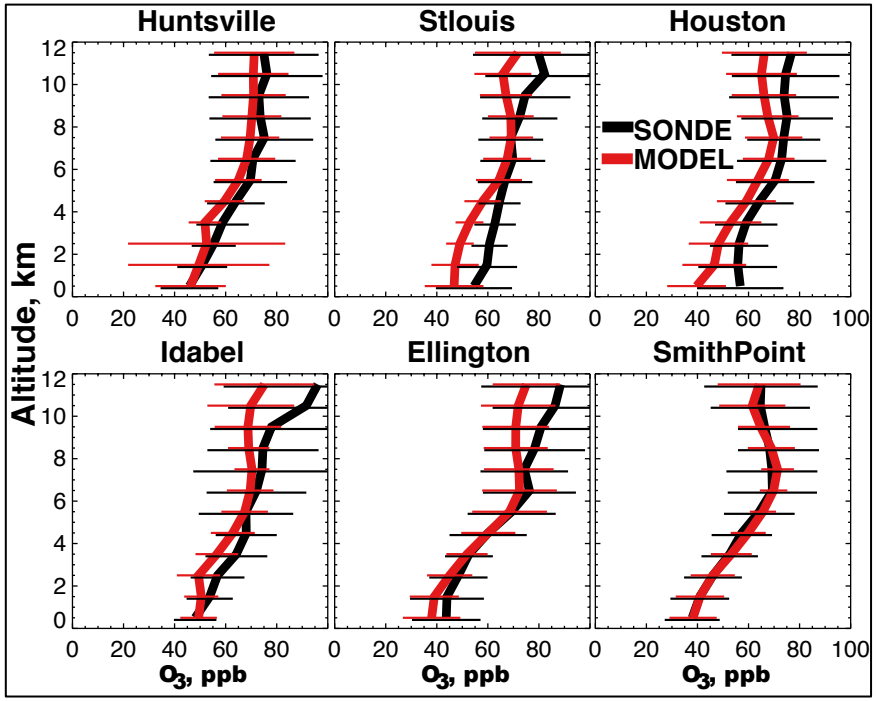
We Successfully Capture The Fate of Isoprene

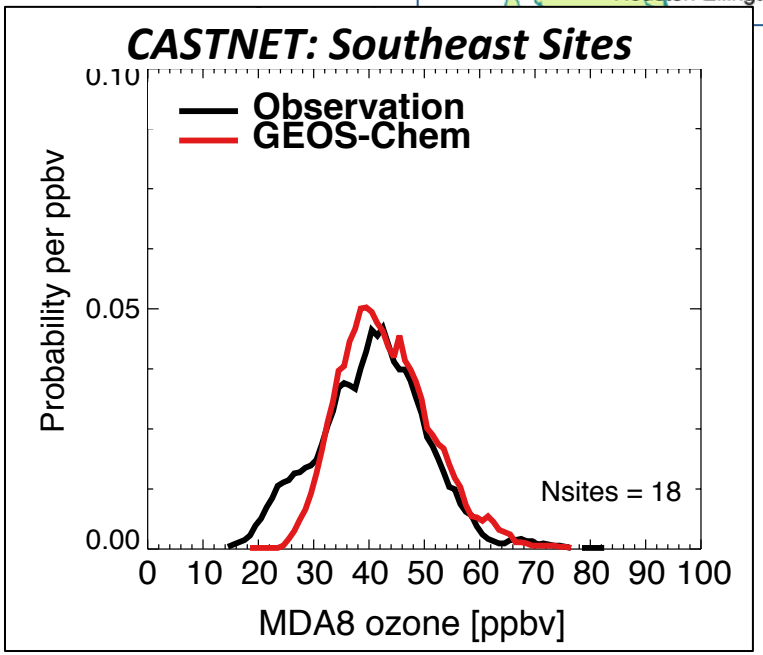


PI. P. Wennberg: ISOPOOH, ISOPN, HPALD;
PI. T. Ryerson: O_3, NOx; PI. T. Hanisco: HCHO

Sonde Comparison Supports Our Free-Tropospheric O_3 Simulation

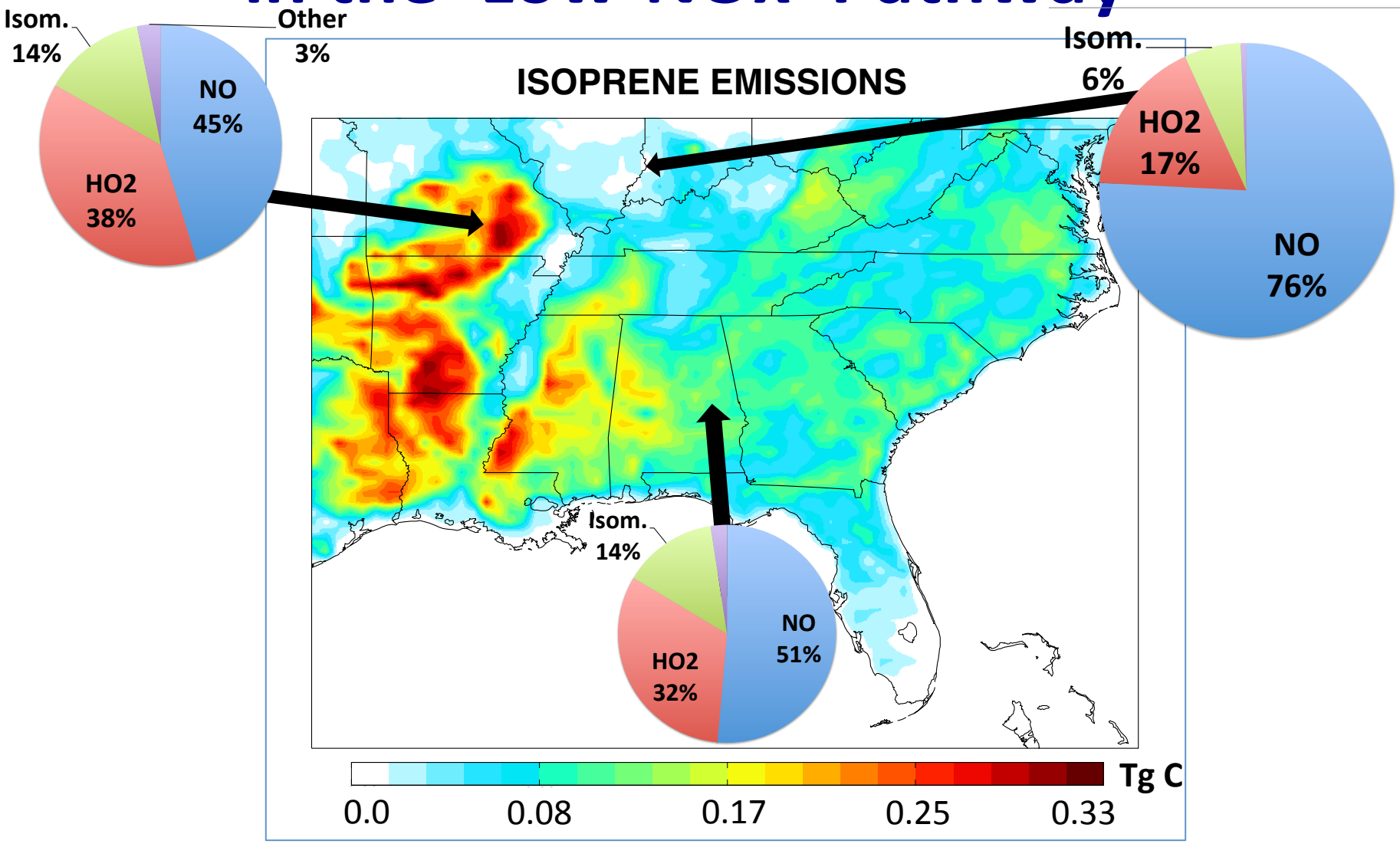






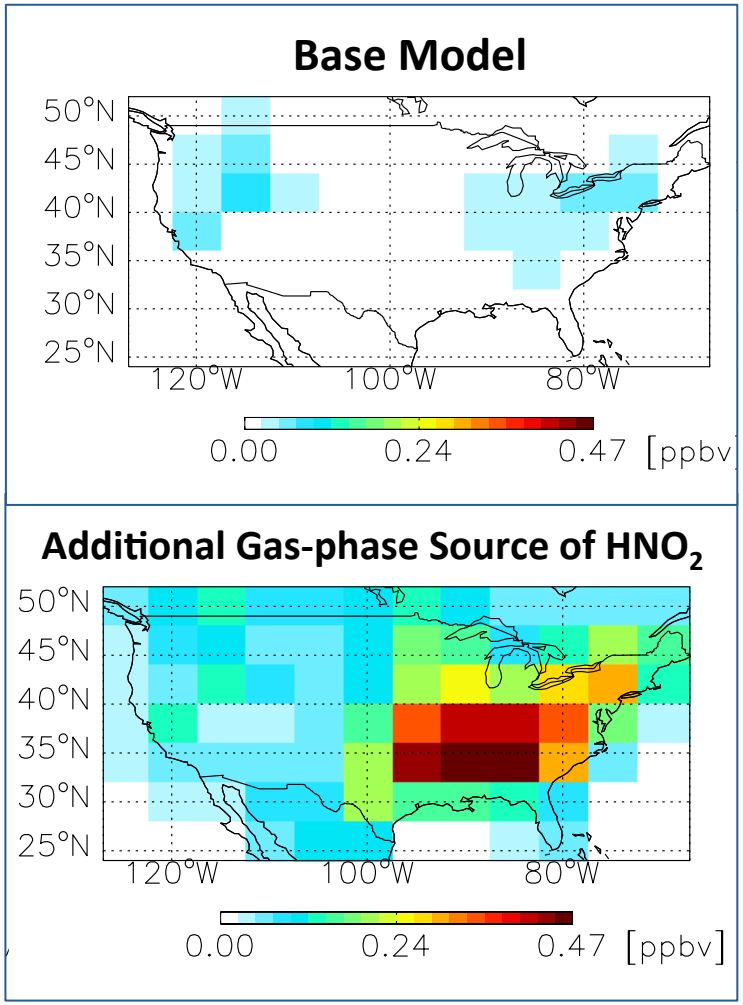
- Fiore et al (2014) found that lightning NOx and isoprene were the largest contributors to differences in modeled background O_3.
- We can use sonde comparisons to build confidence in our background O_3 simulation.
- Against southeast CASTNET sites our bias is 3±4ppb.
- We miss the lowest O_3 in northern Florida on the coast. We also have clear biases in rural areas with low measured MDA8 (ex MO) that may be attributable to soil NOx.

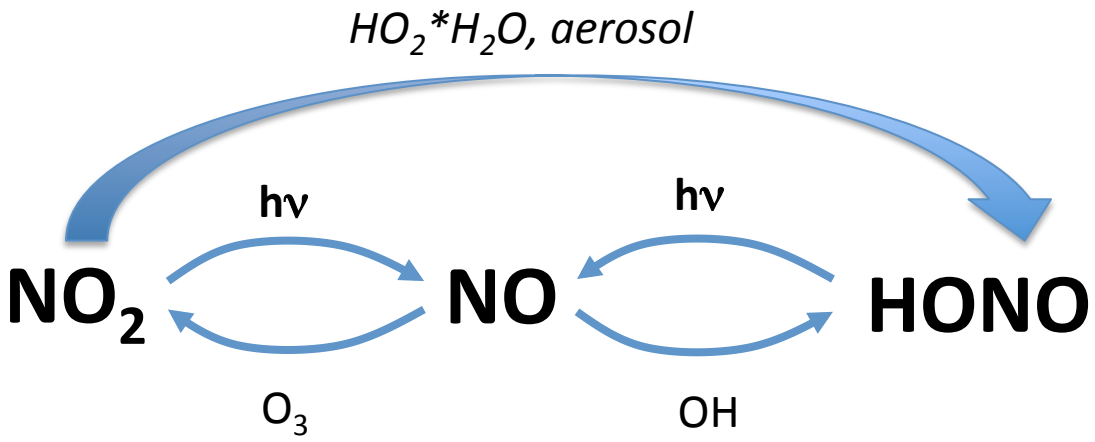
Significant Isoprene Oxidation Occurs in the 'Low-NOx' Pathway



We are able to spatially separate NOx and isoprene emissions, which leads to increased oxidation in the low-NOx pathway (see talk by Karen Yu)

Catalytic O_3 Loss from NO_2→HONO not Supported by SENEX/TROPHONO Data





- Formation of HONO results in conversion of NO_2 to NO without formation of O_3.
- Boundary layer O_3 is reduced ~6ppb and NO_2 is reduced ~100ppt.
- But SENEX observations do not support a large source (pers. com. A. Neumann).
- A gas-phase source of HONO cannot be as large as Suggested by (Li et al, 2014 (Science))

Summary & Conclusions

- Models significantly overestimate observed O_3 in the Southeast U.S.
- We have developed a state-of-the-science model to interpret SEAC^{4}RS aircraft and sonde measurements, as well as satellite observations.
- The NEI mobile NOx inventory is likely overestimated by at least a factor of 2 compared against SEAC^{4}RS data.
- Soil NOx emissions in the midwest are also overestimated by a factor of 2 compared to OMI.
- In order to reconcile SEAC^{4}RS NOx and NOy with model emissions, we must significantly reduce mobile NOx emissions from NEI11.
- With a successful NOx simulation we may be able to model O_3 with minimal bias, and capture the unique pathways of isoprene oxidation in the southeast U.S.
- We will have an improved background O_3 simulation to assist in policy-making.
- A large gas-phase source of HONO is inconsistent with SENEX observations and is not a solution to the modeled O_3 overestimate in the southeast U.S.