O$_3$-NOx-VOC Chemistry in the Southeast U.S. & the Implications of Rapidly Declining NOx Emissions

Katherine Travis
SEAC$^4$RS 4/30/15

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
The Southeast U.S. NOx Emissions Are Rapidly Decreasing

A Modeling Trouble Spot...

In a Region of Rapidly Declining NOx

- 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

- 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$_2$O$_2$, ISOPOOH, ISOPN, HPALDs

OMI NO$_2$
GEOS-Chem Developed to Incorporate the State-of-the-Science Relevant to this Region

- 0.25\textdegree \times 0.3125\textdegree 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:**
  - 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)

- Anthropongenic: 51%
- Soils: 27%
- Lightning: 14%
- Aircraft: 3%
- Biomass Burning: 5%

Total NOx Emission = 0.57 Tg N

Anthropogenic Emissions (NEIv11)

- Mobile: 61%
- Industry: 25%
- EGU: 12%
- Other: 2%

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 \( \text{O}_3 \)

- We reduce the mobile NOx inventory by >50%.

Original NEIv11

<table>
<thead>
<tr>
<th>Category</th>
<th>Original</th>
<th>Reduced</th>
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<tbody>
<tr>
<td>MOBILE</td>
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<td>13%</td>
</tr>
<tr>
<td>INDUSTRY</td>
<td>25%</td>
<td>55%</td>
</tr>
<tr>
<td>EGU</td>
<td>12%</td>
<td>28%</td>
</tr>
<tr>
<td>OTHER</td>
<td>2%</td>
<td>4%</td>
</tr>
</tbody>
</table>

Original NOx: 0-1.5km

Mean Bias = 100ppt

Without scaling by 50%

Pl. T. Ryerson

MODELED - OBSERVED NOx

Mean Bias = <5ppt
We Are Biased Low in Rural Regions Against OMI NO₂

- Midwest NO₂ 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/cm² in rural regions
- OMI NO₂ (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

Ozone and immediate precursors

Unique products of main isoprene oxidation pathways

Altitude, km

SEAC⁴RS Southeast U.S.

- DC8
- GEOS-Chem

O₃, ppbv

HCHO, ppbv

NOₓ, ppbv

ISOPOOH, pptv

ISOPN, pptv

HPALD, pptv

PI. P. Wennberg: ISOPOOH, ISOPN, HPALD;
PI. T. Ryerson: O₃, 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 $NO_2 \rightarrow$ 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.