NO$_X$ emissions, isoprene oxidation pathways, and implications for surface ozone in the Southeast United States

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The Southeast US Is One of the Most Difficult Regions to Model for Surface Ozone

Blame has included isoprene chemistry, isoprene emissions, dry deposition etc.
**SEAC⁴RS** (Aug-Sep 2013) Provided an Unprecedented Dataset to Investigate Air Quality in the Southeast US

- **Data Used for this Study Include:**
  - Thomas Ryerson, NOAA: NOₓ, NO, NO₂, O₃
  - Ron Cohen, Berkeley: NO₂
  - Paul Wennberg, Caltech: isoprene oxidation products
  - Jack Dibb, UNH: HNO₃
  - Sam Hall, NCAR: J-values
GEOS-Chem Incorporates State-of-the-Science Understanding of O₃-NOₓ-VOC Chemistry

- 0.25°x0.3125° resolution over North America.

- **Emissions:**
  - Biogenic from MEGAN (Guenther et al., 2012).
  - See Zhu et al, 2016 (ACP D)
  - Lightning NOₓ according to Murray et al. (2012).
  - Anthropogenic emissions from EPA’s NEI 2011v1.

- **Chemistry:**
  - Chemistry from Mao et al. (2013).
    - With bromine chemistry (Parrella et al., 2012).
    - Improved treatment of low- and high- NOₓ pathways to incorporate recent lab studies.

- **Physical processes:**
  - Faster deposition of isoprene oxidation products (Nguyen et al, 2015).
NO$_x$ and Ozone are Overestimated in the Original GEOS-Chem Simulation

PBL is 60% too high for NO$_x$ and 12ppb too high for ozone.

SEAC$^4$RS PI
Jack Dibb: HNO$_3$, Thomas Ryerson: O$_3$, NO, NO$_2$
Reducing NEI11v1 by 50% Improves Agreement with SEAC$^4$RS NO$_y$ and O$_3$

- Many studies find that NEI mobile NO$_x$ is overestimated –

  - We scale NEI11v1 by 50% by reducing industry and mobile NO$_x$ by 60%.
NOx and O3 Concentrations Below 1.5 km

Spatial Variability Shows No Significant Biases

Mean model bias for ozone is +2 ppb, 9% for NOx

Thomas Ryerson: O3, NO, NO2
Simulation with Scaled $\text{NO}_x$ Successfully Captures Isoprene Oxidation Pathways From SEAC$^4$RS

‘High NOx pathway’

See Fisher et al, 2016 (ACP) for more on ISOPN
Reductions in NO\textsubscript{x} Have a Smaller Impact Due to Spatial Segregation of Emissions

More details in:
Yu, K. et al, ACP (2016)
We Add New Constraints on NO\textsubscript{x} Using Measurements of Deposition

\[
\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3
\]

\[\text{NO}_x = \text{NO} + \text{NO}_2\]

Very soluble
\[\text{H}^+, \text{NO}_3^-\]

"What Goes Up Must Come Down"

Dry deposition of HNO\textsubscript{3}

Wet deposition of NO\textsubscript{3}^-

Measured during Southern Oxidant and Aerosol Study June-July 2013

Measured by the National Atmospheric Deposition Program
Wet Deposition Supports National Scaling of NEI11

US Nitrate Wet Deposition
August-September 2013

Southeast US: Bias = 8%, r=0.71
CONUS: Bias =7%, r = 0.76
Ozone Production Efficiency (OPE) Provides Constraint on Efficiency of Ozone Formation

Without scaling, OPE = 14.7 which means ozone would be produced less efficiently than observed.
How well can we constrain US NO\textsubscript{x} emissions with OMI NO\textsubscript{2}?

OMI NO\textsubscript{2} (BEHR)

OMI NO\textsubscript{2} (NASA v2.1)

GEOS-Chem with reduced NO\textsubscript{x} emissions
-18% vs. BEHR
-11% vs. NASA

Aug-Sep 2013 data with GEOS-Chem shape factors

Low bias in GEOS-Chem is due to upper troposphere, not surface emissions

With original NEI emissions, Bias = +26-31%
Free/upper troposphere makes major contribution to OMI NO\textsubscript{2} tropospheric column in summer

- GEOS-Chem low bias in upper troposphere is caused by NO/NO\textsubscript{2} chemistry; insufficient convection of HO\textsubscript{x} precursors HCHO and CH\textsubscript{3}OOH?

\[ \text{NO} \underset{\text{O}_3, \text{HO}_2, \text{RO}_2}{\overset{h\nu}{\longrightarrow}} \text{NO}_2 \]

- Current OMI retrievals may have large AMF errors

**Mean SEAC\textsuperscript{4}RS NO\textsubscript{2} profiles**

- 25-40% of column

**Mean NO/NO\textsubscript{2} ratio**

- 65-80% of column

**Observed (NOAA + UC Berkeley)**

- GEOS-Chem
- NO-NO\textsubscript{2}-O\textsubscript{3} Equilibrium (PSS)
- Double HO\textsubscript{2} and RO\textsubscript{2} Above 8km

**SEAC\textsuperscript{4}RS PI**
- Thomas Ryerson: NO\textsubscript{2}
- Ron Cohen: NO\textsubscript{2}
Discrepancy Remains Between Surface & Upper PBL $O_3$

- Remaining uncertainties are potential $O_3$ sinks and boundary layer mixing.
Conclusions

• NEI11v1 for NO\textsubscript{x} is biased high across the US by as much as a factor of 2.
• Emissions from industrial and mobile sources must be 30-60\% lower than NEI values.
• Evidence for this comes from (1) SEAC\textsuperscript{4}RS observations of NO\textsubscript{x} and its oxidation products, (2) NADP network observations of nitrate wet deposition fluxes.
• The OPE in the boundary layer is well reproduced.
• There may be large errors in satellite NO\textsubscript{2} columns due to the presence of upper tropospheric NO\textsubscript{2}. Observations show departure from photochemical steady-state.
• MDA8 surface ozone is still biased against the CASTNET observations by approximately 8ppb.

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Additional Papers from SEAC$^4$RS


- **Model Resolution**: Yu, K. et al.: Sensitivity to grid resolution in the ability of a chemical transport model to simulate observed oxidant chemistry under high-isoprene conditions, *Atmos. Chem. Phys.*, 16, 4369–4378, doi:10.5194/acp-16-4369-2016, 2016