Simple chemistry gone wrong: uncertainty in NO-NO₂ cycling in the upper troposphere and the implications for air quality

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with Daniel Jacob¹, Katie Travis², Tomas Sherwen³, Mat Evans³, Ron Cohen⁴, Josh Laughner⁴, Samuel Hall⁵, Kirk Ullmann⁵, John Crounse⁶, Paul Wennberg⁶, Jeff Peischl⁷, Tom Ryerson⁷, and Ilana Pollack⁸

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SEAC$^4$RS aircraft campaign during August-September 2013 provided detailed observations of O$_3$-NO$_x$-VOC chemistry.

Extensive observations over the Southeast US during summer 2013

GEOS-Chem near real time simulation during SEAC$^4$RS at 0.25°×0.3125° resolution with observations overlaid.
Observations show elevated NO\textsubscript{x} concentrations in the upper troposphere mostly present as NO. Median daytime vertical profiles during SEAC\textsuperscript{4}RS:

- NO\textsubscript{x} measurements: T. Ryerson
- NO\textsubscript{2} measurements: R. Cohen
- O\textsubscript{3} measurements: T. Ryerson
- \(J_{NO2}\) measurements: S. Hall

GEOS-Chem overestimates the NO/NO\textsubscript{2} ratio by over a factor of 2 in the upper troposphere.
Conversion of NO to NO\textsubscript{2} balances only half of NO\textsubscript{2} photolysis.

NO-NO\textsubscript{2} cycling in the upper troposphere during SEAC\textsuperscript{4}RS

\[ [O_3], J_{NO_2} \text{ from observations, radical concentrations from GEOS-Chem along the flight tracks} \]

\[ \text{Rate (10}^6 \text{ molecules cm}^{-3} \text{ s}^{-1}) \]

\[ \text{NO} \rightarrow \text{NO}_2 \]

\[ \text{NO}_2 \rightarrow \text{NO} \]
Underestimate of NO/NO₂ ratio cannot be explained by errors in GEOS-Chem radical concentrations.

Underestimate in peroxy and BrO radicals would have to be factor of 5 and 21 to close NO-NO₂ budget.
Uncertainties in NO$_2$ photolysis and the NO+O$_3$ reaction rate are major sources of errors in tropospheric chemistry models.

**NO$_2$ spectroscopic data have 20% uncertainty**

NO$_2$ photolysis frequency:

$$J_{NO_2} = \int F(\lambda)\sigma(\lambda)\phi(\lambda)\,d\lambda$$

- $F$ = actinic flux
- $\sigma$ = absorption cross section
- $\phi$ = quantum yield

$\pm 20\%$ at all temperatures (JPL compilation)

**NO+O$_3$ reaction rate may be biased low at cold temperatures**

NO+O$_3$ Arrhenius rate constant:

$$k = A \exp\left[-\frac{E}{RT}\right]$$

- $A$ = pre-exponential factor
- $E$ = activation energy
- $R$ = ideal gas constant
- $T$ = temperature

Atkinson et al. (2004)
Increasing NO+O₃ reaction rate combined with decreasing $J_{NO2}$ closes NO-NO₂ budget.

Decreasing activation energy of NO+O₃ rate ($k_1$) at low temperatures.

Decreasing $J_{NO2}$ to 1σ uncertainty would affect model and measurements.

Observed
Standard Model
$J_{NO2}$ -20%, 1.4$k_1$
$J_{NO2}$ -20%, 1.9$k_1$
Correction of the NO/NO$_2$ ratio results in large decreases in O$_3$ throughout the troposphere in the Southeast US

- Surface ozone decreases by 5 ppb due to reduction in $J_{NO2}$, improving agreement with observations
- Free troposphere O$_3$ underestimate may be due to insufficient transport from the stratosphere
- Globally, annual mean tropospheric OH decreases by 20%
Satellite measurements of NO$_2$ are particularly sensitive to abundance in the upper troposphere.

OMI observes backscattered solar radiation.

NO$_2$ tropospheric column density observed from NASA.

Travis et al. (2016)
Model underestimates of upper tropospheric NO$_2$ cause positive bias in tropospheric NO$_2$ column retrievals from satellites.

- NO$_2$ columns are 14-23% lower than previously thought;
- The upper troposphere contributes 46% to total column;
- Implies that NO$_x$ emissions are 30-50% lower than NEI.
Conclusions and implications

• An observationally constrained analysis of the NO/NO\textsubscript{2} ratio in the upper troposphere in the Southeast US suggests underestimates in conversion of NO to NO\textsubscript{2} may be due to biases in low-temperature kinetic (NO+O\textsubscript{3}) and spectroscopic ($J_{NO2}$) laboratory data.

• The simulation of surface ozone is improved through decreased NO\textsubscript{2} photolysis but may require increased transport from the stratosphere to correct ozone in the upper troposphere.

• Tropospheric NO\textsubscript{2} columns inferred from satellite observations over the Southeast US decrease by 14-23%, implying lower NO\textsubscript{x} emissions for a given column amount.

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