Reconciling modeled and observed upper tropospheric NO\textsubscript{2} for the interpretation of satellite measurements

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The Bottom Line

- Observed enhancements of upper tropospheric NO\textsubscript{2} in the Southeast US summertime are not captured by models but must be accounted for in the interpretation of satellite observations.
- We show the low temperature kinetics of the NO + O\textsubscript{3} reaction are responsible for the discrepancy between modeled and observed NO/NO\textsubscript{2} concentration ratios during SEAC\textsuperscript{RS}.
- Improved agreement between modeled and observed tropospheric NO\textsubscript{2} columns will allow us to use satellite observations to monitor surface NO\textsubscript{x} emissions.
- Increasing the NO + O\textsubscript{3} rate constant has implications for global tropospheric chemistry.

NO-NO\textsubscript{2}-O\textsubscript{3} Photochemical Steady State

The abundance of NO\textsubscript{2} relative to NO is determined by the rapid cycling between NO and NO\textsubscript{2} that establishes a daytime photochemical steady state (PSS):

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO} + \text{HO}_2/\text{RO} & \rightarrow \text{NO}_2 + \text{OH}/\text{RO} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O}_3
\end{align*}
\]

Approximate the NO/NO\textsubscript{2} concentration ratio:

\[
\frac{\text{NO}}{[\text{NO}_2]} = \frac{j_{\text{NO}_2}}{k_{\text{O}_3}}
\]

Travis et al. (2016) (right) showed a large discrepancy between observations during SEAC\textsuperscript{RS} and PSS in the upper troposphere, possibly due to lack of conversion of NO to NO\textsubscript{2} by HO\textsubscript{2}/RO\textsubscript{2}.

Contribution of deep convection and HO\textsubscript{x} chemistry

The HO\textsubscript{x} underestimate in GEOS-Chem during SEAC\textsuperscript{RS} is largely driven by three flights targeting deep convection the model doesn’t capture (median vertical profiles of HO\textsubscript{x} precursors above). However, the model bias in the NO/NO\textsubscript{2} ratio in the upper troposphere remains (right panel). The doubled HO\textsubscript{x} needed to reconcile the NO/NO\textsubscript{2} ratio is incompatible with measured constraints from SEAC\textsuperscript{RS}.

Implications for interpreting satellite NO\textsubscript{2} columns

Observations of OMI NO\textsubscript{2} columns recalculated using the GEOS-Chem shape factor (top panel) compared to the standard model (middle panel) and the model with the updated rate constant (bottom panel) for JJA 2013. Total NO\textsubscript{2} columns for the Southeast US domain are given inset. The standard model underestimates NO\textsubscript{2} columns by -13.3% due to the underestimate in the upper troposphere while the updated model reduces the model bias to -1%.

Now that we have constrained NO\textsubscript{x} in the upper troposphere, we can use satellite observations to diagnose uncertainties in surface NO\textsubscript{x} emissions including uncertainties in soil NO\textsubscript{x} and the NEI anthropogenic emission inventory.

Global implications for tropospheric O\textsubscript{3} and OH

Newcombe and Evans (2017) recently showed that the uncertainty in rate constants in GEOS-Chem represented a significant source of uncertainty in common climate metrics.

Above, we show the impact of increasing the NO + O\textsubscript{3} rate constant (updated model, dashed lines) on monthly mean global OH (black) and tropospheric O\textsubscript{3} (blue) for 2013 compared to the standard model (solid lines). We find with some month to month variability, the updated model has on average, 6% less OH and 5% less tropospheric O\textsubscript{3} than the standard model, demonstrating an important effect on global tropospheric chemistry.