Observe NO/NO₂ ratios in the upper troposphere imply errors in NO-NO₂-O₃ cycling kinetics or an unaccounted NOₓ reservoir
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The Bottom Line
- Large model overestimates of NO/NO₂ concentration ratios in the upper troposphere imply errors in NO-NO₂-O₃ cycling kinetics or the presence of an unaccounted labile NOₓ reservoir
- The presence of an unaccounted labile NOₓ reservoir would affect the NOₓ lifetime in the upper troposphere and would suggest unrecognized, likely organic, chemistry
- Possible error in NO-NO₂-O₃ cycling kinetics would have large implications for global simulations of tropospheric ozone and for satellite retrievals of tropospheric NO₂

Models overestimate NO/NO₂ concentration ratios in the upper troposphere

The SEAC⁴RS aircraft campaign during August-September 2013 had extensive coverage over the Southeast US (left) and in the upper troposphere (blue). NO₂ measurements in the upper troposphere are prone to positive interferences from inlet decomposition of thermally unstable NOₓ reservoirs. The TD-LIF NO₃ instrument deployed during SEAC⁴RS was specifically designed to minimize and correct for known measurement interferences.

Observations of NO show a “C-shaped” profile (bottom left) reflecting influences from fuel combustion in the boundary layer and lightning in the upper troposphere. The mean observed daytime NO/NO₂ ratios in SEAC⁴RS were approximately half of the values in the GEOS-Chem chemical transport model sampled along the flight tracks (bottom middle). The NO/NO₂ ratio in the model increases rapidly with altitude because of the strong temperature dependence of the NO+O₃ reaction, but in the observations this increase is much less.

NO-NO₂-O₃ cycling in the upper troposphere during SEAC⁴RS

NO and NO₂ cycle according to the reactions shown in the bar chart below. The conversion of NO to NO₂ (left bar) balances only half of the NO₂ photolysis rate (right bar), such that a model using standard kinetics would overestimate the NO/NO₂ ratio observed. Insufficient conversion of NO to NO₂ by peroxo or halogen radicals would be incompatible with measurements of H₂O₂ and model halogen concentrations shown below.

Possible errors in NO-NO₂-O₃ cycling kinetics

The conversion of NO to NO₂ (+OH) is highly temperature- and concentration-dependent and would be affected by errors in the kinetic data used to compute that equilibrium. The left figure shows the temperature-dependent rate constant for the NO+O₃ reaction, k₁, which has large uncertainties at low temperatures of the upper troposphere. At right, the measured and modeled values of the NO₂ photolysis rate constant (J(NO₂)) agree well but rely on the same spectroscopic data such that both would be similarly affected by errors in that data (dotted lines).

Implications for interpreting satellite retrievals of tropospheric NO₂

- Interpretation of tropospheric NO₂ measured by satellites requires information about the vertical distribution of NO₂ from models.
- The NASA operational retrieval (top) uses the GMI model which greatly underestimates NO₂ concentrations in the upper troposphere.
- Compared to tropospheric NO₂ columns computed using the observed profile from SEAC⁴RS (bottom), the NASA retrieval may be biased high by 30%.

Reconciling the NO/NO₂ ratio

The purple lines show the effects in GEOS-Chem of of decreasing J(NO₂) by 20%, and increasing k₁ by a factor 1.4 in the upper troposphere. The resulting NO/NO₂ ratio in the upper troposphere decreases by 40% and the variance in the modeled NO/NO₂ ratio decreases by half (left). One could match the observations if there were in addition a 15 ppt positive bias in the NO₂ measurement due to an unaccounted labile NOₓ reservoir.