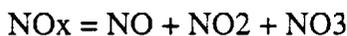


Modeling Nitrogen Oxides in the Lower Stratosphere

Randy Kawa, December 26, 2000

This talk will focus on the status of current understanding (not a historical review) as regards modeling nitrogen oxides (NO_y) in the lower stratosphere (LS). The presentation will be organized around three major areas of process understanding: 1) NO_y sources, sinks, and transport to the LS, 2) NO_y species partitioning, and 3) polar multiphase processes. In each area, process topics will be identified with an estimate of the degree of confidence associated with their representation in numerical models. Several exotic and/or speculative processes will also be discussed. Those topics associated with low confidence or knowledge gaps, weighted by their prospective importance in stratospheric chemical modeling, will be collected into recommendations for further study. Suggested approaches to further study will be presented for discussion. Further details follow.

Definition of nitrogen oxides covered here:



Discussion of NO_y in the LS must start with the primary NO_y source and loss regions in the tropical upper stratosphere. The predominant portion of NO_y in the stratosphere is produced in the region around 30-40 km and transported to the LS region of interest. The production occurs through the reaction $\text{N}_2\text{O} + \text{O}(\text{D}) \rightarrow 2\text{NO}$. Net production is limited by in situ loss through $\text{NO} + h\nu \rightarrow \text{N} + \text{O}$ followed by $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$, which occurs at and above the main production region. This balance creates a maximum in the NO_y mixing ratio of about 18 ppbv near 40 km. NO_y produced in this region is transported poleward and downward by the mean circulation. These processes are very important to correctly modeling NO_y throughout the stratosphere.

Recent modeling work has shown that most current global models do not simulate NO_y distributions very accurately in the stratosphere and that large variation exists among models even when N₂O is constrained. Discrepancies as large as 50-100% are found, indicating that our understanding of the net stratospheric NO_y production is limited. Transport problems may also be contributing.

Other known, but lesser, sources of NO_y should be considered in the lower stratosphere. These include NO_x production by lightning in the upper troposphere (UT) and NO_x emission from aircraft. Transport between the LS and UT is paramount in determining the relative impact of both of these sources as well as the possible importance of surface sources to the LS. Model

transport across the tropopause has limited confidence. In addition, limited confidence is associated with the magnitude of the lightning source strength.

PAN may be a significant component of NO_y in the LS, but the focus of that discussion will be in tropospheric modeling. Most models of stratospheric chemistry do not include PAN or give it little attention and validation. Since PAN is important to O₃ production and the potential impact of aircraft emissions, the question may be raised as to whether it deserves more emphasis in LS modeling.

The primary aspects of modeling NO_y partitioning globally are generally associated with relatively moderate to high confidence, although nagging problems persist in several processes. NO_x (NO/NO₂, NO₂/NO₃) steady state modeling agrees with observations to well within experimental uncertainty. Similar confidence is associated with constrained modeling of NO_x/N₂O₅ and NO₂/ClONO₂ in the LS. NO_x/NO_y, or NO₂/HNO₃, is fairly well simulated under conditions of high-to-moderate aerosol loading provided multiphase hydrolysis reactions (N₂O₅ + H₂O, BrONO₂ + H₂O) are included. This can be seen in post-Pinatubo NO_y simulations. More recent changes to gas-phase NO₂/HNO₃ partitioning rates seem to resolve most of the discrepancy observed for conditions of low aerosol influence. Discrepancies on the order of 10-20% remain, however, in the LS and larger errors are found in the middle stratosphere, suggesting that our understanding is still somewhat limited. A final process, partitioning of NO_x/HO₂NO₂, apparently represents a gap in our knowledge, but the overall importance of this gap has yet to be determined.

Representation of polar processes in models introduces several areas of limited confidence and knowledge gaps. These processes are important because NO_y limits winter polar O₃ loss from chlorine catalysis through a variety of mechanisms. HNO₃-containing particles play a significant, possibly major, role in heterogeneous chlorine activation. We have limited confidence in modeling the various potential polar stratospheric cloud (PSC) compositions (STS, NAT, NAD) and the dependence of their formation on temperature, water, and HNO₃. The overall rates of reactions (ClONO₂ + HCl, ClONO₂ + H₂O) do not appear to depend strongly on composition so these processes may not be a major difficulty in large-scale modeling, however, they are so important to predicting the future of polar O₃, vis a vis chlorine, that they deserve emphasis. An even larger gap in our understanding is modeling the PSC composition and microphysical characteristics that control denitrification and vertical redistribution through sedimentation. These processes are critical for limiting polar ozone loss due to chlorine and may be important to the LS NO_y budget globally. Currently we have only a very limited ability to simulate these processes.

Several other processes have been identified as potentially important to modeling NO_y in the LS for which we have limited confidence, but also a limited expectation of their importance. Such "exotic" processes include a source from energetic particle deposition, source reactions of excited molecular species, NO₂ reduction on soot or metal particles, and conversion of N₂O₅ to HNO₃ in the apparent absence of sulfate particles.

Based on the above compilation, the proposed top priority recommendations for further study are the need to better understand the source/loss NO_y photochemistry in the stratosphere and the role of HNO₃ in polar multiphase processes. Second priority recommendations include NO_y processes near the tropopause and LS NO_x/NO_y partitioning. Potential approaches include lab kinetics studies, model sensitivity tests, and field measurements. These recommendations are posed for discussion; they are subject to change at the workshop.