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 (NOy) in the lower stratosphere (LS). The presentation will be organized around three major areas of process understanding: 1) NOy sources, sinks, and transport to the LS, 2) NOy 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:
NOy = HNO3 + NOx + ClONO2 + N2O5 + HO2NO2 + BrONO2 + PAN
NOx = NO + NO2 + NO3

Discussion of NOy in the LS must start with the primary NOy source and loss regions in the tropical upper stratosphere. The predominant portion of NOy 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 N2O + O1D → 2NO. Net production is limited by in situ loss through NO + hv → N + O followed by N + NO → N2 + O, which occurs at and above the main production region. This balance creates a maximum in the NOy mixing ratio of about 18 ppbv near 40 km. NOy produced in this region is transported poleward and downward by the mean circulation. These processes are very important to correctly modeling NOy throughout the stratosphere.

Recent modeling work has shown that most current global models do not simulate NOy 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 NOy production is limited. Transport problems may also be contributing.

Other known, but lesser, sources of NOy should be considered in the lower stratosphere. These include NOx production by lightning in the upper troposphere (UT) and NOx 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 NOy 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 NOy partitioning globally are generally associated with relatively moderate to high confidence, although nagging problems persist in several processes. NOx (NO/NO2, NO2/NO3) steady state modeling agrees with observations to well within experimental uncertainty. Similar confidence is associated with constrained modeling of NOx/N2O5 and NO2/ClONO2 in the LS. NOx/NOy, 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 NOy 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 NOx/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 NOy 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 NOy 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 NOy 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 NOy photochemistry in the stratosphere and the role of HNO3 in polar multiphase processes. Second priority recommendations include NOy processes near the tropopause and LS NOx/NOy 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.