Modeling of the Partitioning of Reactive Odd Nitrogen in the Lower Stratosphere Using Aircraft Measurements of NO_y, NO, and Other Trace Species

Final Report

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Basic

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Objective: The objective of this research has been to gain a more thorough understanding of the atmospheric processes which control the partitioning of species within the reactive nitrogen (NO_y) reservoir in the lower stratosphere. This understanding is crucial to predicting ozone loss in the stratosphere. NO_y is defined as $NO + NO_2 + HNO_3 + N_2O_5 + ClONO_2 + HO_2NO_2 + NO_3 +$ particulate nitrate. The research focuses on deriving the partitioning among these species using the combined set of measurements from the NASA ER-2 aircraft during recent missions designed to study stratospheric ozone depletion.

Progress and Results: The partitioning of gaseous species in the NO_y and Cl_y (reactive chlorine) reservoirs has been derived in a consistent manner for winter high latitudes in both hemispheres. The latitude distributions of the relative partitionings outside the Arctic vortex region show the least difference from 2-D model distributions calculated with only gas-phase reactions. The distributions inside the Arctic and Antarctic vortices are highly perturbed relative to those outside the Arctic, indicative of extensive heterogeneous reaction presumably on the surfaces of polar stratospheric cloud (PSC) particles. The partitioning in the Antarctic within about 10° outside of the nominal chemically perturbed region also shows clear evidence of heterogeneous reactions but either less intensive or recovering relative to the inside. These findings are published in *Kawa et al.* [1992*a*] (attached). The effect of PSCs on stratospheric chemistry is also discussed in *Brune et al.* [1991] and *Tuck et al.* [1992]. Co-authorship of these papers has been accomplished under this grant.

The particulate phase of NO_y has been studied using in situ aircraft measurements taken in PSCs. The findings confirm that PSC particles contain NO_y but are unable to confirm that the composition is in the stoichiometric 3:1 ratio of nitric acid trihydrate. Exact formulations for the composition and mechanisms of formation of PSCs require further study. These findings are reported in *Kawa et al.* [1992*b*] (attached) and *Dye et al.* [1992]. The grant has also partially supported publication of a review article on PSCs [*Fahey and Kawa*, 1991].

This research has naturally led to study of large scale distributions of NO_y and its relationship to other long-lived species in the lower stratosphere. Variability of NO_y is found to be highly correlated with other long lived species, including ozone under some conditions. Such correlations provide a useful framework for analysis of the performance of large scale models in comparison to measurements. Although 2-D global models appear to perform reasonably well on correlations throughout much of the stratosphere, the comparisons indicate that the models need improvement at high latitudes and near the tropopause. These findings are reported in *Murphy et al.* [1992] and will become part of a NASA report on comparison of models and measurements [*Kawa et al.*, in preparation].

Study of the effects of PSCs on NO_y partitioning has led to analysis of the possible effects of heterogeneous reactions on stratospheric sulfate particles. The use of a new instrument to simultaneously measure both NO and NO_y, along with the usual suite of ER-2 measurements, enables the ratio $(NO+NO_2)/NO_y$ to be derived from the measurements with a high degree of confidence. This ratio should be a sensitive indicator of heterogeneous conversion of N_2O_5 to HNO_3 as expected from laboratory measurements. A flight data-based model of NO_x/NO_y has been derived for comparison to the measured values. Comparison of the model with more general, fully interactive chemistry calculations shows that the flight data model adequately captures the essence of the chemical processes for conditions of the ER-2 flights. Preliminary analysis of data

from the recently completed AASE-II mission indicates that models using only gas-phase reactions are inadequate to explain the measurements and that the comparison is greatly improved by inclusion of the N_2O_5 reaction on background amounts of sulfate aerosol. The comparisons are not fully consistent, however, with those in the presence of particle surface area enhanced by eruption of Mt. Pinatubo. Preliminary results are the subject of conference presentations.

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