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ANNUAL PERFORMANCE REPORT FOR NAGW-413

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Chemistry and Transport in a Multi-Dimensional Model

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PROGRESS REPORT FOR NAGW 413

The focus of our research program is the achievement of a quantitative understanding of the spatial distribution and temporal variation of chemical species in the terrestrial middle atmosphere, with emphasis on ozone. Although not directed at assessments of anthropogenic impacts, our activities contribute to a refinement of model descriptions of chemical and dynamical processes that are needed for assessment tasks. A unique feature of our research effort is a close interaction with the chemical kinetics group at JPL and the field measurement groups at JPL.

The principal tools used in our investigations are 1-D and 2-D photochemical models. The advective component of the meridional transport in these models is approximated by the diabatic circulation, which is derived diagnostically from the net radiative heating rates. We are developing accurate radiative transfer algorithms to find the net heating rates and the diabatic circulation for use in the 2-D model.

I. RESEARCH ACCOMPLISHMENTS IN 1993

A. Summary

1. A Study of the Evolution of Antarctic Polar Ozone from TOMS Data

New results on the evolution of Antarctic polar ozone have come from the analysis of TOMS ozone data by using the area-mapping method, which is designed to filter out synoptic perturbations of the Antarctic polar vortex such as distortion or displacement away from the pole. First, we found that the area of a given ozone column abundance changes with time. The morphology of the ozone hole differs from year to year, but reveals a general trend. The area of the ozone hole expands equatorially at a rate of approximately 0.33 degree per year. At the same time, the transition layer between 250 DU and 300 DU shrinks at a rate of approximate 0.10 degree per year. This proves that the large gradient of ozone between the chemically perturbed region and the dynamically perturbed region effectively hinders the intrusion of ozone-rich air into the ozone hole. Second, by analysis of the general trends of area variation in early Austral spring, we found that ozone begins to decrease in early August. Third, we found that the trend in ozone abundances is continuously interrupted by waves probably generated in the troposphere with a period of around 10 to 20 days.

2. The Heterogeneous Hydrolysis of N_2O_5 on Sulfate Aerosols

Simultaneous *in situ* measurements of stratospheric NO_2 and HNO_3 show, at 24 km, the NO_2 and HNO_3 are 70% lower, and 50% higher, respectively than the results from a purely gas-phase photochemical model. The measured NO/HNO_3 ratio is 5 times smaller than the model result. When the heterogeneous hydrolysis of N_2O_5 of sulfate aerosols was added to the model, calculated values come into good agreement with the observations. At 34 km, where minimal aerosol was thought to be present, the results from the purely gas-

phase chemistry were in good agreement with measurements.

3. A 2-D Model for Stratospheric Ozone

We have completed a 2-D model for stratospheric O₃ with the "standard" gas phase chemistry. The model includes the chemistry of the catalytic cycles due to HO_x, NO_x, and ClO_x. All major species are fixed at the ground at concentrations given by observations of 1985. To first order, the results of our model for O₃ agree quite well with satellite observations, and other 2-D models such as the AER model.

B. Conference Presentations

Y. Jiang, Y.L. Yung, and R.W. Zurek. A Study of the Evolution of Antarctic Polar Ozone from TOMS Data. 1993 Fall AGU Meeting.

C. Publications (supported wholly or in part by this grant)

J. Eluszkiewicz and M. Allen. A Global Analysis of the Ozone Deficit in the Upper Stratosphere and the Lower Mesosphere. *J. Geophys. Res.*, **98**, 1069-1082 (1993).

C.R. Webster, R.D. May, M. Allen, L. Jaeglé, and M.P. McCormick. Balloon Profiles of Stratospheric NO₂ and HNO₃ for Testing the Heterogeneous Hydrolysis of N₂O₅ on Sulfate Aerosols. Submitted to *Geophys. Res. Lett.*

Y. Jiang, Y.L. Yung, and R. Zurek. Decadal Evolution of Antarctic Polar Ozone from TOMS Data. In preparation.

S.L. Nikolaisen, S.P. Sander, L. Jaeglé, J. Lyons, and Y.L. Yung. Photolysis of Chlorine Nitrate and Implications for Atmospheric Chemistry. In preparation.

II. PROPOSED WORK FOR 1994

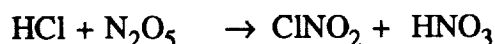
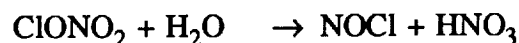
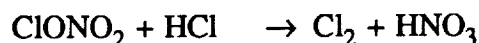
A. The Hydrological Cycle of the Stratosphere

Water vapor is an extremely important species in the middle atmosphere for at least three reasons. It is important for the radiative budget of the atmosphere because of its strong absorption bands in the infrared. It is important, in condensed phase, as a catalytic surface for heterogeneous reactions involving NO_x and halogen species. And most importantly, perhaps, H₂O is a precursor for the HO_x radicals in the upper atmosphere. Until recently we only had data on the principal isotope of H₂O. The ATMOS experiment has obtained vertical profiles of isotopes of H₂O: HDO, H₂¹⁸O, and H₂¹⁷O. The observations suggest that the mixing ratio increases with altitude away from the tropopause. This can be explained as a result of the injection of H₂O into the stratosphere through a cold tropopause where the deuterated species is preferentially depleted. However, since the injection of CH₄ into the

stratosphere is unaffected by condensation, the D/H ratio in stratospheric CH₄ is close to the general tropospheric D/H ratio. As CH₄ is oxidized with increasing altitude, the D/H ratio in H₂O should again rise to the tropospheric value. By modeling the distribution of HDO we can obtain further constraints on the relative contribution of CH₄ and H₂O to the HO_x budget in the upper atmosphere. This is especially important in view of the rise of CH₄ in the atmosphere. We will initially use the transport coefficients deduced by K.K. Tung. Sensitivity studies will be performed by varying the transport coefficients. The results of our 2-D modeling will be compared with LIMS, ATMOS, and UARS observations. The modeling of H₂¹⁸O in the stratosphere is more complicated and will be described in the next task.

B. The Secular Trend in Antarctic Ozone Levels

To understand polar ozone and the secular trend in ozone abundances, we will expand our chemistry package so that the key heterogeneous chemistry can be taken into account. These include reactions such as



Note that ClONO₂ is crucial for stratospheric chemistry. A recent revision in the pressure dependence of the quantum yield of ClONO₂ photolysis (Sander *et al.*, 1993) will be incorporated. Since all these reactions occur on the surface of ice particles, we have to first create a reliable scheme for predicting the ice surface area from the NHC temperature data. This scheme may be checked for its ability for generating free ClO radicals by comparing against the UARS MLS ClO data. We will then check the predicted O₃ loss in our 2-D model for this period. The O₃ results will be compared with UARS data.

C. Cl_y Partitioning in the Non-polar Stratosphere

Current photochemical models reproduce the observations for partitioning among Cl_y species only qualitatively at best. There are three "equilibrium" situations in the stratosphere. In the upper stratosphere, the primary Cl_y species are ClO and HCl. In the lower stratosphere, the individual Cl_y species abundance reflect the partitioning (1) between the short-lived reservoir ClNO₃ and the long-lived reservoir HCl and (2) between reactive ClO and the reservoir ClNO₃. Current calculations for the ClO/HCl ratio in the upper stratosphere exceed observed values, partly contributing to the model/measurement "O₃ deficit." We shall examine the possibility that the inaccurate model simulation of ClO/HCl is the result of 1σ errors in the recommended rate coefficients rather than a missing reaction. For this work the JPL balloon measurements of Stacknik provide a good test. In the lower stratosphere, no calculation reported to date has been constructed to properly test the

ClNO_3/HCl partitioning. We will seek to accomplish this and compare results with the ATMOS measurements. Current model results for the ClO/ClNO_3 appear to agree with observations, but we reserve judgement until the other two issues are resolved.