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The Temporal and Spatial Behavior of Trace Gases: Early Detection of Stratospheric Changes

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The concentrations of several stratospheric and tropospheric trace species are expected to show an upward trend in the next decade or so. These include CO2 (0.5%/yr), CH4 (1-2%/yr), N2O (0.25%/yr), CO (2-4%/yr), and stratospheric total chlorine, ClY (~ 4%/yr). Continued monitoring of the above species is needed for early detection of stratospheric changes. The possible effects on stratospheric ozone of the above trace gases' trends are of particular interest. Although all the above species will affect stratospheric O3 on long time scales, the detectable effect over the next decade or two may be those associated with the chlorine species. We will discuss the future trends of O3, chlorine species (HCl, ClO), HF, and C2H6 (a tracer for Cl in the lower stratosphere). We will also discuss the possible effects on O3 and other species of speculative chemistries and dynamics and suggest observational strategies by which new theories can be tested.

Ozone

The largest percent depletion of local ozone density in the near future are predicted to occur near 40 km. The calculated change in ozone at 40 km in the near future is more sensitive to trends in ClY than those of CH4, CO2, or N2O. Continued monitoring of O3 in this region appears to provide the best possibility for early direct detection of local O3 trends. A meaningful analysis of these measurements also necessitates simultaneous observations of temperature, solar ultraviolet (UV) and chlorine species. Trend analysis of O3 data between 40 and 50 km requires, however, the detrending of other effects affecting the ozone abundance. These effects include variations of 3 to 10 percent due to solar UV changes over an eleven-year solar cycle. Recent studies also indicate possible impact of sodium species on chlorine partitioning, inducing variation in O3

as large as 10-15 percent near 50 km.

The hypothesized photochemical effects on O3 in the lower stratosphere (~ 20 km) could be detected in the stable region of the Antarctic polar vortex during early spring. It is, however, important to implement measurement strategies aimed at distinguishing photochemical effects from radiative-dynamical effects. The photochemical effect seems to require the existence of relatively high abundance of ClO of about 1 ppb at around 20 km during the early spring. Observation of the diurnal variation of ClO in the Antarctic region should shed additional light on the mechanisms controlling ClO and the behavior of reservoir species including OClO, ClNO3, and HOCl. The testing of the proposed radiative-dynamical mechanism involving the upward intrusion of air with low O3 content from the base of the polar vortex would require the simultaneous measurements of the behavior of other long-lived species, including aerosol, during the early spring period.

HCl

Models predict an increase of 3 to 4 percent per year in the column density of HCl above the tropopause. The above estimate depends on the assumed abundance of total chlorine and on the amount of tropospheric HCl. Continued ground-based measurements of total column HCl, tropospheric HCl, stratospheric HCl, and total chlorine are needed.

The expected rate of increase in the total column density of HCl could appreciably slow down if alternate heterogeneous chemical mechanisms such as ClNO3 + HCl --> Cl2 + HNO3 and ClNO3 + H2O --> HOCl + HNO3 were effective in converting various chlorine reservoirs into the more active form of chlorine. These processes, if effective, could lead to nonlinear response of O3 to stratospheric chlorine perturbations.

C2H6

The abundance of ethane above 20 km is very sensitive to the concentration of chlorine. We predict a decrease in the C2H6 concentration of 30 percent at 20 km and a factor of 2 at 24 km between 1985 and 2000, assuming a constant CFC emission rate

after 1980. Measurements of C_2H_6 in this region could be used as an early indication of anomalous increases in Cl and ClO.

HF

Models predict increases of approximately 10 percent per year, in good agreement with observation. Continued monitoring of HF will serve as a check on the expected stratospheric input of fluorocarbons ($CFCl_3$, CF_2Cl_2) versus that of chlorocarbons (CCl_4, CH_3Cl, CH_3CCl_3).