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Changing Composition of the Global Stratosphere

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The current understanding of stratospheric chemistry is reviewed with particular attention to the influence of human activity. Models are in good agreement with measurements for a variety of species in the mid-latitude stratosphere, with the possible exception of ozone (O_3) at high altitude. Rates calculated for loss of O_3 exceed rates for production by about 40 percent at 40 kilometers, indicating a possible but as yet unidentified source of high-altitude O_3. The rapid loss of O_3 beginning in the mid-1970s at low altitudes over Antarctica in the spring is due primarily to catalytic cycles involving halogen radicals. Reactions on surfaces of polar stratospheric clouds play an important role in regulating the abundance of these radicals. Similar effects could occur in northern polar regions and in cold regions of the tropics. It is argued that the Antarctic phenomenon is likely to persist: prompt drastic reduction in the emission of industrial halocarbons is required if the damage to stratospheric O_3 is to be reversed.

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OZONE IS FORMED IN THE STRATOSPHERE BY PHOTOLYSIS of O_2 to atomic oxygen (O),

$$h\nu + O_2 \rightarrow O + O \qquad (1)$$

followed by

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

Its chemistry can be described approximately by reactions 1 and 2 supplemented by

$$h\nu + O_3 \rightarrow O + O_2 \qquad (3)$$

and

$$O + O_3 \rightarrow O_2 + O_2 \qquad (4)$$

Interchange between O_3 and O by reactions 2 and 3 is rapid. It is convenient to consider O_3 plus O as a family, that is, odd oxygen. Reaction 1 provides the source of odd oxygen, the only important source identified to date for the stratosphere. Reaction 4 represents the sink. Reactions 2 and 3 serve to regulate the relative abundances of O_3 and O. Odd oxygen can be removed also by reactions catalyzed by trace quantities of hydrogen (H), hydroxyl radical (OH), and hydrogen superoxide radical (HO_2) (*1*). The dependence of the rate for reaction 2 on the density of the third body, M, ensures

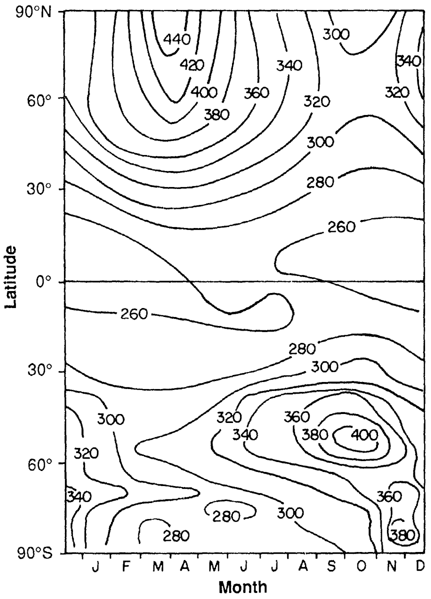

Fig. 1. The global distribution of O_3. The column density of O_3, in Dobson Units (1 DU = 2.7×10^{16} molecules per square centimeter), as a function of latitude and time. Data are from the ground-based Dobson network for years prior to 1974. From Dütsch (*9*).

that the density of O_3 should be significantly larger than that of O at all altitudes below about 70 km.

Much of recent stratospheric research has been concerned with elucidation of additional paths for removal of odd oxygen. Crutzen (*2*) and Johnston (*3*), concerned with possible effects of nitric oxide (NO) released in exhausts of high-flying supersonic aircraft, drew attention to the role of the catalytic sequence involving nitrogen dioxide (NO_2)

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + O &\rightarrow NO + O_2 \end{aligned} \tag{5}$$

equivalent to reaction 4. Reaction 4 can be catalyzed also by chlorine (*4*) and bromine (*5*) radicals (Cl and Br), through

$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O &\rightarrow Cl + O_2 \end{aligned} \tag{6}$$

and

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ BrO + O &\rightarrow Br + O_2 \end{aligned} \tag{7}$$

where ClO is chlorine oxide and BrO is bromine oxide. Since 1972, research in stratospheric chemistry has been directed toward identifying the sources of nitrogen and halogen radicals and understanding the complex suite of reactions that regulate the abundances of the key radicals involved in reactions 5 through 7.

Nitrogen radicals are introduced into the stratosphere by oxidation of microbially produced nitrous oxide (N_2O) through

$$O(^1D) + N_2O \rightarrow NO + NO \tag{8}$$

and by reactions triggered by absorption of cosmic rays (*6*) and energetic solar protons (*7*). The metastable $O(^1D)$ is formed by photolysis of O_3. Decomposition of natural and anthropogenic halocarbons provides the dominant source of chlorine and bromine. The seminal study by Molina and Rowland (*8*) drew attention to the importance of industrial chlorocarbons, notably CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2), as a source of chlorine radicals. Their hypothesis, now largely confirmed, has provided the focus for much of stratospheric research over the past decade, resulting in 1987 in the landmark Montreal Protocol on Substances that Deplete the Ozone Layer. The Montreal Protocol, ratified recently by more than 40 nations, provides a standard for responsible global environmental regulation, a tribute to the ability of industry and governments to act in the face of carefully marshalled scientific argument.

Atmospheric motions play a critical role in determining the global distribution of O_3, as shown in Fig. 1. Largest column abundances of O_3 are observed at high northern latitudes in spring where chemical production is relatively inefficient. This is not to say that chemistry is unimportant. Chemistry should determine the abundance of O_3 in a region covering the higher altitudes, extending down to about 25 km at the equator and sloping up towards the poles. Bordering this region at lower altitudes we expect a zone where both chemistry and motions should be important; leakage of O_3 from this intermediate region should determine the quantity of O_3 available for redistribution by transport at lower altitudes and O_3 should behave as a quasi-conservative tracer of the motion field. This picture persisted up to about 4 years ago: it is called into question, however, by the large losses of O_3 detected in recent years at low altitudes in spring over Antarctica.

The abundance of radicals implicated in O_3 removal depends on a complex suite of reactions implicating, with current models, some 40 distinct chemical species. The important radicals can be temporarily removed by reactions such as

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{9}$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \tag{10}$$

$$ClO + NO_2 + M \rightarrow ClNO_3 + M \tag{11}$$

(where HNO_3 is nitric acid, CH_4 is methane, CH_3 is methyl radical, HCl is hydrogen chloride, and $ClNO_3$ is chlorine nitrate), and

$$BrO + NO_2 + M \rightarrow BrNO_3 + M \tag{12}$$

where $BrNO_3$ is bromine nitrate. Removal of radicals is transitory, however. Radicals involved in loss of odd oxygen, temporarily tied up in species such as HNO_3, HCl, $ClNO_3$, and $BrNO_3$, are regenerated by reactions such as

$$h\nu + HNO_3 \rightarrow OH + NO_2 \tag{13}$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{14}$$

$$OH + HCl \rightarrow H_2O + Cl \tag{15}$$

$$h\nu + ClNO_3 \rightarrow Cl + NO_3 \tag{16}$$

and

$$h\nu + BrNO_3 \rightarrow Br + NO_3 \tag{17}$$

The importance of a particular scheme for removal of odd oxygen depends on the abundance of radicals implicated in the rate-limiting steps of the catalytic sequences in reactions 5 through 7, specifically on the abundances of NO_2, ClO, and BrO. Reactions 5 are most important for the current atmosphere, reflecting the relatively large abundance of NO_2, as discussed below. The influence of reaction 6 is greatest at higher altitudes, between about 35 and 45 km, and is inhibited at lower levels by conversion of ClO to $ClNO_3$ and HCl. In the stratosphere, $BrNO_3$ and HBr are less stable than $ClNO_3$ and HCl, allowing the loss of odd oxygen by reaction 7 to proceed over a more extensive region than that due to reaction 6: the overall significance of reaction 7 is limited by the relatively small abundance of inorganic bromine, about 10 pptv (parts per trillion by volume) for the current epoch (*10*), as compared with about 3 ppbv (parts per billion by volume) of chlorine (*11*).

The present understanding of gas-phase chemistry at mid-latitudes is also discussed. The models appear to provide a satisfactory representation of radical concentrations observed at mid-latitudes, and they suggest that the chlorine-catalyzed reaction sequence 5 should lead to significant loss of O_3 between about 30 and 45 km. Indeed, there is evidence that this loss has been observed. There is a difficulty, however, in that calculated rates for loss of O_3 appear to exceed rates for production of O_3 in regions where photochemical steady state (where chemical production equals chemical loss) would be expected to provide an excellent approximation.

There is evidence that the loss of O_3 over Antarctica at high latitudes proceeds by reaction paths in addition to reactions 5 through 7. Ozone is lost by reactions equivalent to

$$O_3 + O_3 \rightarrow 3\ O_2 \qquad (18)$$

Chlorine and bromine radicals are again implicated, with heterogeneous processes involving polar stratospheric clouds (PSCs) setting the stage for rapid springtime removal of O_3 over an extensive region of the Southern Hemisphere. Changes in O_3 levels at mid-latitudes observed in recent years are also discussed below, including a brief comment on the implications for other latitudes.

Chemistry of the Stratosphere at Mid-Latitudes

A variety of techniques, in situ and remote, have been developed to allow measurement of almost all of the key chemical species of the stratosphere. Measurements have been taken from aircraft, rockets, and balloons, providing detailed snapshots of conditions in local regions. These data are complemented by intensive spectroscopic studies of selected species both from the ground and from space (*11*). The data are most complete for a latitude of 32°N, the location of the National Scientific Balloon Facility at Palestine, Texas. In what follows, we consider measurements derived from analysis of the high-resolution interferometric data obtained with the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment launched by Spacelab 3 on 30 April 1985 (*12*). These data have the advantage that they provide simultaneous information on a number of the key species involved in catalysis of O_3 loss.

The results obtained from a simulation of the ATMOS measurements at 30°N between 30 April and 1 May 1985 are shown in Fig. 2, A and B. Profiles of total odd nitrogen [$NO_y = NO + NO_2 + HNO_3 + ClNO_3 + N_2O_5$ (nitrogen pentoxide) + HNO_4 (peroxonitric acid)], total inorganic chlorine [$Cl_x = HCl + ClNO_3 + ClO + HOCl$ (hypochlorous acid)], O_3, H_2O, and CH_4 were adopted from the ATMOS data (*12*). Profiles for individual species were obtained by solving the appropriate set of coupled time-dependent reaction equations (*13, 14*). Good agreement is obtained for all species, with the exception of $ClNO_3$, for which the model profile falls off much more slowly with altitude than the observed (*15*). The observations refer to local sunset. Minor discrepancies between model and observation for NO at low altitudes may reflect the procedure used to correct the observations to allow for the rapid time variation of NO and NO_2 at the large solar zenith angles relevant for the observing conditions of ATMOS. It is unlikely, however, that this effect will resolve the discrepancy for $ClNO_3$.

The calculated and measured profiles for ClO are shown in Fig. 2C. These measurements were taken at about the same location as the ATMOS data, but at different times. There is considerable scatter in the observational data for ClO. The results for 28 July 1976 and 14 July 1977 appear to be higher than would be expected. The best agreement between model and observation is obtained with the data taken in 1986 and 1987. The shape of the calculated profile in this case is similar to that observed, although the calculated curve appears to be displaced downward relative to the observed. The model shown here assumed that reaction of ClO with OH formed HO_2 and Cl and ignored the possible role of this reaction as a sink for chlorine radicals. Agreement for ClO would be improved significantly if we assumed that this reaction had a path to HCl with a branching ratio of 0.1, consistent with the upper limit given by DeMore *et al.* (*14*).

Model and observed concentrations for OH are in good agreement as shown in Fig. 2D. The early measurements by Anderson (*17*) are about a factor of 2 greater than the data of Heaps and McGee (*18*) and Carli and Park (*19*). The model agrees well at low altitudes with the recent data of Stimpfle and Anderson (*20*). The agreement exhibited in Fig. 2D would not be significantly altered if we allowed for the production of HCl through the ClO + OH reaction.

Given the agreement for the various species shown in Fig. 2, we might expect a similar pattern for O_3. The relative importance of the several loss mechanisms for odd oxygen is illustrated in Fig. 3. The results in Fig. 3 were obtained with the ATMOS data for O_3. There is a discrepancy between calculated rates for production and removal of odd oxygen (*21*). Photochemical rates for loss of odd oxygen exceed rates for production at all altitudes above about 27 km, by as much as 40% at 40 km. The difference is significant since reaction rates are rapid and we would expect a steady state at these altitudes; chemical production should balance loss to a close approximation.

It seems unlikely that the discrepancy can be attributed to errors in calculated densities for the important radicals. Reactions 5 account for 42% of the net loss of odd oxygen calculated at 40 km, with about 23%, 18%, and 13% from reactions 6, 4, and odd hydrogen chemistry, respectively. Model results for NO_2 are in good agreement with the essentially simultaneous measurements by ATMOS, and the comparisons for ClO in Fig. 2C suggest that the problem cannot be attributed to errors in ClO. If we allow for production of HCl with a 10% yield in the ClO + OH reaction, the discrepancy is reduced but not significantly. The issue merits further attention. It may indicate that the calculated rates for production of odd oxygen are too small, by about 40% between about 30 and 45 km.

Attempts to find additional sources of odd oxygen have met with limited success. Photolysis of $O_2(a^1\Delta_g)$ is too slow to play a role (*22*). Slanger *et al.* (*23*) pointed out that photolysis of O_3 could provide a significant source of vibrationally excited O_2. If quenching of the vibrationally excited states is slow, additional production of odd oxygen could occur by photolysis of the excited states, either through the Schumann-Runge bands or the excited $1^3\Pi_u$ state. The net effect would be autocatalytic, equivalent to production of three molecules of O_3 by photolysis of one:

$$\begin{gathered} h\nu + O_3 \rightarrow O_2{}^* + O \\ h\nu + O_2{}^* \rightarrow O + O \\ 3\,[O + O_2 + M \rightarrow O_3 + M] \end{gathered} \qquad (19)$$

where * denotes an excited molecule. The idea is interesting and merits further study in light of the problem exhibited in Fig. 3.

Chemistry of the Antarctic Stratosphere

The report by Farman *et al.* (*24*), appearing in *Nature* a little more than 11 years after the paper by Molina and Rowland (*8*), provided the first clue that the problem of stratospheric O_3 loss was not simply confined to mid-latitudes and high altitudes. They indicated that the column density of O_3 over Halley Bay on the coast of Antarctica (76°S) in October fell from about 320 Dobson Units (DU) in 1975 to almost 200 DU in 1984. Similar decreases were observed at Syowa (69°S) (*25*). Satellite measurements (*26*) showed that the phenomenon was not confined to a small region: in 1982 it covered an area almost twice the size of the United States.

Levels of O_3 over Antarctica in the Austral spring of 1987 reached values as low as 120 DU, approximately half the average value at the equator (*27*). Removal of O_3 was almost total between about 12 and 20 km (*28*). Loss began in late August, was most rapid in September, and was essentially complete by early October. Loss of O_3 was much less severe in 1988 than in 1987 (*29*): O_3 reductions appear to exhibit a quasi-biennial oscillation (QBO) in tune with a similar pattern observed for global stratospheric winds (*30*).

In situ observations of ClO and BrO (*31*), in combination with remote-sensing data for ClO (*32*), OClO (*33*), and BrO (*34*), confirm the importance of the O_3 loss mechanisms suggested by Molina and Molina (*35*),

$$\begin{aligned} ClO + ClO + M &\rightarrow Cl_2O_2 + M \\ h\nu + Cl_2O_2 &\rightarrow Cl + ClOO \\ ClOO + M &\rightarrow Cl + O_2 + M \\ 2\,[Cl + O_3 &\rightarrow ClO + O_2] \end{aligned} \tag{20}$$

and McElroy *et al.* (*36*),

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + BrO &\rightarrow Cl + Br + O_2 \end{aligned} \tag{21}$$

With values of the rate constants for the various key reactions recommended by DeMore *et al.* (*14*), about 80% of the loss of O_3 in 1987 would be attributed to reaction 20, with most of the balance due to reaction 21, as illustrated in Fig. 4 (*37*). The relative importance of reations 20 and 21 should vary from year to year, reflecting changes in the abundances of ClO and BrO. We might expect greater interannual variability in ClO than in BrO because of the larger dependence of the concentration of the former on the abundance of NO_2.

The high concentration of chlorine radicals in the springtime Antarctic stratosphere may be attributed to the importance of reactions on the surface of particles composing PSCs (*36, 38*). Four reactions have been suggested and studied in the laboratory (*39*):

$$ClNO_3 + HCl(s) \rightarrow Cl_2 + HNO_3(s) \tag{22}$$

$$ClNO_3 + H_2O(s) \rightarrow HOCl + HNO_3(s) \tag{23}$$

$$N_2O_5 + HCl(s) \rightarrow ClNO_2 + HNO_3(s) \tag{24}$$

where $ClNO_2$ is chlorine nitrite, and

$$N_2O_5 + H_2O(s) \rightarrow 2HNO_3(s) \tag{25}$$

where (s) denotes a species in the solid phase. Photolysis of Cl_2, HOCl, and $ClNO_2$ results in production of Cl and ClO. So long as the abundance of NO_2 is low, reactions 22 through 24 can lead to essentially complete conversion of inorganic chlorine to radicals (*40*).

Three types of PSCs have been identified. Type 1 PSCs are thought to be composed of nitric acid trihydrate ice (NAT), which is formed by condensation of HNO_3 and H_2O at temperatures of about 195 K (*41*). Type 2 PSCs are composed mainly of H_2O ice

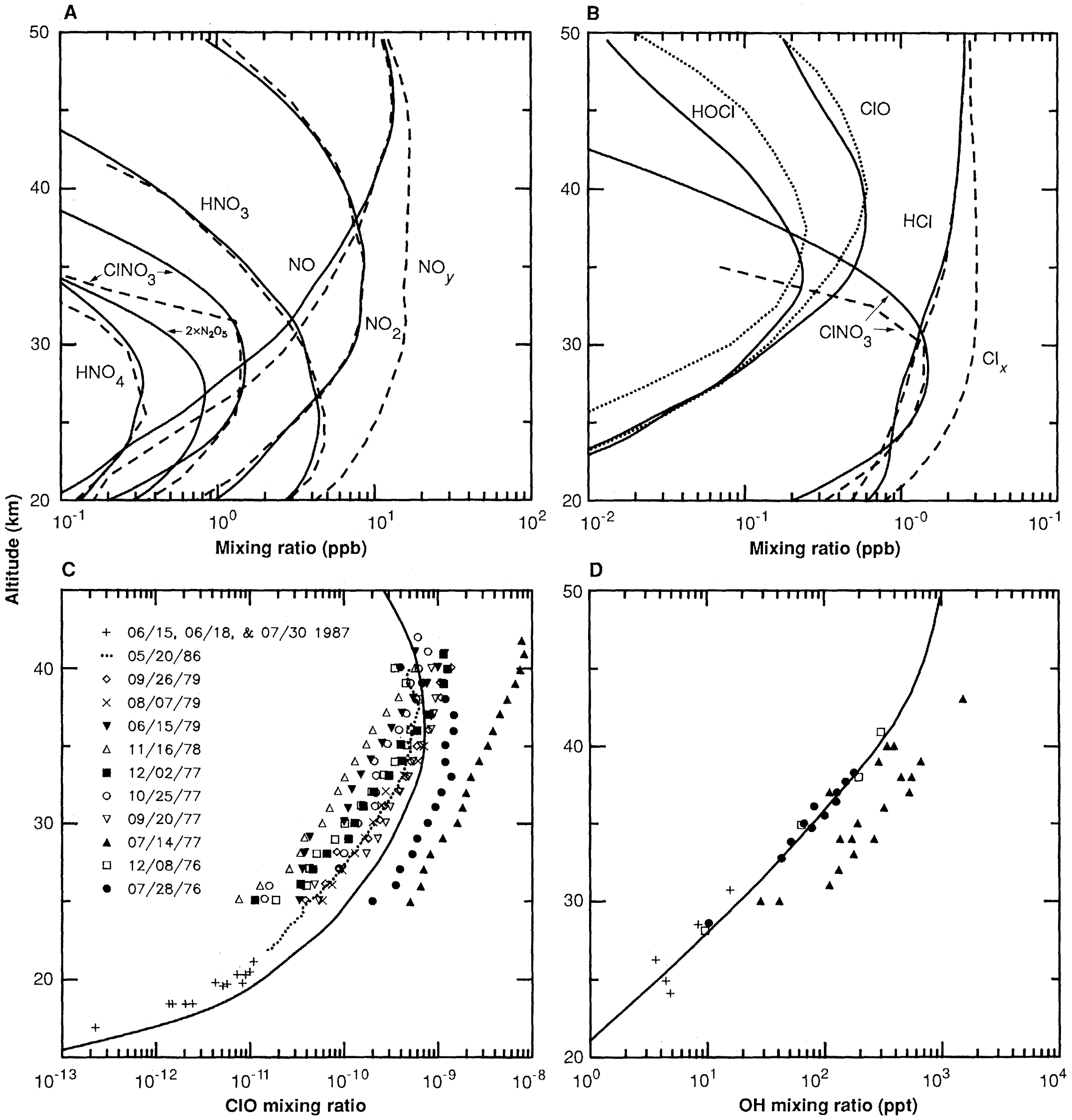

Fig. 2. (**A**) Calculated and observed concentrations for the odd nitrogen family. Data from the ATMOS experiment, for local sunset at 30°N on 30 April and 1 May 1985 are shown by the dashed lines. Model results that used values for NO_y, Cl_x, O_3, H_2O, CH_4, and temperature measured by ATMOS are shown by the solid curves. (**B**) Calculated and observed concentrations for the inorganic chlorine family. Experimental conditions are as in (A). The ATMOS data for ClO and HOCl, shown by dotted lines, define upper limits. The Cl_x model profile was obtained by combining measured values for HCl and $ClNO_3$ with model profiles for ClO and HOCl. (**C**) Theoretical and observed ClO. The calculated profile for ClO, shown by the solid line, is for midday and was derived with constraints on NO_y, Cl_x, O_3, and temperature defined by ATMOS measurements as for (A) and (B). In situ profiles measured by Anderson and co-workers (*16*) using resonance fluorescence are shown for various dates as indicated. (**D**) Theoretical and observed OH. The calculated profile for OH at noon, consistent with constraints imposed by ATMOS measurements, is shown by the solid line. In situ profiles, measured at midlatitudes, are shown by the indicated symbols. The data of Anderson (*17*) and Heaps and McGee (*18*) are taken from Stimpfle and Anderson (*20*), who adjusted the published results to allow for recent measurements of the fluorescence efficiency of OH.

and condense at temperatures of about 190 K. Type 3 PSCs are associated with topographic features and are believed to form primarily under conditions where cooling rates are rapid. Growth of NAT in spring, for at least part of the time, appears to involve only a small fraction (between 10^{-2} and 10^{-4}) of the available stratospheric aerosols (*42*). This suggests that formation of NAT may result in production of particles large enough to precipitate, providing a sink for stratospheric HNO_3. Large-scale depletion of HNO_3 and H_2O observed in the Antarctic stratosphere in the spring of 1987 (*43*) has been attributed to precipitation of NAT and H_2O ice (*44*).

The efficiency with which O_3 is lost in spring is a sensitive function of the residual level of HNO_3, as illustrated in Fig. 5. Photolysis of HNO_3 provides a source of NO_2 that can immobilize chlorine and bromine radicals through reactions 11 and 12. The magnitude of the sink for O_3 is sensitive also to the continued presence of Type 1 PSCs. Chlorine radicals are removed by

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (27)$$

Loss of radicals by this mechanism can be compensated by continued production, primarily by reaction 22. The results in Fig. 5 indicate that interannual variability in O_3 may be due primarily to fluctuations in HNO_3, leading to variability in NO_2, affecting the supply of halogen radicals (*40*). According to Salawitch *et al.* (*44*), levels of HNO_3 inside the chemically perturbed region in spring should depend primarily on the extent of mixing with the external environment after about the middle of July. Temperatures should be cold enough earlier to permit significant loss of HNO_3 as a regular phenomenon. Wave activity, which interrupts the vortex and adds HNO_3 and O_3 while raising temperature, may be largely responsible for the observed interannual variation in O_3.

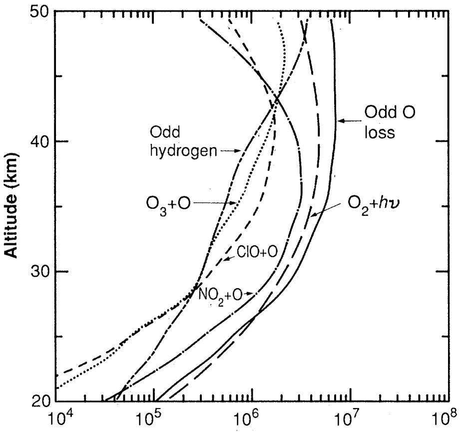

Fig. 3. Diurnally averaged rates for the important sources and sinks of odd oxygen computed using constraints imposed by ATMOS, as for the computations in Fig. 2. Loss of odd oxygen summarized with the curve labeled odd hydrogen includes contributions from reaction 28, important only at lower altitudes, and contributions from the several HO_x cycles involved in catalyzing reaction 4, significant only at higher altitudes. The total rate for odd oxygen production (O_2 + $h\nu$) is less than the computed loss rate for all altitudes above 27 km.

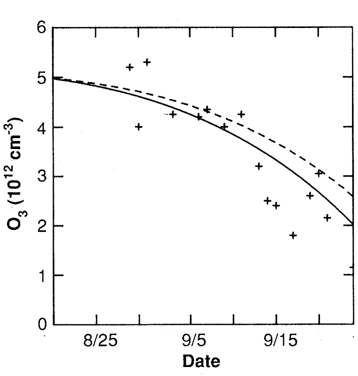

Fig. 4. Ozone density at 18 km over Antarctica, 1987. The crosses, taken from Barrett and coworkers (*32*), show measurements of O_3 at 18 km over McMurdo Station during 1987. The curves summarize reductions in O_3 obtained in an illustrative calculation, using preliminary values for ClO and BrO obtained in situ as reported by Anderson and coworkers (*31*). The dashed curve represents loss by cycle 20 only. The solid curve incorporates effects from bromide-chlorine chemistry (cycle 21). Cycle 21 contributes about 20% of the total accumulated O_3 loss by the end of the simulation. Note, however, as discussed in (*37*), that recent laboratory data may require a downward revision in the rate for production of Cl_2O_2.

Temporal Trends in O_3 Levels

A key test of the significance of the anthropogenic influence on stratospheric O_3 would be to find unambiguous evidence for a decline in O_3 attributable to input of industrial gases. The task is not easy. There is a limited long-term record of the column density of O_3 from Dobson instruments located at a small number of stations, mainly in the Northern Hemisphere. There are difficulties associated with lack of reliable calibration of the Dobson instruments. Satellite observations can fill the void in spatial coverage, but data for the total O_3 column are available only for the period since 1978. There are problems due to temporal drifts in instrumental sensitivity, and it has been necessary to calibrate satellite instruments by reference to ground-base data. Finally, to isolate a trend due to industrial activity, there is need to correct for a variety of natural influences that may be expected to contribute variability comparable or larger than the signal due to anthropogenic emissions.

Natural influences on O_3 include changes in the flux of ultraviolet radiation from the sun, changes in the source of NO_y due to variations in the flux of cosmic rays and solar protons, and inputs of gases and particulate material from volcanic eruptions. In addition, we must allow for fluctuations in stratospheric dynamics relating to, among other factors, effects of the QBO and the El Niño–Southern Oscillation (ENSO). A panel of experts convened by NASA attempted to allow for these effects using statistical techniques (*45*). They concluded that the best current analysis, using mainly data from the ground-based Dobson network, indicates that the annually averaged column density of O_3 declined by between 1.7 and 3.0% in the latitude band 30° to 64°N between 1969 and 1986. The decrease was most marked for the winter months, for which they reported a drop of between 2.3 and 6.2%. We may note, however, that the period covered by this analysis occupies less than one major solar cycle and includes two significant geophysical events, the eruption of El Chichon and the unusually large ENSO of 1983. Results of the statistical study should be interpreted with caution.

The anthropogenic influence on O_3 is itself complicated. In addition to the increase in the burden of stratospheric chlorine and bromine, we must allow for effects of increases in CH_4, N_2O, and CO_2. Methane levels are currently increasing at an annual rate of between 1 and 2% (*11*). The increase in CH_4 may be expected to compensate partially for the rise in chlorine, thus shifting chlorine from radical forms to HCl by enhancing the rate for reaction 27. The rise in CH_4 should result also in an enhanced abundance of stratospheric H_2O, with possible implications for the density and persistence of stratospheric clouds (*46*). The increase in N_2O, about 0.3% per year (*11*), reflecting subtle influences on the global nitrogen cycle, should result in a slow secular rise in the abundance of stratospheric NO_y. The increase in CO_2 (*11*), due largely to combustion of fossil fuels, has an indirect effect, causing a reduction in stratospheric temperatures. Lower temperatures in the stratosphere would lead to changes in rates of a number of key reactions: model studies suggest that thermal feedback should cause a small increase in the abundance of O_3. Lower temperatures could enhance also the conditions favoring loss of O_3 at high latitudes. All of these competing influences must be included in models seeking to describe the temporal trend in O_3.

The recent NASA report (*45*) concludes that "model calculations are broadly consistent with the observed changes in column O_3, except that the mean values of the observed decreases at mid- and high latitudes in winter are larger than the mean values of the predicted decreases. The observed changes may be due wholly, or in part, to the increased atmospheric abundance of trace gases, primarily chlorofluorocarbons." In light of the problems in balancing production and loss of odd oxygen described above, the difficulty in accounting for meteorological variability in models, problems in accommodating effects of volcanic activity, uncertainties in the secular variability of solar ultraviolet radiation, and difficulties implicit in the statistical analysis of the observational data, it would appear that further work is required before this complex issue can be resolved.

Information concerning temporal trends in O_3 is presented as a function of altitude in Fig. 6. Extensive and relatively direct information from the Stratospheric Aerosol and Gas Experiment (SAGE) suggests a reduction in O_3 for an extensive range of altitudes from about 25 to 45 km over latitude bands between 20° and 50° in both hemispheres between 1979 and 1986. The reduction averages about 3% between 30 and 40 km, in good agreement with results from models. Models appear to overestimate the reductions observed above 40 km, while they seem to err in the opposite sense below 30 km. The difficulty at high altitudes could reflect, in part at least, problems in simulating the secular variation of solar radiation: the time period of interest in Fig. 6 covers the transition from maximum to minimum solar activity. The problems at low altitude are more intriguing. If confirmed by further analysis, they could provide an early indication that low-altitude loss of O_3, dramatically evident over Antarctica in spring, is not simply confined to high southern latitudes.

A preliminary study by Sze *et al.* (*47*) suggests that mixing of low O_3 air from Antarctica with air from outside the chemically perturbed region, following breakup of the vortex in spring, could have an influence on the abundance of O_3 to latitudes as low as about 40°S. This model could provide at least a partial explanation for the low-altitude trend observed by SAGE in the Southern Hemisphere.

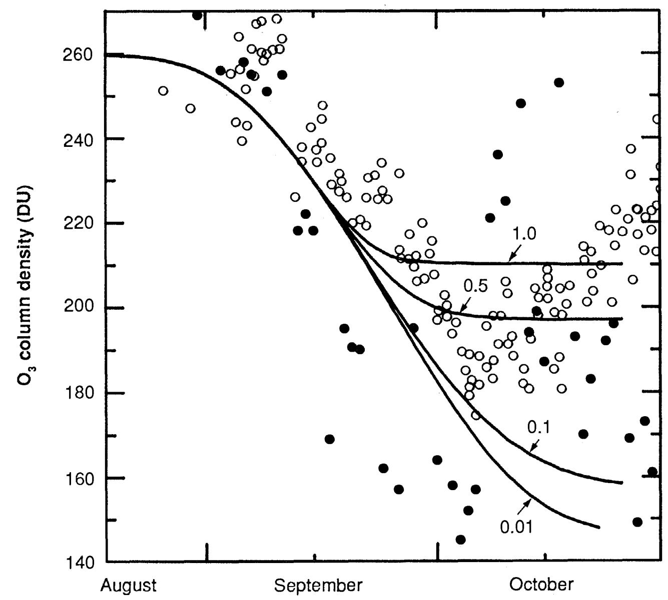

Fig. 5. Ozone column density as a function of time for a model allowing for effects of heterogeneous chemistry and denitrification. Heterogeneous chemistry on PSCs was modeled based on laboratory results (*39*), and was assumed to persist until PSCs evaporated in mid-September. Nitric acid was assumed absent from the gas phase prior to PSC evaporation. Labels on the curves define the fraction of the initial HNO_3 returned to the gas phase at the time of PSC evaporation, simulating the effect of denitrification (*40*). The open circles represent data for 1983 near Halley Bay (*26*); the closed circles summarize data for 1987 near McMurdo Station as reported by Harder *et al.* (*53*).

The findings with respect to depletion of O_3 in the south polar region, as well as the findings of the NASA report (*45*), emphasize the importance of investigating the possible role of heterogeneous chemistry in the northern polar region. PSCs are observed, albeit less frequently than in the south (*48*). Densities of NO_2 are suppressed, most probably due to heterogeneous reactions involving N_2O_5 (*49*). It is possible that HNO_3 could be removed at least locally in the north by precipitation, despite the fact that the vortex in the north is less stable than its southern analogue. Air parcels depleted in NO_y, when released into lower latitudes, could be poised to lose O_3 through reactions 20 and 21 and the analogous cycle proposed by Solomon *et al.* (*38*):

$$\begin{gathered}\mathrm{ClO} + \mathrm{HO_2} \rightarrow \mathrm{HOCl} + \mathrm{O_2}\\ \mathrm{HOCl} + h\nu \rightarrow \mathrm{OH} + \mathrm{Cl}\\ \mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}\\ \mathrm{OH} + \mathrm{O_3} \rightarrow \mathrm{HO_2} + \mathrm{O_2}\end{gathered} \tag{27}$$

It would be particularly instructive to search for evidence of O_3 loss in the tropics. The calculations of Sze *et al.* (*47*) suggest that the influence of the polar regions should be confined to latitudes higher than about 40°. Temperatures are low enough, however, in the tropics to permit condensation and possible precipitation of HNO_3 (*50*). The dependence of odd oxygen loss on NO_y at 20 km at the equator is illustrated in Fig. 7A. Two-dimensional model results (*51*), considering only gas-phase chemistry, indicate a mixing ratio of NO_y at this altitude of about 0.5 ppbv. The O_3 concentration is determined primarily by a balance of production and transport (*52*). The results in Fig. 7A indicate that chemical loss, through a combination of reactions 20, 21, and 27, and the sequence

$$\begin{gathered}\mathrm{OH} + \mathrm{O_3} \rightarrow \mathrm{HO_2} + \mathrm{O_2}\\ \mathrm{HO_2} + \mathrm{O_3} \rightarrow \mathrm{OH} + 2\,\mathrm{O_2}\end{gathered} \tag{28}$$

could be significant if the abundance of NO_y were less than about 0.2 ppbv. Chemical loss could be even more important, comparable to photochemical production, if HCl were converted to either Cl_2, HOCl, or $ClNO_2$ through reactions 22 through 24, with subsequent photolytic release of radicals, as illustrated in Fig. 7B.

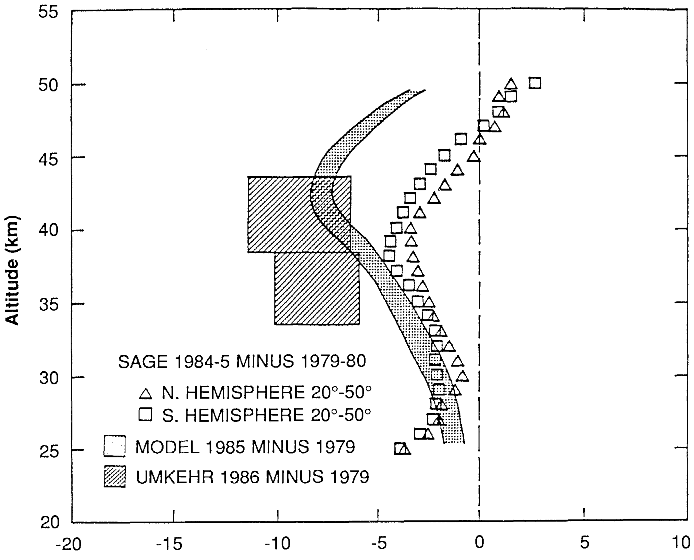

Fig. 6. Percent changes in O_3 observed over the period 1979 to 1987. The data from the Stratospheric Aerosol and Gas Experiment (SAGE) were averaged over the latitude band indicated. The Umkehr data are for northern mid-latitudes. The range of model values and the comparisons shown here are taken from (*45*).

Concluding Remarks

The past 15 years have witnessed a remarkable advance in our understanding of stratospheric chemistry. Progress has occurred on all fronts, with significant achievements in the investigation of kinetic processes in the laboratory, development of imaginative techniques to study the composition of the stratosphere both in situ and by remote sensing, and implementation of powerful computer models to simulate the combined effects of transport and chemistry.

Our understanding of the chemistry of free radicals at mid-latitudes is well advanced, although problems persist in attempts to balance the budget for O_3. Ozone changes occur on a variety of time and space scales. A much better understanding of the interactive chemistry and meteorology of the stratosphere is required to separate effects of anthropogenic and natural changes.

The discovery of a major sink for O_3 over Antarctica was unexpected, but much progress has been made in less than 4 years to meet this challenge. There is definitive evidence that the decline in O_3 over Antarctica is caused by industrial chemicals, in combination with distinct meteorological conditions, although further work is required to define the detailed mechanism and to clarify the impact of the Antarctic phenomenon on O_3 at other latitudes.

There is a need to explore whether the unusual chemistry observed over Antarctica can have an influence on other regions of the stratosphere. As noted, temperatures are low enough in the northern polar region and in the tropics to allow condensation of HNO_3. These regions merit special attention. The northern polar region is to be subjected to careful scrutiny in 1989 with a campaign similar to that mounted in 1987 for Antarctica; future plans should include similar careful investigations of the tropics.

The Montreal Protocol made the connection of science to policy, providing a framework for major global reductions in the emission of industrial halocarbons (*55*). It was formulated in advance of the most recent information from Antarctica. It includes, however, provisions for review and, if necessary, for implementation of even more stringent control strategies. Implications of the present control strategy for future burdens of stratospheric chlorine and bromine are illustrated in Fig. 8. Loss of O_3 was evident over Antarctica first in the mid-1970s when the abundance of stratospheric chlorine was about 2.5 ppbv. For the stratosphere to return to these levels, even on a time scale of a century or so, requires a drastic and immediate reduction in emission of halocarbons. The Montreal Protocol should be amended not only to require more stringent controls on emissions of the specified chemicals, but also to include controls on emission of CH_3CCl_3, $CHClF_2$, CCl_4, and CH_3Br that were not incorporated in the original formulation.

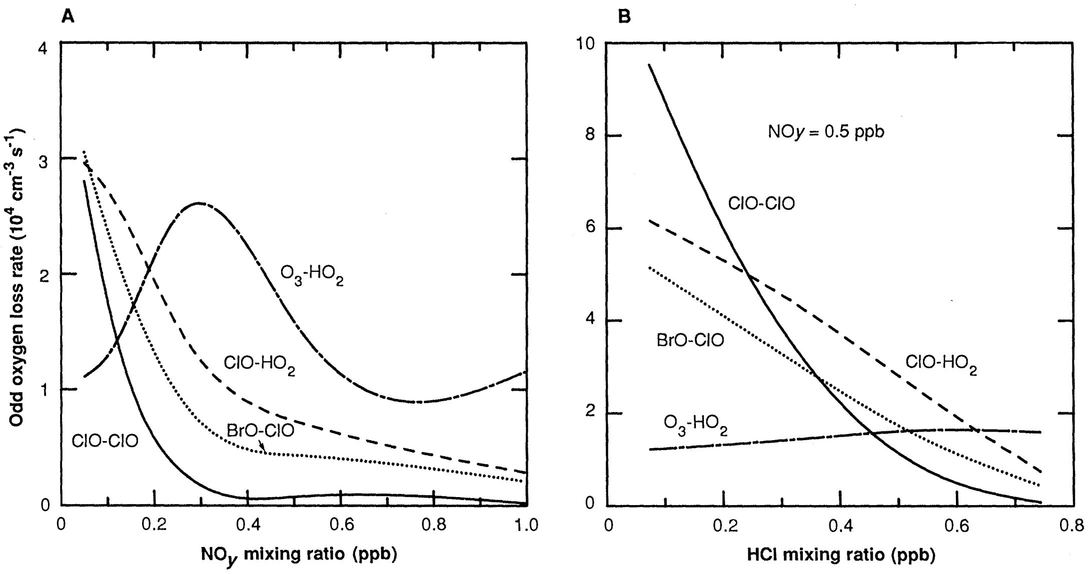

Fig. 7. Calculated odd oxygen loss rate, for 20 km, at the equator. The calculation was constrained by using O_3 and temperature measurements at Natal, Brazil (6°S), for the period 25 March to 15 April 1985, as reported by Barnes *et al.* (*54*). Constraints for NO_y and Cl_x were obtained with two-dimensional model results (*51*). (**A**) The effects of denitrification on odd oxygen loss were simulated by adjusting the level of NO_y, calculating individual Cl_x species for a total Cl_x mixing ratio of 0.84 ppbv, and solving in steady state for the loss of odd oxygen, with results for individual cycles as indicated. (**B**) The possible effects of heterogeneous conversion of HCl to radicals was simulated by varying the level of HCl, keeping total Cl_x and NO_y fixed, assuming that species other than HCl adjust to their photochemical steady state values.

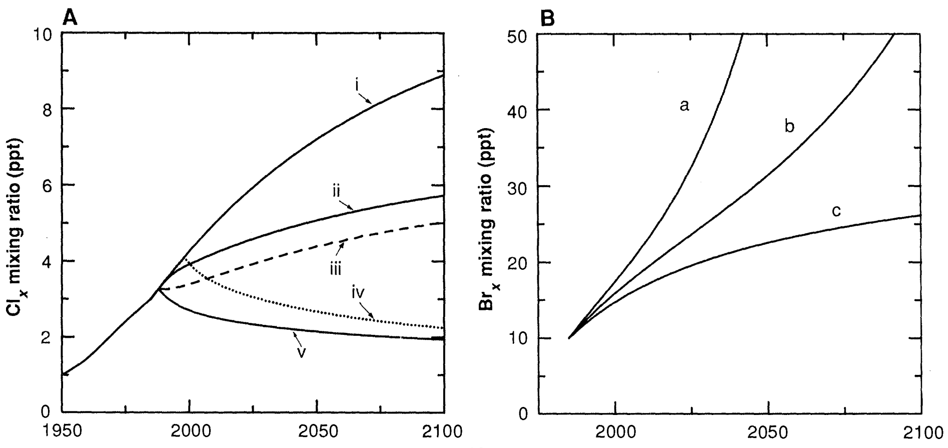

Fig. 8. Halogen growth projections. Increases in stratospheric (**A**) inorganic chlorine and (**B**) inorganic bromine are shown for a variety of emission scenarios. Levels of Cl_x and Br_x in 1985 are taken as 3.0 ppbv and 10.0 pptv, respectively. Projections for chlorine were obtained by using industrial emission rates and atmospheric lifetimes for CCl_3F, CCl_2F_2, $C_2Cl_3F_3$, and $CHClF_2$ from the WMO report (*11*). The scenarios in (A) refer to: (i) continued growth at 1986 emission rates; (ii) implementation of the Montreal Protocol; (iii) a 50% reduction in chlorocarbon emissions effective 1989; (iv) a 90% reduction in emissions 10 years from present; and (v) an immediate 90% reduction, effective 1989. Scenarios (iv) and (v) illustrate the consequence of a 10-year delay in implementing reductions in emissions. There is a 50-year delay in the time required for Cl_x to return to a particular value, a consequence of the long atmospheric lifetimes of the chlorocarbon gases. For bromine, three scenarios are shown in (B). All of the scenarios assume constant release of $CBrF_3$ and $CBrClF_2$ at 1986 rates. Scenario (a) allows for an increase in emission of CH_3Br at 4% per year; scenario (b) considers such an increase at 2% per year; scenario (c) keeps CH_3Br fixed at 6.7 pptv.

Studies of stratospheric O_3 demonstrate that the global environment is fragile. The human influence extends from pole to pole, from the troposphere to the mesosphere. They attest to the persistence of our impact. What we have wrought in the past can affect the environment for centuries to come. But it is a story not without hope; our science has made notable progress and governments and industry have demonstrated at least the initial will to act as required.

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